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LIQUID-LIQUID EXTRACTION OF IRON^{III} WITH TRIBUTYLPHOSPHATE

SEPARATION FROM MIXTURES

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Summary—A method is presented for rapid solvent extraction of iron^{III} with tributylphosphate (TBP). Quantitative extraction results from 3–6*M* hydrochloric acid, using 100% TBP. The effects of TBP concentration, salting-out agent and diverse ions on the extraction behaviour of iron^{III} have been investigated. The extractable species are $FeCl_3 \cdot 3TBP$ and $H[FeCl_4 \cdot (TBP)_2]$ from 2*M* and 6*M* hydrochloric acid respectively.

TRIBUTYLPHOSPHATE, commonly known as TBP, has been widely used for the extraction of actinide and also lanthanide elements.[1,2] But very little work has as yet been done on the extraction of common elements with TBP. Recently Musil and Weidmann[3] reported the separation of cobalt from nickel by extraction with TBP. Specker and Cremer[4] described the solvent extraction of iron^{III} from hydrochloric acid with 1-5% TBP in benzene. They concluded from their studies that the species extracted from 7–9*M* hydrochloric acid is $H[FeCl_4(TBP)_2]$ and from 4*M* acid, $FeCl_3 \cdot 3TBP$. The maximum partition coefficient value obtained from 9*M* hydrochloric acid was 9·27. Aven and Freiser[5] described the removal of iron interference in steel analysis by extraction of ferric thiocyanate with TBP. This work was extended by Melnick *et al.*[6] who obtained clear-cut extraction using a TBP-carbon tetrachloride mixture.

It has been found by the present authors that almost quantitative extraction of iron^{III} is possible from hydrochloric acid using undiluted TBP (100%), leading to a very high partition coefficient. In this paper, systematic quantitative studies on the liquid-liquid extraction behaviour of iron^{III} from hydrochloric acid by means of TBP are described. The optimum conditions for extraction, separation and analytical measurement have been evaluated from a critical study of the various factors involved such as acidity, salting-out agent and TBP concentration.

EXPERIMENTAL

Apparatus

Separatory funnels (250 ml) were used for extraction.

Reagents

All the chemicals used were chemically pure or reagent grade materials unless otherwise mentioned.

A stock solution of ferric chloride was prepared by dissolving 12·5 g of the hexahydrate salt (E. Merck) in 500 ml of water, 1% in hydrochloric acid. The solution, standardised by the dichromate titrimetric method, was found to contain 4·614 mg of iron^{III} per ml.

Tributylphosphate (Matheson, Coleman and Bell, Cincinnati, Ohio, U.S.A.), b.p. 143–145° at 5 mm, was employed as an extractant after purification according to the method of Peppard *et al.*[7]

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General procedure

The general extraction and measurement procedures were as follows.

An aliquot (5 ml) of ferric chloride solution containing 4·614 mg of iron^{III} per ml was mixed with a calculated volume of hydrochloric acid of known strength to give the desired acid concentration, diluted with water to 25 ml and introduced into a separatory funnel. For the study of salting-out agents, the appropriate salt and for that of diverse ions, the selected foreign ion, were added before making up the final volume of the aqueous phase to 25 ml. The aqueous phase, thus prepared, was shaken for 5 min with 10 ml of TBP (100%). For the study of the effect of TBP concentration, TBP was diluted with chloroform as desired and 20 ml of the chloroform solution were used. After extraction the layers were allowed to settle and the aqueous layer was carefully withdrawn. Iron^{III} was then stripped from the TBP layer by shaking this with 2 × 20 ml of water for 10 min; the aqueous extracts were combined in a beaker and iron^{III} was determined by direct dichromate titration.

RESULTS AND DISCUSSION

Effect of acidity

The system was investigated at concentrations of hydrochloric acid in the range 0·25*M*–9·6*M*. The partition coefficients (*D*) were calculated from the concentration ratios:

$$D = \frac{[\mathrm{Fe^{III}}]_{\mathrm{org.\ phase}}}{[\mathrm{Fe^{III}}]_{\mathrm{aq.\ phase}}}$$

The results are shown in Table I and Fig. 1.

The concentration of iron^{III} in the organic phase was obtained by titration

TABLE I.—EXTRACTION OF IRON^{III} AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION (Fe^{III}, 23·07 mg; TBP, 100%)

HCl, *M*	0·25	0·5	1·0	1·5	1·92	3·0	4·0	6·0
Extraction, %	0	17·9	73·1	90·4	97	97·2	97·2	98·6
Partition coefficient, *D*	0	0·22	2·77	9·42	32·33	34·34	34·34	70·4

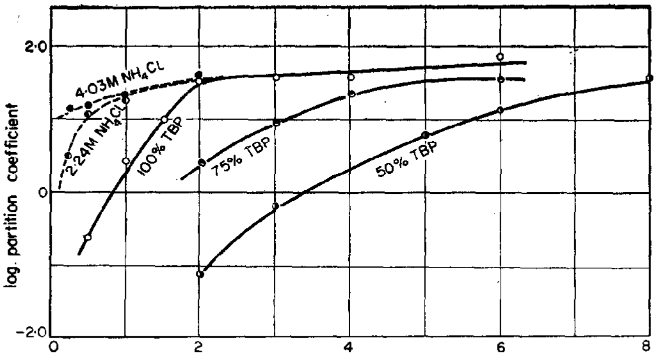

FIG. 1. Extraction of iron^{III} with TBP as a function of hydrochloric acid concentration in the aqueous phase.

according to the general procedure; that in the aqueous phase was calculated by difference from the total amount of iron^{III} taken. Extraction with 100% TBP starts from about 0·5*M* hydrochloric acid and becomes almost quantitative (>97%) from 1·92*M* acid onwards. In the extraction curve (Fig. 1) there is an initial steep rise at low acidities, presumably due to salting-out from the aqueous phase by chloride ion; whereas at higher acidities the extraction curve levels off, passing through a maximum value of the partition coefficient. The latter effect may be attributed to the formation of chloro-complexes and to hydrochloric acid competition for the available TBP. It is obvious from Fig. 1 that 97–100% extraction of iron^{III} is possible from 3–6*M* hydrochloric acid. The maximum partition coefficient obtained was 70 (6*M* acid) which can be compared to the value 9·27 (9*M* acid) reported by Specker and Cremer.[4] Hence the use of 100% TBP as an extractant definitely improves the extraction process.

Salting-out agent

The presence of ammonium chloride or barium chloride in the aqueous phase enhances the extraction in each case and permits almost complete extraction (>96%) even from 1*M* hydrochloric acid. The effect of these two salts on the extraction was observed at different acidities in the aqueous phase, as shown in Table II and Fig. 1. At lower acid concentrations *i.e.*, 0·25*M*–0·5*M*, the partition coefficients increase by several orders of magnitude. This may be explained by the fact that under this condition less of the TBP is combined with the acid, and therefore more TBP is available for extraction. Moreover, the presence of an inextractable chloride in the aqueous layer serves to maintain the salting-out function of the chloride ion. Increase in salt concentration, and replacement of a univalent by a bivalent cation in the salt, always lead to an increased extraction.

TBP concentration

Using chloroform as a diluent, the concentration of TBP was varied from 19% (0·69*M*) to 75% (2·75*M*) and the effect on extraction was observed at varying acid concentrations (Table III). Dilution of the TBP lowers the extraction, as shown in Fig. 1. The composition of the extractable species was ascertained from a log D — log C_{TBP} plot (Fig. 2). The best line through the points for 2*M* hydrochloric acid indicates a slope of 3·1 so that the species involved is $FeCl_3 \cdot 3TBP$; whereas the plot at 6*M* acid corresponds to a slope of 1·7 giving the extractable species approximately as di-solvate, *viz.*, $H[FeCl_4 \cdot (TBP)_2]$. Presumably at 2*M* hydrochloric acid the extraction system follows a limiting cube law which holds good up to 4*M* acid; and a limiting square law from 6*M* acid onwards. This result agrees fairly well with that of Specker and Cremer[4] who found a cube law at 4*M* acid and a square law at 7–9*M* acid.

In order to make Fig. 2B complete, a few runs were made with 30% TBP at 6*M* hydrochloric acid. The extraction was 55·7% giving $D = 1·26$. Extraction was negligible from 2*M* acid.

Diverse ions

The following ions were tested for interference (Table IV): Cu^{2+}, Hg^{2+}, UO_2^{2+}, Co^{2+}, Ni^{2+}, Ba^{2+}, Al^{3+}, Cr^{3+}, Bi^{3+}, Th^{4+}, VO_3^-, $Mo_7O_{24}^{6-}$, PO_4^{3-}, citrate, tartrate and EDTA. The aqueous phase in each case was maintained at 4*M* in hydrochloric acid.

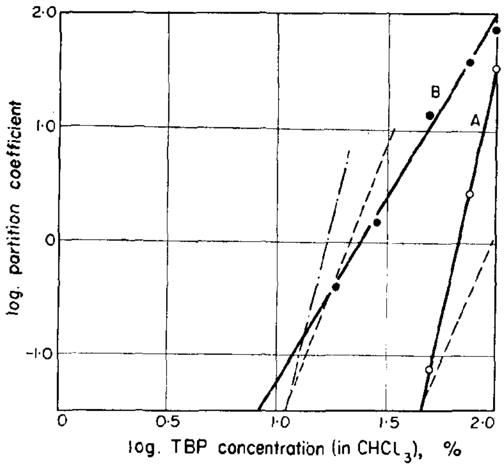

FIG. 2. Partition coefficient as a function of TBP concentration: A. Aqueous phase, 2*M* HCl. Line of slope 3·1 B. Aqueous phase, 6*M* HCl. Line of slope 1·7.

TABLE II.—SALTING-OUT AGENTS

A. NH_4Cl. Fe^{III}, 23·07 mg; TBP, 100%

HCl, *M*	0·25			0·5			1·0			1·92	
NH_4Cl, *M*	2·24	4·03	5·0	2·24	4·03	5·0	2·24	4·03	5·0	2·24	4·03
Extraction, %	76·5	93·4	94·6	92·2	93·4	94·6	94·6	95·2	96·4	97·0	97·2
Partition coefficient, *D*	3·26	14·16	17·52	11·82	14·16	17·52	17·52	19·84	26·79	32·33	34·34

B. $BaCl_2 \cdot 2H_2O$. Fe^{III}, 23·07 mg; TBP, 100%

HCl, *M*	0·25	0·5	1·0
$BaCl_2 \cdot 2H_2O$, *M*	1·24	1·24	1·24
Extraction, %	83·2	88·6	93·4
Partition coefficient, *D*	4·95	7·77	14·16

Iron^{III} is readily extracted in the presence of excess of copper^{II}, mercury^{II}, nickel^{II}, barium^{II}, aluminium^{III}, chromium^{III}, bismuth^{III}, phosphate and EDTA. Copper^{II}, although co-extracted to a slight extent, does not interfere with the determination of iron^{III}. Iron^{III} can tolerate 5 mg of uranium^{VI} and 25 mg of thorium^{IV}. Larger amounts of uranium^{VI} seriously interfere, whereas comparable amounts of thorium do not affect the iron^{III} determination. However, in the presence of thorium a large

TABLE III.—EXTRACTION AS A FUNCTION OF TBP CONCENTRATION.

A. 19% TBP (0·69*M*) IN CHLOROFORM

HCl, *M*	4·0	6·0	8·0	9·6
Extraction, %	1·19	28·6	94·6	98·2
Partition coefficient, *D*	0·01	0·4	17·52	54·55

B. 50% TBP (1·83*M*) IN CHLOROFORM

HCl, *M*	1·0	2·0	3·0	5·0	6·0	8·0
Extraction, %	6·58	6·58	38·2	84·8	92·7	97
Partition coefficient, *D*	0·07	0·07	0·62	5·58	12·7	32·33

C. 75% TBP (2·75*M*) IN CHLOROFORM

HCl, *M*	2·0	3·0	4·0	6·0
Extraction, %	72·2	89·88	95·8	97
Partition coefficient, *D*	2·6	8·88	22·81	32·33

excess of TBP should be used to ensure extraction of iron^{III} since thorium is also considerably extracted under the same conditions. Serious interferences are found in cases of cobalt^{II}, vanadate, molybdate, citrate and tartrate.

The lack of interference due to copper^{II}, aluminium^{III} and chromium^{III} is interesting since these are commonly associated with iron^{III} in ores and industrial products. It is also worth while to note that iron^{II} is not extracted at all under the experimental condition and hence the method is suitable for the extraction of iron^{III} in the presence of iron^{II}.

Recommended procedure

The solution should contain about 25 mg of iron^{III} as chloride. Adjust to 4*M* with respect to hydrochloric acid in a volume of 25 ml. Introduce the solution into a 250-ml separatory funnel and extract for 5 min with 10 ml of 100% TBP. Separate the layers, back-extract iron^{III} from the organic layer by shaking with two 20-ml portions of water and determine iron^{III} in the combined aqueous extracts with dichromate.

From ten such runs (iron = 23·07 mg) an average recovery of 96·7 ± 2·2% was obtained, so that the standard deviation was ± 2·3%. The total operations—consisting of extraction, stripping and analysis—in each run require only 30 min. The time-factor, however, can be cut down by 50% if manual shaking is replaced by a mechanical shaker in the extraction and back-extraction steps. The method possesses the advantages of simple and rapid operation with fairly good reproducibility and should be applicable to the determination of iron in ores and industrial products.

TABLE IV.—DIVERSE IONS
Fe^{III}, 23·07 mg

Foreign ion	Amount added, *mg*	Source	$Iron^{III}$ extracted, %	Remarks
Cu^{2+}	95	$CuSO_4{\cdot}5H_2O$	97	No interference[b]
Hg^{2+}	100	$HgCl_2$	97	No interference
Co^{2+}	25	$Co(NO_3)_2{\cdot}6H_2O$	TBP layer coloured green	Interference[a]
Ni^{2+}	94	$NiSO_4{\cdot}6H_2O$	98·2	No interference
Ba^{2+}	100	$BaCl_2{\cdot}2H_2O$	95·8	No interference
Bi^{3+}	100	$BiOCl$	97	No interference
Al^{3+}	98	$Al_2(SO_4)_3{\cdot}18H_2O$	95·8	No interference
Cr^{3+}	100	$Cr(NO_3)_3{\cdot}6H_2O$	98·2	No interference
Th^{4+}	25	$Th(NO_3)_4{\cdot}4H_2O$	97	No interference
UO_2^{2+}	5	$UO_2(NO_3)_2{\cdot}6H_2O$	99	No interference
VO_3^-	50	NH_4VO_3	V^{5+} co-extracted	Interference[a]
$Mo_7O_{24}^{6-}$	50	$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$	co-extraction of Mo^{6+}	Interference[c]
PO_4^{3-}	100	$NaH_2PO_4{\cdot}12H_2O$	97	No interference
$(EDTA)^{4-}$	100	EDTA (disodium salt)	97	No interference
$Tart^{3-}$	100	Tartaric acid	—	Interference[c]
Cit^{3-}	100	Citric acid	—	Interference[c]

[a] Colour interference.
[b] Cu^{2+} was also extracted giving a deep yellow TBP phase but there was no interference with analysis of $iron^{III}$.
[c] Interference with $iron^{III}$ analysis.

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Zusammenfassung—Eine Methode zur schnellen Solventextraktion von Fe(III) mit Tributylphosphate (TBP) wird beschrieben. Die Extraktion ist quantitativ aus Lösungen 3–6 molar in Salzäure, wenn 100% TBP verwendet wird. Der Einfluss der TBP-konzentration, Aussalzeffekte sowie Anwesenheit verschiedener Ionen wurde studiert. Die extrahierten Partikeln sind $FeCl_3{\cdot}3TBP$ und $H[FeCl_4{\cdot}(TBP)_2]$ aus 2 bzw. 6m Salzsäure.

Résumé—Les auteurs présentent une méthode d'extraction rapide du fer(III) par le tributyl phosphate (T.B.P.). L'extraction quantitative se fait en milieu acide chlorhydrique 3 M à 6 M, en utilisant du T.B.P. à 100 pour cent. Les effets de la concentration du T.B.P., de l'agent de relarguage et des divers ions sur le comportement de l'extraction du fer(III) ont été étudiés. Les espèces que l'on peut extraire sont $FeCl_3$, 3 T.B.P. et $H[FeCl_4(T.B.P.)_2]$ en milieu acide chlorhydrique 2 M et 6 M respectivement.

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CATION-EXCHANGE STUDIES OF LEAD^{II} ON DOWEX 50W-X8

SEPARATION FROM MIXTURES

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Summary—Quantitative studies are reported on the behaviour of lead^{II} at milligram level, using cation-exchange resin Dowex 50W-X8. Various eluents, such as nitric acid, ammonium acetate, sodium nitrate, tartaric acid, citric acid, ethylenediaminetetra-acetic acid (disodium salt) and perchloric acid, are used for column operation. Two hundred ml of $2M$ nitric acid or ammonium acetate is sufficient for quantitative elution of lead from 1·4 × 14·5 cm of Dowex 50W-X8 resin. The efficiency of the various eluents is evaluated in terms of their elution constants. Lead^{II} is separated from barium, strontium and aluminium by selective elution with ammonium acetate ($1M$) and from cerium^{IV}, zirconium^{IV}, thorium^{IV}, bismuth^{III} and iron^{III}, by converting the latter into suitable anionic complexes.

WITH the increasing application of nuclear energy for peaceful purposes in recent years, the study of lead has assumed considerable significance. Lead is invariably used as an excellent shielding material for reactors and for general work involving highly radioactive isotopes. Industrial uses of lead are also well-known. Hence it was thought worthwhile to investigate the ion-exchange behaviour of lead using the cation-exchange resin, Dowex 50W-X8.

Bonner and Loussmith[1] determined the cation-exchange equilibrium involving ions like lead^{II} on Dowex 50, and derived a selectivity scale for bivalent ions on the basis of their affinity for the resin. Minami and Ishimori[2] separated barium from lead by eluting first lead with ammonium acetate at pH 6·1 and then barium with 10% ammonium chloride solution. Ethylenediaminetetra-acetic acid (disodium salt) was used as a complexing agent for lead.[3] In this method lead was eluted as the lead-EDTA complex at pH 4·0–4·5 and subsequently barium was eluted with EDTA at pH 10·5. Gabrielson[4] devised a method for the determination of lead sulphate in storage battery plates. Lead sulphate was digested with sodium carbonate, the precipitate of lead carbonate was removed by filtration and the resulting sodium sulphate solution (after elimination of excess of carbonate in solution) was passed through a cation-exchange resin. The issuing sulphuric acid was determined.

But thus far systematic cation-exchange studies of lead are lacking. This paper describes systematic quantitative studies of the cation-exchange behaviour of lead^{II} on Dowex 50W-X8 (hydrogen form). Nitric acid, ammonium acetate, sodium nitrate, tartaric acid, citric acid, ethylenediaminetetra-acetic acid (disodium salt) and perchloric acid have been studied as the eluting agents. Lead has been also separated from barium, strontium, aluminium, cerium^{IV}, zirconium, bismuth, iron^{III}, and thorium.

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APPARATUS AND REAGENTS

Apparatus

Ion-exchange column and Cambridge pH indicator.

The ion-exchange column was similar to the one described before.[5,6] A resin bed 1·4 cm × 14·5 cm was used.

Reagents

Lead nitrate solution (~5 mg lead per ml): 3·9965 g of lead nitrate (Merck and Co. Inc., Rahway, N.J.) were dissolved in 500 ml of water. The solution was standardised by the chromate precipitation method.[7]

Buffer solution (pH 9·96): 67·5 g of ammonium chloride (E. Merck & Co., Analar) were dissolved in 570 ml of ammonium hydroxide (sp.gr. 0·88) and diluted to 1 litre with water.

Dowex 50W-X8 (Dow Chemical Co., Midland, Mich. U.S.A.): 50-100 mesh hydrogen-form cation-exchange resin. The resin was conditioned by repeated washes with $4M$ nitric acid, followed by water. After being filled, the column was washed at a flow rate of 2 ml per min with $4M$ nitric acid and then with water till the effluent became acid-free. At the conclusion of the runs, the resin was withdrawn from the column, air-dried, dried in an oven at 100° for 1–2 hr and weighed.

RESULTS AND DISCUSSION

Ion-exchange behaviour studies

An aliquot of the lead nitrate solution containing 26·5 mg of lead was passed through the column at a rate of 2 ml per min. The resin was washed with 50 ml of water and then the lead was eluted with 200 ml of different eluents. The latter included nitric acid (1, 2, 3, 4, and $6M$), ammonium acetate (1, 3, and $4M$), sodium nitrate ($1M$, $2M$ and $2M$ + $0{\cdot}5M$ nitric acid), tartaric acid (5% at pH 4 and at pH 6), citric acid (5% at pH 3 and at pH 5), ethylenediaminetetra-acetic acid (disodium salt, $0{\cdot}01M$ at pH 4·5) and perchloric acid ($2M$). In each case the elution rate was 2 ml per min and the eluate was collected in 50-ml fractions. With the mineral acid eluents, each fraction was evaporated to dryness in a beaker. The residue was taken up with 5 ml of water, and 10 ml of buffer (pH 9·96) were added. A twentyfive-ml excess of ethylenediaminetetra-acetic acid (disodium salt) was added and the excess of EDTA was back titrated with standard magnesium sulphate solution using Eriochrome Black T (1:100 in sodium chloride) as an indicator.[8] The complexometric titration was also carried out in the analyses of products involving tartrate and EDTA as eluents, but avoided in the other elutions (Nos. 2, 3 and 5) because of the difficulty in pH adjustment. In these cases lead was directly precipitated from each fraction of the eluate as lead chromate and was determined iodometrically.[8] It was found that the chromate method could equally well be applied to runs with nitric acid after evaporating the eluate to dryness to remove the acid.

The elution constant, E, for each eluting agent is calculated from the relation[9]

$$E = \frac{d\,.\,A}{V}$$

where V is the volume of eluent (corrected for free column volume of liquid in the resin bed) which is required to displace lead under essentially equilibrium conditions through a distance d cm in a column of cross-sectional area A cm^2. The free column volume in this work was found to be 10·8 ml. An additional correction (7 ml) for V is required in order to make allowance for the volume of liquid existing from the bottom of the resin bed to the tip of delivery tube. The results are shown in Table I. The elution curves obtained with nitric acid, ammonium acetate and sodium nitrate are illustrated as histograms in Fig. 1.

Quantitative elution of lead^{II} was possible with 200 ml of nitric acid (2–$6M$), ammonium acetate (1–$4M$), sodium nitrate ($2M$) as the eluting agents. In Fig. 1 the elution peak is seen to be gradually shifted towards the left with increased eluent concentration. Where the elution peak was observed in the second fraction, the latter was further fractionated into fractions of 25 ml each to trace the exact position of the peak (*e.g.*, $2M$ nitric acid and $1M$ ammonium acetate). When the peak was observed in the first 50-ml fraction, it was inevitably in the second 25-ml portion of this lot since the first 17·8 ml of the effluent was due to free column volume plus the extra liquid in the column. In Nos. 4 and 6 of Table I the lead recovery was incomplete with 200 ml of the eluting agents and the

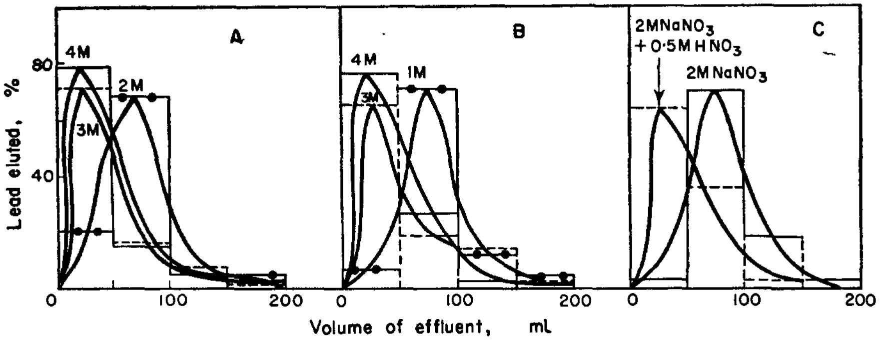

FIG. 1.—Elution of lead^{II} on Dowex 50W-X8
A. HNO_3 B. CH_3COONH_4 C. $NaNO_3$

TABLE I. BEHAVIOUR OF LEAD^{II} TOWARDS VARIOUS ELUTING AGENTS.
Lead = 26·5 mg.
Wt. of oven dried resin = 9·230 g.

No.	Eluting agents	Lead recovery, % 50-ml fractions of effluent				Total lead recovery, %	Elution constant
		I	II	III	IV		
1	HNO_3, 1*M*	2·3	2·3	5·7	5·1	15·4	—
	HNO_3, 2*M*	16·7	70·1	6·2	5·1	98·1	0·390
	HNO_3, 3*M*	72·6	16·4	7·0	1·3	97·3	0·693
	HNO_3, 4*M*	78·9	15·0	5·1	3·7	102·7	0·693
	HNO_3, 6*M*	84·6	7·6	10·1	3·7	106·0	0·693
2	CH_3COONH_4, 1*M*	5·3	74·8	15·1	2·1	97·3	0·390
	CH_3COONH_4, 3*M*	68·1	18·7	16·0	2·1	104·9	0·693
	CH_3COONH_4, 4*M*	78·5	25·1	1·3	0·5	105·4	0·693
3	$NaNO_3$, 1*M*	3·3	3·6	4·6	6·0	17·5	—
	$NaNO_3$, 2*M*	3·5	73·9	18·5	2·9	98·8	0·271
	$NaNO_3$, 2*M* with 0·5*M* HNO_3	67·1	36·0	1·3	0·8	105·2	0·693
4	Tartaric acid 5% (pH = 4·0)	...	...	...	...	19·0	—
	Tartaric acid 5% (pH = 6·0)	1·7	12·8	42·2	11·6	68·3	0·169
5	Citric acid 5% (pH = 5·2)	5·4	29·1	51·5	7·5	93·5	0·169
6	$HClO_4$, 2*M*	...	...	...	...	5·7	—
7	CH_3COOH, 4*M*	—	—	—	—	2·5	—
8	EDTA, 0·01*M* (pH = 4·5)	48·4	23·9	16·9	6·6	95·8	0·693

Each result represents the average of at least duplicate runs.

elution peaks were not ascertained, since a large volume of eluent was required for this purpose. The elution constants (Table I) give a measure of the relative efficiencies of the various eluents, and from them the eluting agents can be arranged in order of decreasing efficiency: ammonium acetate > nitric acid > sodium nitrate > EDTA > citric acid > tartaric acid. For routine work ammonium acetate (1–4M) is preferred owing to ease of direct precipitation and determination of lead as chromate. The whole operation takes from 4 to 5 hr. Among organic acid eluents acetic acid has been found to be a very poor eluting agent.

Ion-exchange separations

The separations are based on the fact that ammonium acetate is a good eluent for lead^{II} but fails to elute some cations like barium, strontium and aluminium. Secondly, lead^{II} does not form a complex with citric acid at pH ~ 3·0 or with EDTA (disodium salt) at pH ~ 2–3. Hence cations which give rise to anionic complexes with these reagents at proper pH can easily be separated from lead^{II} by passage through a cation-exchange column.

Separation from strontium, barium and aluminium

A mixture of lead^{II} and an excess of strontium, barium or aluminium nitrate was adsorbed on the ion-exchange column. After washing with water (50 ml), lead^{II} was selectively eluted with 200 ml of 1M ammonium acetate. This was followed by elution of the other cations in the resin bed with 200 ml of 4M hydrochloric acid. Lead^{II} was determined as chromate, as before. In this manner lead can be separated from four times its amount of barium, strontium and aluminium.

Separation from cerium and zirconium

Cerium^{IV} (as ceric nitrate) and zirconium^{IV} (as zirconyl nitrate) were converted to anionic complexes[10] with 5% citric acid at pH 2·7. The mixture with lead^{II}, after this pre-treatment, was poured down the Dowex 50 bed upon which the anionic complex was eluted. The resin was washed with water (50 ml) and lead^{II} was eluted with ammonium acetate as usual. Clear-cut separations were achieved in this way.

TABLE II. ION-EXCHANGE SEPARATIONS

No.	Taken, *mg*		Lead found, *mg*	Lead recovery, %
1	Pb	34·73	32·83	94·5
	Ba	132·12		
2	Pb	14·88	14·30	96·1*
	Ba	132·12		
3	Pb	34·73	34·89	100·2
	Sr	132·12		
4	Pb	34·73	32·72	94·2
	Al	138·8		
5	Pb	34·73	33·98	97·9
	Ce^{IV}	132·12		
6	Pb	34·73	34·37	99·0
	Zr^{IV}	69·60		
7	Pb	14·88	14·62	98·2*
	Bi^{III}	29·0		
8	Pb	34·73	32·82	94·5
	Fe^{III}	68·0		
9	Pb	14·88	14·15	95·1*
	Th^{IV}	67·50		
10	Pb	14·88	15·10	101·4*
	Th^{IV}	140·0		

* Lead determined iodometrically.
Each result represents the average of at least duplicate runs.

Separations from bismuth, iron and thorium

Mixtures of lead^{II} with bismuth^{III}, iron^{III} or thorium^{IV} nitrate were treated with 0·01*M* EDTA and adjusted to pH 2·0–2·2. This transformed the cations other than lead into anionic complexes, rendering the separation quite easy. The mixtures were passed through the resin bed (Na^+ form). In each case the effluent fraction containing lead^{II} was evaporated to dryness with nitric and perchloric acids to destroy any EDTA present, since this interferes in the chromate precipitation.

The separation of lead from barium is significant since the latter is the principal interference in the routine analysis of lead as chromate. Iron, and, to a less extent, bismuth, are associated with lead in minerals and some industrial products, and therefore their elimination by ion-exchange is important. Attempts to separate copper^{II}, mercury^{II} and zinc from lead by complexing the former as cyanide at pH 10 in presence of tartrate were not successful, since at this pH tartrate itself was found to elute lead. The recovery of the latter was therefore poor. However, the isolation of lead from large amounts of thorium provides an attractive feature of this method because the former is the stable end-product of radioactive minerals. The total operations in the proposed method require only 3–4 hr. The results are reproducible to within ±3%.

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Zusammenfassung—Das Verhalten von Bleiionen an einem Kationenaustauscher wurde studiert, wobei verschiedene eluierende Reagenzien verwendet wurden. Trennung von Ba, Sr, Al, Ce(IV), Zr, Bi, Fe(III) und Th wurde ermöglicht.

Résumé—Le comportement du plomb(II) sur un échangeur de cations a été étudié, en utilisant une série d'éluants. Des séparations de Ba, Sr, Al, Ce(IV), Zr, Bi, Fe(III) et Th ont été réalisées.

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DIE CHELOMETRISCHE TITRATION DES TITANS IN GEGENWART VON NIOB UND TANTAL

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Zusammenfassung—Es wird über die Existenz eines Komplexes des Peroxytitanylions mit 1,2-Diaminocyklohexan-N,N,N',N'-tetraessigsäure berichtet. Diese Chelatverbindung wird für eine titrimetrische Bestimmungsmethode des Titans ausgenutzt, bei der eine überschüssige DCTA-Menge mit Kupferlösung zurückgemessen wird. Als Indikator wird PAN verwendet. Die Methode ist im Gegansatz zu den sonst gebräuchlichen chelatometrischen Titanbestimmungen auch in Gegenwart von Niob und Tantal anwendbar.

EINE Trennung des Titans von Niob und Tantal zählt auch heute noch zu den schwierigen und zeitraubenden Aufgaben der analytischen Chemie. Es sollte daher untersucht werden, ob man durch eine chelometrische Titration des Titans neben Niob und Tantal in der Lage ist, eine Trennung der Elemente zu umgehen.

Es ist bekannt, dass Ionen des vierwertigen Titans mit ÄDTA Chelate bilden[1], die jedoch nur innerhalb eines relativ geringen pH-Bereiches beständig sind.[2] Die Reaktionsgeschwindigkeit des Titans mit ÄDTA ist gering und es besteht Neigung zur Hydrolyse, wobei es zur Ausfällung von Titanoxydhydrat kommt.

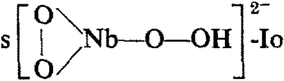
Obwohl nur Rücktitrationsverfahren und keine direkten Methoden angewendet wurden, führte dies oft zu empfindlichen Störungen der ÄDTA-Titration des Titans.[3]

Niob und Tantal fallen unter den Bedingungen der Titantitration beinahe vollständig aus. Zusatz von Hilfskomplexbildnern wie Tartrat, Citrat, Oxalat oder Fluorid verhindert wohl die Ausfällung sämtlicher drei Elemente, jedoch sind die entsprechenden Titankomplexe mit diesen Ionen stabiler als das Titankomplexonat.

Es wurde bereits von Sweetser u. Bricker[14] sowie von Lieber[4] gefunden, daß sich Titanlösungen mit Wasserstoffperoxydzusatz im Vergleich zu Titanylsalzlösungen wesentlich besser titrieren lassen, und daß keine Neigung zur Hydrolyse besteht. Das im sauren Milieu existente Peroxytitanyl-Ion[5,6] ist offenbar befähigt mit ÄDTA ein stabileres Chelat zu bilden. Diese Annahme wird durch die Angaben von Musha und Ogawa[7] bestätigt, die für den Komplex $[TiO(H_2O_2)Y]^{2-}$ einen log. K-Wert von 20,43 angeben, während für [TiY] 17,7 bzw. $[TiOY]^{-2}$ 17,3 gefunden wurden.[1] Obige Autoren berichten auch als einzige über eine direkte ÄDTA-Titration des Titans, wobei die Endpunktsindikation auf photometrischem Wege erfolgt. Auch über eine photometrische Bestimmungsmethode des Ti als $[TiO(H_2O_2)Y]^{-2}$ wird berichtet.

Sajo[8] und Wilkins[9] benützten ebenfalls die Existenz des Peroxytitanyl-ÄDTA-Komplexes zur Titanbestimmung mit ÄDTA über Rücktitrationsverfahren mit Zn- bzw. Cu-Lösungen. Das Peroxytitanyl-ÄDTA-Chelat ist nur im schwach sauren Bereich stabil. Musha und Ogawa[7] stellten fest, daß dieser Bereich zwischen pH 0,4 und 4 liegt. Im alkalischen Milieu liegt das Titan als $[Ti(O_2)_4]^{4-}$- Anion vor[5], welches nicht mehr mit ÄDTA zu reagieren vermag. Dieser Umstand wurde von Wehber[10] zur

Maskierung des Titans bei komplexometrischen Titrationen anderer Metalle bei pH 10 ausgenützt.

Über eine etwa vorhandene Komplexbildung zwischen Niob und ÄDTA bzw. Tantal und ÄDTA wurde unseres Wissens noch an keiner Stelle berichtet. Wir konnten jedoch feststellen, daß das Niob, dessen Reaktionsanalogie zum Titan bekannt ist, in wasserstoffperoxydhaltiger Lösung ein dem Titan sehr ähnliches Verhalten zeigt. Nach Sieverts und Müller[11] bzw. Adler u. Hiskey[12] liegt in schwach saurem Medium das Niob in Gegenwart von Wasserstoffperoxyd als  $\left[\begin{array}{l} O\diagdown \\ |\quad Nb{-}O{-}OH \\ O\diagup \end{array}\right]^{2-}$-Ion vor. Wir konnten nun feststellen, daß solche Lösungen auf Zusatz von ÄDTA eine deutliche Gelbfärbung aufweisen. Ferner verdrängen Peroxyniobylionen bei pH 3–4 Kupferionen aus ihrem ÄDTA-Komplex. Damit ist eindeutig erwiesen, daß zwischen ÄDTA und Peroxyniobylionen Komplexbildung eintritt.

Versuche, diesen Umstand zu einer komplexometrischen Titrations-methode des Niobs auszunützen, in dem ein gemessener ÄDTA-Überschuß mit Kupferlösung gegen PAN-Indikator rücktitriert werden sollte, scheiterten an einem über 1 ml Maßlösung schleppendem Umschlagt. Ebenfalls führten Versuche mit verschiedenen anderen Indikatoren und anderen Metallsalzlösungen als Rücktitriermittel zu keinem besseren Ergebnis.

An Tantallösungen konnten keinerlei derartige Erscheinungen festgestellt werden.

Aus dem oben Gesagten geht bereits hervor, daß eine Titanbestimmung auf komplexometrischem Weg in Gegenwart von Niob nicht möglich ist. Arbeitet man ohne Wasserstoffperoxydzusatz, so treten Fällungen auf, während in Gegenwart von Wasserstoffperoxyd Niob zumindest teilweise an ÄDTA gebunden wird und außerdem der Indikatorumschlag am Titrationsendpunkt sehr schleppend und unbrauchbar wird.

Die erwähnten Peroxytitanyl- bzw. Peroxyniobyl-ÄDTA-Chelate sind gelb gefärbt, während Tantal unter denselben Bedingungen keinerlei Färbung aufweist. Im weiteren wurde versucht, durch photometrische Messungen einerseits die Beständigkeitsbereiche dieser Verbindungen in Abhängigkeit vom pH-Wert festzustellen, andererseits an Stelle von ÄDTA einige andere, bekannte Aminopolycarbonsäuren hinsichtlich ihrer Reaktionen mit Titan und Niob zu untersuchen.

In Abb. 1 ist die Extinktion der Peroxytitanyl- und Peroxyniobyl-ÄDTA-Chelate in Abhängigkeit vom pH-Wert eingetragen. Wie bereits auf Grund der oben erwähnten Titrationsversuche zu erwarten war, haben beide Komplexe ungefähr denselben Beständigkeitsbereich. Im Gegensatz zu Musha und Ogawa[7] steht die Tatsache, daß die Kurve des $[TiO(H_2O_2)Y]^{2-}$ erst bei pH 8 einen deutlichen Knick aufweist, was bedeutet, daß das Chelat auch über pH 4 stabil ist. Dies wird auch durch die Erfahrungen von Sajo[8] und Wilkins[9] bestätigt, die bei Rücktitrationsverfahren immer einen pH-Wert von etwa 4–5 angewandt haben.

Abb. 2 zeigt dieselben Untersuchungen an Lösungen, die statt ÄDTA Dipicolinsäure (DPS), Nitrilotriessigsäure (NTE), Äthylenglykol-bis-(β-amino-äthyläther-(ÄGTA) und 1,2-Diaminocyklohexan-N,N,N^1,N^1-tetraessigsäure (DCTA) enthielten. Es ist ersichtlich, daß DPS, ÄGTA und NTE im untersuchten Bereich keine sehr stabilen Komplexe mit Peroxytitanylionen bilden, wohl aber DCTA. Peroxyniobylionen zeigen mit DCTA ebenfalls jedoch nur zwischen pH 1 und 5 Chelatbildung, während das Titanchelat zwischen pH 2 und 7 stabil ist.

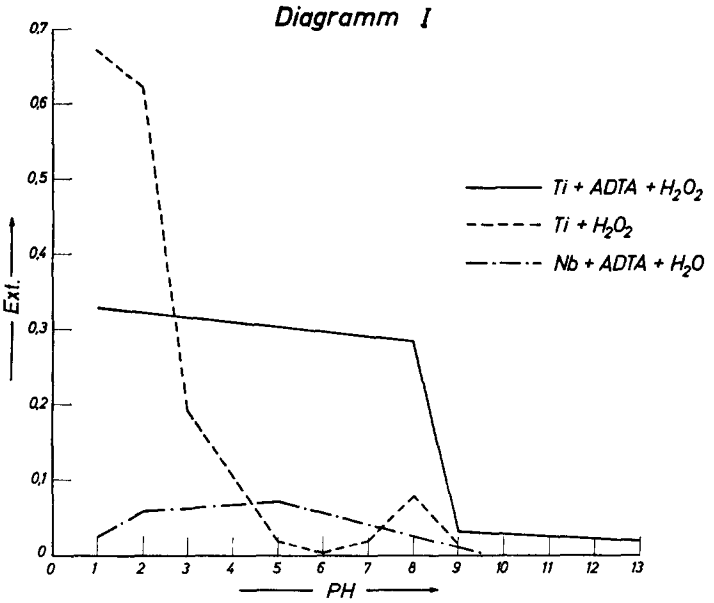


ABB. 1.—2 ml 0,05 m Ti-Lösung, 1 ml 5% ig ÄDTA-Lösung, 1 ml H_2O_2 30% ig in 100 ml. ELKO II Photometer, Küvette 2 cm, Filter Hg 436

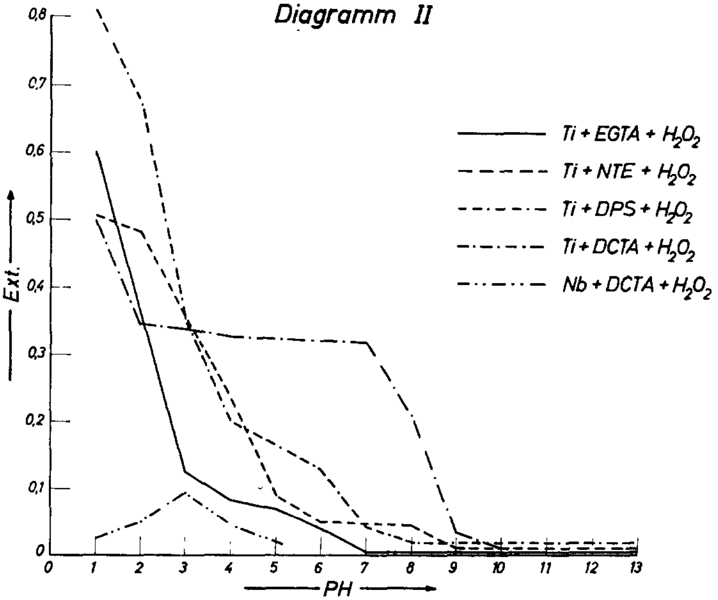


ABB. 2.—2 ml 0,05 m Ti-Lösung, 1 ml 5% ige Aminopolycarbonsäure, 1 ml H_2O_2 30% ig in 100 ml
ELKO II Photometer, Küvette 2 cm, Filter Hg 436

Daraus ergab sich die Möglichkeit mit DCTA Titan neben Niob und Tantal entweder auf photometrischem Weg bei pH 5–6 oder auf maßanalytischem Weg bei pH 4–5 zu bestimmen.

Über Untersuchungen zur photometrischen Bestimmung werden wir in Kürze in einer weiteren Veröffentlichung berichten.

Versuche wasserstoffperoxydhaltige Titanlösungen mit einem gemessenen Überschuß an DCTA-Lösung zu versetzen und anschließend mit Kupfermaßlösung gegen PAN rückzutitrieren, verliefen befriedigend. Als günstiger pH-Wert wurde 5–5,2 festgestellt. Dieser pH-Wert kann auch leicht durch Acetatpufferung konstant gehalten werden.

Bei Niob- und Tantal-haltigen Lösungen wird in Gegenwart von H_2O_2 eine vorgelegte DCTA-Menge bei Titration mit Kupferlösung vollstänständig wiedergefunden. Eine Beeinträchtigung des Indikatorumschlages durch Niob und Tantal konnte nicht festgestellt werden.

Auf Grund der bereits bekannten, im Vergleich zu ÄDTA geringeren Reaktionsgeschwindigkeit der DCTA[13] und der geringen Wasserlöslichkeit des Cu-PAN-Chelats ist einerseits erhöhte Temperatur (70–90°C), andererseits langsameres Titrieren, als bei ähnlichen Titrationsmethoden mit ÄDTA erforderlich.

Bei Verwendung von 0,05 m Lösungen ist der Farbumschlag am Titrationsendpunkt noch schärfer als bei der Titration von Cu mit ÄDTA und auf Bruchteile eines Tropfens genau erkennbar. Auf Grund der relativ intensiven Gelbfärbung des Peroxytitanyl-DCTA-Chelats erscheint der Farbumschlag des Indikators nicht wie normal von Gelb nach Blauviolett, sondern von Gelb nach Rotviolett. Bei höheren Titankonzentrationen empfiehlt es sich daher in größerer Verdünnung zu arbeiten.

Dicarbonsäuren, wie z.B. Weinsäure, Oxalat, ferner Fluorid, wirken störend, da sie das Titan teilweise oder vollständig maske iren.

Da man gezwungen is bei erhöhter Temperatur zu arbeiten, ist es nicht unbedingt notwendig, Alkohol zur besseren Löslichkeit des Cu-PAN-Chelats zuzusetzeh. Be Gegenwart von Niob und Tantal kommt es auf Alkoholzusatz oft zu Trübungen der Lösung durch ausfallende Erdsäurehydrate. Trotzdem werden richtige Resultate für Ti erhalten und auch der Farbumschlag erscheint in der gewohnten Schärfe.

Störungen durch Fremdionen wurden nicht untersucht, da sich eine Abtrennung der Elemente Nb, Ta und Ti von übrigen Begleitelementen meist nicht umgehen läßt. Die Methode laßt sich in den Mikrobereich übertragen, gibt jedoch dabei in Gegenwart von Nb und Ta keine genauen Resultate.

Apparate und Reagenzien

Sämtliche photometrischen Messungen wurden mit einem ELKO-II-Photometer der Fa.C.Zeiss, Oberkochen, durchgeführt. Zu den pH-Messungen diente ein Titrator TTT1 der Fa.Radiometer, Kopenhagen. Die Maßlösungen wurden in Halbmikrobüretten (Teilung in 0,02 ml) gehandhabt.

0,05 *m-Kupferlösung:* 12,485 g $CuSO_4 \cdot 5H_2O$ wurden in Wasser gelöst und im Meßkolben auf 1 Liter aufgefüllt. Die genaue Titerstellung erfolgte durch Titration mit ÄDTA.

0,05 *m-DCTA-Lösung:* 17,3173 g der freien Säure wurden in Wasser durch Zugabe von NaOH in Lösung gebracht und zum Liter aufgefüllt. Die Titerstellung erfolgte durch Titration mit obiger Cu-Lösung bei pH 5,5 und PAN-Indikator.

0,05 *m Titanlösung:* 12,005 g $K_2[TiF_6]$ wurden in der Platinschale mit H_2SO_4 abgeraucht und sodann mit verdünter Schwefelsäure im Meßkolben zum Liter aufgefüllt.

PAN-Indikatorlösung: 0,1 % ige Lösung in Alkohol. Lösungen von Niob und Tantal wurden aus einsten Metallen durch Lösen mit Salpetersäure-Flußsäure und nachherigem Abrauchen mit Schwefelsäure hergestellt.

Essigsäure (1:1), Ammoniaklösung (35% ig), Methanol, Wasserstoffperoxyd (30% ig), Natriumacetat fest.

Arbeitsvorschrift

Die stark schwefelsäure Probelösung (5–20 mg Ti) wird mit 1–2 ml Wasserstoffperoxyd und einem gemessenen Überschuß an DCTA-Lösung versetzt. Nach Zugabe von 2–3 g Natriumacetat bringt man mit Wasser auf ein Volumen von etwa 150 ml. Mit Ammoniak bringt man auf pH 5,0–5,2 (Spezialindikatorpapier) und erwärmt auf 70–90°C. Die heiße Lösung wird nun nach Zusatz von 7–8 Tropfen PAN langsam mit Kupferlösung bis zum bleibenden Farbumschlag von Gelb nach Rotviolett und dann mit DCTA-Lösung auf Gelb titriert. Mehrmalige Endpunktseinstellung empfiehlt sich zur Verringerung des Fehlers. Es sei nochmals darauf hingewiesen, daß langsames Titrieren unbedingt erforderlich ist. Enthält die Probelösung mehr als 15 mg Ti, so verdünnt man auf etwa 300 ml.

Berechnung: (ml 0,05 m DCTA-ml 0,05 m Cu) . 2,3 g 5 = mg Ti.

Resultate

In Tabelle I sind eine Reihe von Ergebnissen, die nach obiger Arbeitsvorschrift erhalten wurden, zusammengestellt. Wei ersichtlich, ist im Mittel mit einer Abweichung von ±0,012 ml 0,05 m DCTA-Lösung zu rechnen. Dies entspricht einem mittleren absoluten Fehler von ±0,025 mg Ti bzw. bei Titanmengen von 5–20 mg einem relativen Fehler von 0,1–0,5%.

TABELLE I. VERSUCHSERGEBNISSE, MITTELWERTE AUS JE ZWEI ENDPUNKTSEINSTELLUNGEN

ml 0,05 m Lösungen			mg Ti			neben mg
Ti	DCTA	Diff.	geg.	gef.	Diff.	
2,63	2,635	+0,005	6,30	6,310	+0,010	—
4,80	4,780	−0,020	11,50	11,450	−0,050	—
0,50	0,515	+0,015	1,20	1,235	+0,035	10 Nb
2,00	2,010	+0,010	4,79	4,815	+0,025	10 Nb
2,00	2,010	+0,010	4,79	4,815	+0,025	56 Nb
2,97	2,970	—	7,12	7,120	—	28 Nb
2,98	2,965	−0,015	7,14	7,105	+0,035	10 Nb
4,00	4,010	+0,010	9,58	9,600	+0,020	20 Nb
6.00	5,990	−0,010	14,37	14,345	−0,025	28 Nb
8,00	7,990	−0,010	19,16	19,135	−0,025	37 Nb
2,00	2,000	—	4,79	4,790	—	72 Ta
2,00	1,990	−0,010	4,79	4,775	−0,025	72 Ta
2,00	2,010	+0,010	4,79	4,815	+0,025	109 Ta
2,00	1,990	−0,010	4,79	4,765	−0,025	18 Ta, 10 Nb
2,00	1,990	−0,010	4,79	4,765	−0,025	36 Ta, 19 Nb
2,00	1,980	−0,020	4,79	4,740	−0,050	109 Ta, 19 Nb
ml 0,005 m Lösungen						
1,00	1,01	+0,01	0,239	0,241	+0,002	—
2,00	2,015	+0,015	0,479	0,483	+0,004	—
5,00	4,99	−0,01	1,197	1,195	−0,002	—
8,00	7,98	−0,02	1,916	1,912	−0,004	—

Gegenwart von 50 mg Niob und 100 mg Tantal zeigt keinerlei Störungen.

Die neue Methode bietet gegenüber den bisher gebräuchlichen Verfahren (Trennung durchmehrmaliges Fällen, Chromatografie, Extraktion usw.) zweifellos durch ihre Einfachheit und dem geringen Zeitbedarf große Vorteile, ohne daß dadurch ein größerer Fehler in Kauf genommen werden muß.

Summary—The existence of a complex between diaminocyclohexanetetra-acetic acid and the peroxytitanyl ion is reported. This chelate compound is used in a titrimetric procedure for titanium, in which excess of DCTA is back-titrated with copper solution to a PAN end-point. In contrast with other chelometric procedures for titanium, there is no interference from niobium and tantalum.

Résumé—Les auteurs indiquent l'existence d'un complexe entre l'acide diaminocyclohexane tétracétique et l'ion peroxytitanyl. Ce chelate est utilisé dans une titrimétrie du titane où l'excès de DCTA est titré en retour par une solution de cuivre jusqu'au point équivalent (PAN) A l'opposé des autres méthodes de dosage du titane par formation de complexes, celle-ci n'est pas gênée par le niobium ou le tantale.

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CONTRIBUTIONS AU PROBLEME DE LA DETERMINATION DU POINT D'EQUIVALENCE—I

UNE NOUVELLE METHODE DE CALCUL DU POINT D'EQUIVALENCE DANS LES TITRAGES LINEAIRES

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Résumé—On décrit une nouvelle méthode générale pour la détermination du point d'équivalence dans la titration linéaire, fondée sur le calcul analytique du point d'intersection des deux droites. Les coefficients des équations des deux droites (l'ordonnée à l'origine et le coefficient angulaire) sont déterminés par la méthode des moindres carrés, indépendamment des adjonctions de réactif. De cette manière, on opère aux droites les plus probables (les droites optima), de sorte qu'on ôte tout facteur subjectif qui pourrait intervenir dans le traçage graphique et qui se concrétise parfois par des erreurs bien fortes.

DANS l'analyse titrimétrique on suit la variation d'une certaine propriété de la solution comme fonction de l'addition de la solution de réactif. Si la propriété étudiée est proportionnelle (variation linéaire) à la concentration d'un des composants de la solution, la courbe de titrage est exprimée par deux droites, ayant un point commun (le point d'intersection) dont les coordonnées sont le volume de réactif qui correspond à l'équivalence, c'est-à-dire le point d'équivalence, d'autre part la valeur de la propriétée étudiée, au point d'équivalence.

De cette catégorie de titrages, dits linéaires[1], nous rappelons les titrages conductométriques, réfractométriques, radiométriques[2], ampérométriques, hétérométriques[3], chronopotentiométriques[4], etc.

Pour déterminer le point d'équivalence dans le titrage linéaire, ont été proposés les procédés suivants:

(1) *La méthode graphique*

Après avoir exécuté le titrage on trace à l'aide d'une règle les deux droites; celle jusqu'au point d'équivalence et celle après ce point.

Il arrive que surtout dans le voisinage du point d'équivalence il y a des points qui ne sont pas compris ni par l'une des droites, ni par l'autre. Généralement on laisse ces points de côté.

On voit bien que le procédé graphique pour déterminer le point d'équivalence dans le titrage linéaire est sujet à des erreurs bien fortes.

Une source d'erreurs est due à l'échelle de la courbe. Pour montrer ceci, considérons le titrage conductométrique suivant[5], dont les valeurs figurent dans le tableau no. I.

Il en résulte que le volume d'équivalence sera compris entre 1,2 et 2,4 ml.

Nous ferons deux graphiques. Dans tous les deux, on prendra, sur l'abscisse 50 mm pour 1 ml. Sur l'ordonnée, pour l'un des cas on prendra 2 mm pour chaque unité de n (n + la valeur lue au galvanométre); le volume d'équivalence obtenu par l'intersection des deux droites sera de 1,8 ml (courbe a, fig. 1). Pour le second cas, on prendra sur l'ordonnée 10 mm pour chaque unité de la valeur lue (n). Le volume d'équivalence graphiquement déterminé sera de 2,20 ml (courbe b, fig. 1), donc de 23,6 % plus fort qu'au premier cas et de 0,5 % plus fort que la valeur (2,19 ml) indiquée dans le présent mémoire.

TABLEAU I.
LA TITRATION DU KCl AU $NaClO_4$

$NaClO_4$, *ml*	$\sqrt{n}$	$NaClO_4$, *ml*	$\sqrt{n}$	$NaClO_4$, *ml*	$\sqrt{n}$
0,2	9,05	1,2	6,33	3,2	8,00
0,4	8,70	2,4	6,58	3,4	8,53
0,6	8,30	2,6	6,78	3,6	9,02
0,8	7,98	2,8	7,11	3,8	9,58
1,0	6,60	3,0	7,50	4,0	10,05

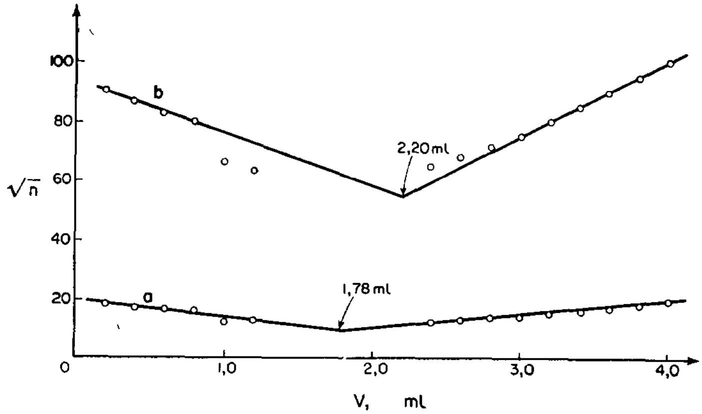

FIG. 1.

Cette grande différence provient du fait, qu'au deuxième cas, les deux derniers points avant le point d'équivalence et les deux premiers après, ne se rangent pas sur la droite et ont été abandonnés.

Même en employant une grande échelle on commet des erreurs lorsqu'on trace les deux droites, donc lorsqu'on détèrmine le point d'équivalence selon cette méthode très employée encore, il faut l'avouer à regret.

(2) *La méthode par calcul*

(a) D'après la méthode de J. H. Boulard[6], on calcule analytiquement le point d'intersection des deux droites, en tenant compte seulement des deux derniers points avant l'équivalence et des deux premiers après.

Cette méthode peut conduire à des résultats fort erronés, comme nous l'avons constaté précédemment.

(b) La méthode de E. Grünwald[7] s'applique seulement aux courbes linéaires de titration, qui n'ont pas un point final anguleux pour indiquer un changement de pente. C'est le cas où le composé résultant de la réaction est peu stable; hydrolysé, soluble, dissocié, etc.

La méthode emploie la partie de la courbe de titration voisine du point d'équivalence. Elle est basée sur le fait que pour n'importe quels deux points de la courbe de titrage avant et tout près de l'équivalence, il y a deux points conjugués sur la courbe, après l'équivalence, de la sorte que les droites tracées par ces deux paires de points se coupent au point d'équivalence.

On choisit d'abord trois points voisins du point d'équivalence (deux avant et un après le point d'équivalence, déterminé graphiquement), puis on détermine par calcul le quatrième point (le deuxième conjugué, après le point d'équivalence). Par interpolation on obtient le quatrième point.

On exprime les quatre points conjugués (volumes de solution titrante) par fractions du volume d'équivalence (déterminé d'abord par voie graphique). Puis on établit les équations des deux droites et on calcule analytiquement leur intersection; on obtient une première valeur pour le point d'équivalence, sous- ou surunitaire. En multipliant par le volume d'équivalence obtenu par voie graphique, on établit maintenant la première valeur calculée pour le volume d'équivalence.

En continuant, on répète le procédé, en employant la nouvelle valeur calculée du point d'équivalence et en prenant d'autres points voisins du volume d'équivalence. On continue avec les approximations jusqu'à ce que plusieurs valeurs du point d'équivalence ainsi calculées soient suffisamment rapprochées; on considère leurs moyenne arithmétique comme valeur définitive du volume d'équivalence.

Il est facile de voir que cette méthode ressemble à celle de Boulard[6], dont elle diffère seulement par le fait que le second point (le quatrième conjugué) par lequel passe la droite après le point d'équivalence, est obtenu par calcul.

On doit remarquer que la formule de calcul pour le quatrième point conjugué a été établie seulement pour le domaine voisin du point d'équivalence, domaine où la pente de la courbe de titration est variable. De plus, la déduction suppose qu'on se trouve dans l'immédiat voisinage de l'équivalence (on néglige la concentration de l'un des participants à la réaction). Tout ceci nous oblige à avoir suffisamment de points expérimentaux pour nous en servir dans les calculs.

Pour finir, cette méthode, sans employer la méthode des moindres carrés ne peut être appliquée qu'aux titrations linéaires, où il y a une variation de la pente près du point d'équivalence et suffisamment de points expérimentaux.

(c) La méthode de J. Mika[8] emploie la méthode des moindres carrés, d'après le procédé du centre de pesanteur de A. Milasovszky[9].

Quoique cette méthode ait un fondement théorique irréprochable, elle peut être employée seulement pour des adjonctions égales de réactif.

(d) Dans ce qui suit, nous exposerons les principes d'une méthode générale pour déterminer le point d'équivalence dans la titration linéaire, en employant la méthode des moindres carrés, à des adjonctions quelconques de réactif.

De toutes ses courbes qu'on peut tracer à l'aide de plusieurs points, la plus probable, la courbe optimum est celle qui satisfait à la relation

$$\sum_{k=1}^{n} (y - y_k)^2 = \text{minimum} \qquad (1)$$

où y_k sont des valeurs expérimentales et y sont les valeurs de la fonction

$$y = A_0 + A_1 x + A_2 x^2 + \ldots + A_m x^m$$

obtenues en substituant x par les valeurs expériment les x_k.

Supposons que la dépendance des valeurs lues x_k des additions de réactif x_k, puisse être représentée par une fonction du type:

$$y = f(x) = A_0 + A_1 x + A_2 x^2 + \ldots + A_m x^m$$

où $A_0, A_1, \ldots, A_m$ sont des coéfficients constants qu'on doit déterminer.

Le phénomène étudié, c'est-à-dire un titrage linéaire, peut être représenté par une équation du premier degré $y = A_0 + A_1 x$, comme c'est le cas dans le titrage linéaire, après avoir écrit la condition (1) sous la forme:

$$f(x) = [(A_0 + A_1 x) - y_1]^2 + [(A_0 + A_1 x_2) - y_2]^2 \\ + \ldots + [(A_0 + A_1 x_m) - y_n]^2 = \text{minimum}$$

on annule les dérivées partielles par rapport à A_0 et A_1; on obtient[10] les équations suivantes, dites normales, en A_0 et A_1:

$$nA_0 + A_1 \sum_{k=1}^{n} x_k = \sum_{k=1}^{n} y_k$$

$$A_0 \sum_{k=1}^{n} x_k + A_1 \sum_{k=1}^{n} x_k^2 = \sum_{k=1}^{n} x_k y_k$$

Si on se sert de n_1 points expérimentaux pour le calcul de l'équation de la droite ($y = A_0 + A_1 x$) avant le point d'équivalence et de n_2 points expérimentaux pour la droite après le point d'équivalence ($y' = A_0' + A_1' x$), les solutions de ce système d'équations normales, seront:

$$A_0 = \frac{\sum_{k=1}^{n_1} x_k^2 \sum_{k=1}^{n_1} y_k - \sum_{k=1}^{n_1} x_k \sum_{k=1}^{n_1} x_k y_k}{n_1 \sum_{k=1}^{n_1} x_k^2 - \left(\sum_{k=1}^{n_1} x_k\right)^2} \tag{2}$$

$$A_1 = \frac{n_1 \sum_{k=1}^{n_1} x_k y_k - \sum_{k=1}^{n_1} x_k \sum_{k=1}^{n_1} x_k}{n_1 \sum_{k=1}^{n_1} x_k^2 - \left(\sum_{k=1}^{n_1} x_k\right)^2} \tag{3}$$

respectivement

$$A_0' = \frac{\sum_{k=1}^{n_2} x_k^2 \sum_{k=1}^{n_2} y_k - \sum_{k=1}^{n_2} x_k \sum_{k=1}^{n_2} x_k y_k}{n_2 \sum_{k=1}^{n_2} x_k^2 - \left(\sum_{k=1}^{n_2} x_k\right)^2} \tag{4}$$

$$A_0' = \frac{n_2 \sum_{k=1}^{n_2} x_k y_k - \sum_{k=1}^{n_2} x_k \sum_{k=1}^{n_2} y_k}{n_2 \sum_{k=1}^{n_2} x_k^2 - \left(\sum_{k=1}^{n_2} x_k\right)^2} \tag{5}$$

On calcule le point d'équivalence analytiquement en mettant

$$A_0 + A_1 x = A_0' + A_1' x,$$

d'où

$$x = \frac{A_0 - A_0'}{A_1' - A_1} = \text{le volume d'équivalence } V_e. \qquad (6)$$

Mode opératoire

On fait un graphique à une échelle suffisamment grande et on effectue les calculs pour déterminer les coefficients A_0, A_1, A_0' et A_1' en laissant de côté les points qui s'en écartent trop. Puis à l'aide de la formule (6), on calcule le volume d'équivalence comme le point d'intersection des deux droites.

Calculons maintenant le point d'équivalence dans quelques titrages linéaires en employant la méthode proposée.

(*a*) *Le titrage thermométrique de* 100 ml *de sulfate acide de biguanidine* 10^{-1} N *par* NaOH N^{11}; V = 11,70 ml

TABLEAU II

NaOH, *ml*	Variation de la température, °C	NaOH, *ml*	Variation de la température, °C	NaOH, *ml*	Variation de la température, °C
1,0	0,11	8,0	0,61	13,0	0,83
2,0	0,20	9,0	0,67	13,5	0,83
3,0	0,29	10,0	0,73	14,0	0,825
4,0	0,35	11,0	0,78	14,5	0,82
5,0	0,43	11,5	0,82	15,0	0,82
6,0	0,49	12,0	0,83	16,0	0,81
7,0	0,55	12,5	0,83	16,5	0,81

Dans le calcul des coefficients A_0 et A_1, on a laissé de côté deux points (1,0 — 0,11; 2,0 — 0,20), les plus écartés d'une droite.

Les résultats obtenus sont: $A_0 = 11{,}3333$; $A_1 = 6{,}1565$; $A_0 = 89{,}5347$; $A_1' = -0{,}5176$ et $V_e = 11{,}72$ ml; donc une différence de +0,17% (par rapport à 11,70 ml).

(*b*) *Le titrage thermométrique de* 100 ml *de* H_2SO_4 1,266 . 10^{-1} N *par* NaOH N^{11}. V_e = 14,80 ml

TABLEAU III

NaOH, *ml*	Variation de la température, °C	NaOH, *ml*	Variation de la température, °C	NaOH, *ml*	Variation de la température, °C
1,0	0,06	8,0	0,77	14,0	1,38
2,0	0,17	9,0	0,87	14,5	1,43
3,0	0,27	10,0	0.97	15,0	1,46
4,0	0,37	11,0	1,07	15,5	1,46
5,0	0,48	12,0	1,17	16,0	1,46
6,0	0,58	13,0	1,28	17,0	1,45
7,0	0,67	13,5	1,34	18,0	1,45

Dans les calculs, nous nous sommes servis de tous les points. Les résultats obtenus sont: $A_0 = -3{,}4048$; $A_1 = 10{,}0948$; $A_0' = 152{,}3440$; $A_1' = -0{,}4130$ et $V_e = 14{,}82$ ml, donc une différence de $+0{,}14\,\%$ (par rapport à 14,80 ml).

(*c*) *Le titrage de l'acide bilianique* (*solution alcoolique*) *par* NaOH[12]; $V_e = 1{,}065$ ml.

TABLEAU IV

NaOH, *ml*	0,4	0,6	0,8	1,0	1,2	1,6	2,0	2,4
n (divisions au galvanomètre)	1,1	1,8	2,4	2,9	4,0	6,4	8,55	11,3

Dans le calcul, nous avons tenu compte de tous les points. En voilà les résultats: $A_0 = -0{,}05$; $A_1 = 3{,}00$; $A_0' = -3{,}32$; $A_1' = 6{,}088$ et $V_e = 1{,}059$ donc une différence de $+0{,}6\,\%$ (par rapport à 1,065 ml).

(*d*) *Le titrage de* 100 ml *de* H_3PO_4 5 . 10^{-2} N *par* NaOH 5,6 . 10^{-1} N[13] $V_e' = 0{,}75$ ml; $V_e'' = 1{,}55$ ml.

TABLEAU V

NaOH, *ml*	$\frac{100-a}{a}$	NaOH, *ml*	$\frac{100-a}{a}$
0,2	27,88	1,6	24,15
0,4	20,77	1,8	29,45
0,6	13,98	2,0	35,20
0,8	10,04	2,2	41,10
1,0	13,48	2,4	46,80
1,2	16,81	2,6	52,80
1,4	20,12	2,8	58,70

Pour le calcul, nous nous sommes servis de tous les points. Les résultats pour le premier point d'équivalence, sont les suivants: $A_0 = 33{,}3766$; $A_1 = -31{,}7500$; $A_0' = -3{,}3565$; $A_1' = 16{,}7900$ et $V_e' = 0{,}76$ ml, donc une différence de $+1{,}3\,\%$ (par rapport à 0,75 ml). Voilà les résultats pour le deuxième point d'équivalence: $A_0 = -3{,}3565$; $A_1 = 16{,}7900$; $A_0' = -22{,}4517$; $A_1' = 28{,}9196$; $V_e = 1{,}57$ ml, donc une différence de $+1{,}3\,\%$ (par rapport à 1,55 ml).

(*e*) *Le titrage de* 5 ml *de* I_2 10^{-1} N + 30 ml *d'eau par* $Na_2S_2O_3$ 10^{-1} N[14] $V_e = 4{,}35$ ml.

TABLEAU VI

$Na_2S_2O_3$, *ml*	$\frac{100-a}{a}$	$Na_2S_2O_3$, *ml*	$\frac{100-a}{a}$
0,7	0,626	4,9	1,013
1,4	0,710	5,6	1,063
2,1	0,770	6,3	1,107
2,8	0,835	7,0	1,151
3,5	0,894	7,7	1,238
4,2	0,942	9,1	1,283

Nous avons fait usage de tous les points dans le calcul. Les résultats sont les suivants: $A_0 = 0{,}5765$; $A_1 = 0{,}0905$; $A_0' = 0{,}7045$; $A_1' = 0{,}0636$ et $V_e = 4{,}76$ ml, donc une différence de $+8{,}6\%$ (par rapport à 4,35 ml).

CONCLUSIONS

Nous donnons une nouvelle méthode générale pour la détermination du point d'équivalence dans le titrage linéaire, fondée sur le calcul analytique du point d'intersection des deux droites. Les coefficients des équations des deux droites (l'ordonnée à l'origine et le coefficient angulaire) sont déterminés par la méthode des moindres carrés, indépendamment des adjonctions de réactif. De cette manière, on opère aux droites les plus probables (les droites optima), de sorte qu'on ôte tout facteur subjectif qui pourrait intervenir dans le tracé graphique et qui se concrétise parfois par des erreurs bien fortes.

Le point d'équivalence ainsi déterminé représente la valeur la plus probable (optimum); il reflète véritablement les conditions de travail et peut être considéré comme ayant le caractère d'une moyenne arithmétique.

Il faut mentionner le fait que la méthode décrite peut être employée aussi pour calculer les coordonnées du point de changement dans tout procès dont le développement peut être figuré par une "courbe" constituée de deux droites ayant un point d'intersection (propriété-action) (propriété-composition).

Summary—A new general method is described for the determination of the point of equivalence in a linear titration, based on the calculation of the point of intersection of two straight lines. The coefficients of the equations of the two straight lines (the ordinate at the origin and the angular coefficient) are determined by the method of least squares, independently of additions of reagent. In this way the most probable straight lines are used, thus removing any subjective factors which might affect a graphical derivation, and which on occasion can produce quite large errors.

Zusammenfassung—Eine neue, allgemeine Methode wird beschrieben um den Äquivalenzpunkt in einer linearen Titration zu ermitteln. Die Berechnung hat die Ermittelung des Schnittpunktes zweier Geraden zum Ziele. Die Koeffizienten in den Gleichungen der beiden Geraden (Ordinatenhöhe für Nullwert der Abscisse sowie Steigung) werden nach der Methode der kleinsten Quadrate bestimmt, unabhängig von der Zugabe von Reagens. Hierdurch wird erzielt, dass die wahrscheinlichsten Geraden verwendet werden. Subjektive Faktoren in der graphischen Auswertung werden vermieden, und so manchmal recht beträchliche Ausmasse erreichende Fehler ausgeschlossen.

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CONTRIBUTIONS AU PROBLEME DE LA DETERMINATION DU POINT D'EQUIVALENCE—II

UNE NOUVELLE METHODE POUR DETERMINER LE COEFFICIENT REEL D'ASYMETRIE DANS LES TITRAGES POTENTIOMETRIQUES

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Résumé—On donne une nouville methode pour le calcul du coefficient réel d'asymétrie u dans la titration potentiométrique. Dans ce but on calcule par la méthode des moindres carrés les coefficients angulaires A_1 et A_1' des deux droites obtenues par la linéarisation de la courbe potentiométrique avant et après le point d'équivalence.

Suivant la méthode décrite, le coefficient réel d'asymétrie est calculé par la méthode des moindres carrés et à l'aide des données de titration éloignées du point d'équivalence; sa valeur a le caractère d'une moyenne arithmétique.

On sait de la théorie générale du titrage potentiométrique que le point d'inflexion de la courbe (volume d'inflexion V_i) ne coïncide avec le point d'équivalence (volume d'équivalence V_e) qu'au cas des titrage dits symétriques[1].

Si on considère le titrage général $mA + nB$, c'est-à-dire le titrage de la substance A par B, le rapport $\frac{m}{n} = \mu$ s'appelle coefficient d'asymétrie[1] et il faut en tenir compte dans le calcul du point d'équivalence[1-3].

On considère comme symétrique un titrage lorsque la courbe en est symétrique, c'est-à-dire si on faisait tourner de 180° le titrage de la courbe d'après le point d'inflexion, celle-ci serait l'image (au moins dans le voisinage de ce point) dans un miroir, passant par le point d'inflexion et perpendiculaire au plan de la figure, de l'autre branche de la courbe.

Considérons deux points sur la courbe de titrage, d'un côté et de l'autre du point d'équivalence, deux points dits équivalents, de telle sorte que dans ce stade du titrage ou les concentrations des réactif soient égales, par exemple Cl^- à Ag^+, ou les rapports de leurs concentrations à leur produit de réaction soient égaux (réactions rédox), par exemple:

$$\frac{[Fe^{2+}]}{[Fe^{3+}]} \quad \text{et} \quad \frac{[MnO_4^-]}{[Mn^{2+}]}$$

Si on a la titration

$$m\,\mathrm{red}_2 + n\,\mathrm{ox}_1 \rightleftharpoons m\,\mathrm{ox}_2 + n\,\mathrm{red}_1$$

on considère deux points d'un côté et de l'autre du point d'équivalence, de sorte que dans ces stades on ait:

$$\frac{[\mathrm{red}_2]}{[\mathrm{ox}_2]} = \frac{[\mathrm{ox}_1]}{[\mathrm{red}_1]}$$

Pour une certaine valeur de ces rapports, les potentiels seront E_n et E_m, c'est-à-dire:

$$E_n = E_{0_2} - \frac{0{,}058}{n} \log \frac{[\mathrm{red}_2]}{[\mathrm{ox}_2]} = E_{0_2} - \frac{B}{n}, \text{ respectivement}$$

$$E_m = E_0 +_1 \frac{0{,}058}{p} \log \frac{[\mathrm{ox}_1]}{[\mathrm{red}_1]} = E_{0_1} + \frac{B}{n}$$

(nous avons pris $0{,}058 \log \frac{[\mathrm{red}_2]}{[\mathrm{ox}_2]} = 0{,}058 \log \frac{[\mathrm{ox}_1]}{[\mathrm{red}_1]} = B$)

Pour le potentiel au point d'équivalence, on a l'expression $E_e = \frac{mE_{0_1} + nE_{0_2}}{m+n}$, de sorte qu'on peut calculer le rapport des différences du potentiel d'équivalence et des potentiels correspondants aux deux points équivalents.

$$\frac{E_e = E_n}{E_m - E_e} = \frac{\frac{mE_{0_1} + nE_{0_2}}{m+n} - \left(E_{0_2} - \frac{B}{n}\right)}{E_{0_1} + \frac{B}{n} - \frac{mE_{0_1} + nE_{0_2}}{m+n}} = \frac{\frac{m(E_{0_1} - E_{0_2}}{m+n} + \frac{B}{n}}{\frac{m(E_{0_1} - E_{0_2})}{m+n} + \frac{B}{n}} = \frac{m}{n} = \mu$$

Il en résulte que

$$E_0 - E_e = u(E_m - E_n) \tag{1}$$

Donc, pour symétriser la courbe de titrage, c'est-à-dire les variations de potentiel après le point d'équivalence, il faut les multiplier par le coefficient d'asymétrie.

F. L. Hahn et M. Frommer ont montré[1] que généralement le coefficient réel d'asymétrie, calculé en employant la notion de points équivalents, ne coïncide pas avec le coefficient théorique.

Le coefficient réel d'asymétrie sera celui des valeurs du rapport $(E_e - E_n)/(E_m - E_e)$, pour lequel, en prenant deux valeurs E_n et E_m, on obtient deux résultats rapprochés. Aux deux valeurs E_n et E_m correspondent deux adjonctions de réactif avant, et deux après le point d'équivalence.

La différence entre le coefficient théorique et celui réel d'asymétrie est facile à comprendre pour les titrages où apparaissent des réactions d'un degré de molécularité supérieur à trois. Le plus souvent la réaction globale est la somme de plusieurs réactions et probablement que la plus lente détermine le coefficient réel d'asymétrie.

Même au cas des plus simples réactions comme les neutralisations ou les précipitations, le coefficient réel d'asymétrie peut être différencié de celui théorique. L'instauration lente des équilibres (réactions de précipitation, etc.), l'asymétrie de fonctionnement de l'électrode indicatrice sont causes générales de l'asymétrisation même des titrations qui font usage de réactions symétriques, c'est-à-dire où $m = n$.

Dans le même ordre d'idées, nous mentionnons[4] l'oxydation de l'électrode de platine pendant la titration rédox a Ce^{4+} et CrO_4^{2-}.

Dans ce qui suit nous donnerons une autre méthode pour le calcul du coefficient réel d'asymétrie, basé sur la méthode des moindres carrés.

Le fondement théorique de la méthode est constitué par la transformation de la courbe logarithmique (coordonnées $E - V$) en courbe linéaire d'après le procédé

G. Gran[5], non seulement jusqu'au point d'équivalence en coordonnées $\Delta V/\Delta E - (V + \frac{1}{2}\alpha \cdot \Delta V)$, mais aussi après ce point, en coordonnées $\Delta V/\Delta E - (V - \frac{1}{2}\alpha \cdot \Delta V)$, ou $\alpha = \dfrac{\Delta V}{|v_i - V|}$

Le volume d'inflexion v_i peut être déterminé avec une précision suffisante par l'une des méthodes de calcul connues.[6,7,etc]. Au besoin et surtout au cas d'adjonctions inégales de réactif au voisinage du point d'équivalence, le volume d'infléxion v_i peut être déterminé aussi graphiquement, en figurant la courbe de titrage à une échelle suffisamment grande.

On passe maintenant à la représentation graphique et on calcule par la méthode des moindres carrés les équations de deux droites, $y = A_0 + A_1 x$ et $y = A_0' + A_1' x$ en laissant de côté les points trop écartés de la droite.

Puisque $\dfrac{E_e - E_n}{E_m - E_e} = u$, il en résulte que pour symétriser la courbe de titrage logarithmique, c'est-à-dire pour que la droite après le point d'équivalence ait la même pente que la droite avant ce point, $y = A_0 + A_1 x$, on doit multiplier par les variations de potentiel après le point d'équivalence. On obtient ainsi la droite $y = A_0'' + A_1'' x$.

Il faut prendre, dans les solutions des équations normales, $\dfrac{\Delta V}{u \cdot \Delta E} = y_{\text{sym}}$ au lieu de $\dfrac{\Delta V}{\Delta E} = y$. Par conséquent

$$\sum_{k=1}^{n_2} y_{\text{sym}} = \frac{y_1}{u} + \frac{y_2}{u} + \ldots + \frac{y_{n2}}{u} = \frac{1}{u} y_k$$

On obtient ainsi

$$A_0'' = \frac{\frac{1}{u}\left(\sum\limits_{k=1}^{n_2} x_k^2 \sum\limits_{k=1}^{n_2} y_k - \sum\limits_{k=1}^{n_2} x_k \sum\limits_{k=1}^{n_2} x_k x_k\right)}{n_2 \sum\limits_{k=1}^{n_2} x_k^2 - \left(\sum\limits_{k=1}^{n_2} x_k\right)^2} = \frac{A_0'}{u} \tag{3}$$

et

$$A_1'' = \frac{\frac{1}{u}\left(\sum\limits_{k=1}^{n_2} x_k y_k - \sum\limits_{k=1}^{n_2} x_k \sum\limits_{k=1}^{n_2} x_k\right)}{n_2 \sum\limits_{k=1}^{n_2} x_k^2 - \left(\sum\limits_{k=1}^{n_2} x_k\right)^2} = \frac{A_1'}{u} \tag{4}$$

comme conclusion

$$u = \frac{A_0'}{A_0''} = \frac{A_1'}{A_1''}$$

Il est évident qu'après la symétrisation, la droite $y = A_0'' + A_1'' x$ aura la même pente que la droite avant le point d'équivalence $y = A_0 + A_1 x$. Il en résulte que $A_1'' = A_1$ et donc

$$u = \frac{|A_1'|}{|A_1|} \tag{5}$$

(Puisque les signes n'ont aucune signification dans ce cas, on prend les valeurs absolues des coefficients angulaires des deux droites).

Donc le coefficient réel d'asymétrie est le rapport des pentes des deux droites résultant de la linéarisation de la courbe logarithmique.

Si pour calculer le coefficient on a pris pour le volume d'inflexion v_i une valeur approximative il est évident que la valeur de u contiendra elle-même une certaine incertitude. Un calcul rigoureux du point d'inflexion s'impose. Dans ce but on calcule les coefficients A_0, A_1, A_0' et A_1' des deux droites: $y = A_0 + A_1 x$ avant le point d'équivalence et $y = A_0' + A_1' x$ après à l'aide des n_1 paires de valeurs $x - y$, $\left[\frac{\Delta V}{\Delta E} - (v + \frac{1}{2}\alpha \cdot \Delta V)\right]$ respectivement n_2 paires de valeurs $x - y$, $\left[\frac{\Delta V}{\Delta E} - (v - \frac{1}{2}\alpha \cdot \Delta V).\right]$ On obtient (Note I-ère, même revue p.

$$A_0 = \frac{\sum_{k=1}^{n_1} x_k \sum_{k=1}^{n_1} y_k - \sum_{k=1}^{n_1} x_k \sum_{k=1}^{n_1} x_k y_k}{n_1 \sum_{k=1}^{n_1} x_k^2 - \left(\sum_{k=1}^{n_1} x_k\right)^2} \tag{6}$$

$$A_1 = \frac{n_1 \sum_{k=1}^{n_1} x_k y_k - \sum_{k=1}^{n_1} x_k \sum_{k=1}^{n_1} y_k}{n_1 \sum_{k=1}^{n_1} x_k^2 - \left(\sum_{k=1}^{n_1} x_k\right)^2} \tag{7}$$

$$A_0' = \frac{\sum_{k=1}^{n_2} x_k^2 \sum_{k=1}^{n_2} y_k - \sum_{k=1}^{n_2} x_k \sum_{k=1}^{n_2} x_k y_k}{n_2 \sum_{k=1}^{n_2} x_k^2 - \left(\sum_{k=1}^{n_2} x_k\right)^2} \tag{8}$$

$$A_1' = \frac{n_2 \sum_{k=1}^{n_2} x_k y_k - \sum_{k=1}^{n_2} x_k \sum_{k=1}^{n_2} y_k}{n_2 \sum_{k=1}^{n_2} x_k^2 - \left(\sum_{k=1}^{n_2} x_k\right)^2} \tag{9}$$

On trouve le point d'intersection, c'est-à-dire le volume d'inflexion v_i en calculant analytiquement, en mettant

$$A_0 + A_1 x = A_0' + A_1' x.$$

On obtient

$$x = \frac{A_0 - A_0'}{A_1' - A_1} = V_i \tag{10}$$

V_i ainsi obtenu sert à calculer le coefficient α et les nouvelles abscisses y, $V + \frac{1}{2}\alpha \cdot \Delta V$ respectivement $V - \frac{1}{2}\alpha \cdot \Delta V$. A l'aide des nouvelles valeurs A_1' et A_1 on calcule la valeur définitive de u.

Calculons maintenant le coefficient réel d'asymétrie dans le cas de quelques titrages potentiométriques.

(1) *Le titrage de* 10 ml *de solution de l'acide gluconique* $7{,}687 \cdot 10^{-2}$N *par* NaOH $2{,}5 \cdot 10^{-1}$N[8]

TABLEAU I

NaOH, *ml*	1,50	2,00	2,50	2,75	3,00	3,06	3,12	3,18	3,25	3,50	4,00
E, mV	212	229	256	284	341	392	632	664	674	698	721

Pour le calcul des abscisses, respectivement pour le calcul d'α, on prend la valeur $v_i = 3{,}09$ ml, déterminée d'après F. L. Hahn et G. Weiller[6]

TABLEAU II

V, ml	E, mV		
3,00	341		
		> 51	
3,06	392		> 189
		> 208	
3,12	632		> 208
		> 32	
3,18	664		——
			397

$$v_i = 3{,}06 + 0{,}06\,\frac{189}{397} = 3{,}06 + 0{,}029 \approx 3{,}09 \text{ ml.}$$

Les résultats de l'élaboration mathématique sont contenus dans le tableau no. III, Les points 2,533 — 89,2 et 3,205 — 70,0 n'ont pas été employés.

TABLEAU III

NaOH ml	E mV	$\alpha = \dfrac{\Delta V}{\lvert v_i - V\rvert}$	$\frac{1}{2}\alpha \cdot \Delta V$	$V + \frac{1}{2}\alpha \cdot \Delta V$ $V - \frac{1}{2}\alpha j \cdot \Delta V$ x	$\dfrac{\Delta V}{\Delta E} \cdot 10^4$ y	Résultats
1,50	212	0,314	0,079	1,579	294,1	($v_i = 3{,}09$ ml)
2,00	229	0,459	0,116	2,115	185,2	
2,50	256	0,424	0,053	2,553	89,2	$A_1 = -195{,}87$
2,75	284	0,735	0,093	2,842	43,8	
3,06	392	0,667	0,020	3,020	11,8	$A_1' = 279 \cdot 65$
3,12	632	0,667	0,014	3,166	18,7	$M = \dfrac{279{,}65}{195{,}87} = 1{,}42$
3,18	664	0,438	0,015	3,235	70,0	
3,25	674	0,610	0,076	3,424	104,2	$A_0 = 601{,}53$
3,50	698					
4,00	721	0,549	0,137	3,863	217,3	$A_0 = -860{,}77$

A l'aide de la formule (10), on obtient pour le volume d'inflexion $v_i = 3{,}075$ ml, valeur qui par élaboration ultérieure conduit à $A_1 = -195{,}48$; $A_1' = 250{,}54$ et $u = 1{,}44$.

Il en résulte donc qu'il suffit d'un seul calcul utilisant le v_i obtenu par la méthode Hahn-Weiller ou graphiquement (en cas d'adjonctions inégales de réactif au voisinage immédiat du point d'équivalence).

Si on met en oeuvre le même titrage, mais en prenant les volumes de 0,50 en 0,50 ml ($\Delta V = 0{,}50$ ml) et qu'on emploie pour le calcul de α, $v_i = 3{,}225$ ml (d'après Hahn-Weiller), on obtient $A_1 = -212{,}65$; $A_1' = 309{,}19$ et $u = 1{,}45$.

(2) *Le titrage du sulfate ferreux par* $KMnO_4$ 10^{-1}N *en solution de* H_2SO_4 1N[9]

On prend $v_i = 21{,}175$ ml (calculé d'après Hahn-Weiller). Les résultats de l'élaboration mathématique de cette titration sont contenus dans le tableau no. IV.

TABLEAU IV

$KMnO_4$ *ml*	ω (ohms comp.)	$\alpha = \frac{\Delta V}{\lvert v_t - V \rvert}$	$\frac{1}{2}\alpha \cdot \Delta V$	$V + \frac{1}{2}\alpha \cdot \Delta V$ $V - \frac{1}{2}\alpha \cdot \Delta V$	$\frac{\Delta\omega}{\Delta V} \cdot 10^4$	Résultats
20,00	200	0,5106	0,1534	20,1534	600,0	(v_t = 21,175 ml)
20,60	210					
		0,6087	0,1065	20,7065	350,0	
20,95	220					
		0,4444	0,0222	20,9722	100,0	
21,05	230					$A_1 = -603,13$
		0,4000	0,0100	21,0600	50,0	
21,10	240					
		0,6667	0,0167	21,1167	50,0	
21,15	250					$A_1' = 1053,15$
21,18	360					
		0,8571	0,0129	21,1971	3,3	
21,21	450					$u = \frac{1053,15}{603,13} = 1,75$
		0,5333	0,0107	21,2393	13,3	
21,25	480					
		0,4444	0,0133	21,2967	60,0	
21,31	490					$A_0 = 12 \cdot 776,17$
		0,6823	0,0989	21,5011	290,0	
21,60	500					
		0,7384	0,4430	22,3570	1200,0	$A_0' = -22 \cdot 348,75$
22,80	510					

Pour ce même titrage, F. L. Hahn et M. Frommer[10], par leur méthode d'approximations successives à l'aide des valeurs du voisinage immédiat du point d'équivalence ont trouvé $u = 1,85$.

CONCLUSIONS

On donne une nouvelle méthode pour le calcul du coefficient réel d'asymétrie dans les titrages potentiométriques. Dans ce but on calcule par la méthode des moindres carrés les coefficients angulaires A_1 et A_1' des deux droites obtenues par la linéarisation de la courbe potentiométrique avant et après le point d'équivalence.

Il est évident que le calcul du coefficient réel d'asymétrie seulement à l'aide des données du voisinage immédiat du point d'équivalence[1], où les variations du potentiel sont bien fortes, des erreurs même négligeables dans l'évaluation des volumes de réactif entraînent de fortes erreurs dans la valeur de u.

Suivant la méthode décrite, le coefficient réel d'asymétrie est calculé par la méthode des moindres carrés et à l'aide des données de titrage éloignées du point d'équivalence; sa valeur a le caractère d'une moyenne arithmétique.

Summary—A new method is described for determining the real coefficient of asymmetry, u, in a potentiometric titration. For this purpose, the angular coefficients, A_1 and A_1' of the two straight lines obtained by linearising the potentiometric curve before and after the point of equivalence by the method of least squares are calculated. Using the method described, the real coefficient of asymmetry is calculated by the method of least squares with the help of titration results obtained some distance from the equivalence point. The value of the coefficient has the nature of an arithmetic mean.

Zusammenfassung—Eine neue Methode wird beschrieben um den tatsächlichen Assymetriekoeffizienten, u, in einer potentiometrischen Titration zu ermitteln. Zu diesem Zwecke werden die Steigungen, A_1 und A_1' der beiden Geraden ermittelt die man durch Linearisierung der Titrationskurve vor und nach dem Äquivalenzpunkte erhält. Die Methode der kleinsten Quadrate wird angewendet, wobei die experimentallen Punkte in einiger Entfernung vom Äquivalenzpunkt herangezogen werden. Die Koefficienten sind ihrer Natur nach arithmetische Mittel.

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CONTRIBUTIONS A LA DETERMINATION DU POINT D'EQUIVALENCE—III

UNE NOUVELLE METHODE POUR LE CALCUL DU POINT D'EQUIVALENCE DANS LES TITRAGES POTENTIOMETRIQUE

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Résumé—On décrit une nouvelle méthode pour le calcul du point d'équivalence dans la titration potentiométrique. Dans ce but on calcule les équations des deux droites obtenues par la linéarisation de la courbe potentiométrique, avant et après le point d'équivalence, en employant la méthode des moindres carrés. Puis on détermine analytiquement le point d'intersection des deux droites, point que correspond au volume d'inflexion V_i de la courbe de titration. On calcule après, le coefficient réel d'asymétrie u et finalement le volume d'équivalence V_e.

Aucune des méthodes pour la détérmination du poind d'équivalence dans les titrages potentiométriques ne fait usage de la méthode des moindres carrés, pourtant seule une methode de ce genre serait vraiment rigoureuse.

Le fondement théorique de la méthode c'est la transformation de la courbe logarithmique à un point d'infléxion (coordonnées E–V), en courbe linéaire d'après le procédé G. Gran[1], mais pas seulement jusqu'au point d'équivalence, en coordonnées

$$\Delta V/\Delta E - \left(V - \tfrac{1}{2}\alpha \cdot \Delta V\right); \text{ où } \alpha = \frac{\Delta V}{|v_i - V|}$$

Le volume d'inflexion v_i peut être déterminé avec une exactitude suffisante par l'une des méthodes connues[2,3etc]. Au besoin et surtout en cas d'adjonctions inégales de réactif au voisinage du point d'équivalence, le volume d'inflexion v_i peut être déterminé avec une exactitude suffisante graphiquement, après avoir représenté la courbe de titrage à une échelle suffisamment forte, en employant surtout les valeurs au voisinage de l'équivalence.

On trace maintenant les deux droites. On laisse de côté les points trop écartés, on calcule par le procédé des moindres carrés les équations des deux droites: $y = A_0 + A_1x$ jusqu'au point d'inflexion et $y = A_0' + A_1'x$ après ce point. C'est-à-dire on calcule pour n_1 paires de valeurs avant le point d'équivalence les coefficients A_0 et A_1; les coefficients A_0' et A_1' seront calculés à l'aide de n_2 paires de valeurs après le point d'équivalence.

$$A_0 = \frac{\sum_{k=1}^{n_1} x_k^2 \sum_{k=1}^{n_1} y_k - \sum_{k=1}^{n_1} x_k \sum_{k=1}^{n_1} x_k y_k}{n_1 \sum_{k=1}^{n_1} x_k^2 - \left(\sum_{k=1}^{n_1} x_k\right)^2} \tag{1}$$

$$A_1 = \frac{n_1 \sum_{k=1}^{n_1} x_k y_k - \sum_{k=1}^{n_1} x_k \sum_{k=1}^{k_1} y_k}{n_1 \sum_{k=1}^{n_1} x_k^2 - \left(\sum_{k=1}^{n_1} x_k\right)^2} \tag{2}$$

$$A_0' = \frac{\sum_{k=1}^{n_2} x_k^2 \sum_{k=1}^{n_2} y_k - \sum_{k=1}^{n_2} x_k \sum_{k=1}^{n_2} x_k y_k}{n_2 \sum_{k=1}^{n_2} x_k^2 - \left(\sum_{k=1}^{n_2} x_k\right)^2} \tag{3}$$

$$A_1' = \frac{n_2 \sum_{k=1}^{n_2} x_k y_k - \sum_{k=1}^{n_2} x_k \sum_{k=1}^{n_2} y_k}{n_2 \sum_{k=1}^{n_2} x_k^2 - \left(\sum_{k=1}^{n_2} x_k\right)^2} \tag{4}$$

On calcule analytiquement le point d'intersection des deux droites (voir cette revue, p. 21), en mettant $A_0 + A_1 x = A_0' + A_1' x$; il en résulte

$$x = \frac{A_0 - A_0'}{A_1' - A_1} = V_i \tag{5}$$

x représente le volume d'inflexion V_i et non pas le volume d'équivalence V_e, comme dans le cas du titrage linéaire.

$V_i = V_e$ seulement au cas des titrage symétriques$^{4-6}$. Il est évident que par la symétrisation préalable de la courbe de titrage potentiométrique en employant la méthode de linéarisation et le calcul qui s'ensuit et en calculant analytiquement le point d'intersection, on obtiendra le volume d'équivalence et non pas celui d'inflexion.

Pour symétriser la courbe de titrage potentiométrique, il suffit de multiplier les variations de potentiel après le point d'équivalence, par le coefficient réel d'asymétrie u; donc $y_{\text{sym}} = \frac{\Delta V}{\mu \cdot \Delta E} = \frac{y}{u}$.

On obtient ainsi une nouvelle droite $y = A_0'' + A_1'' x$, dont les coefficients A_0'' et A_1'' peuvent être déterminés à l'aide des formules (3) et (4) en y remplaçant les valeurs expérimentales des ordonnées y, par les nouvelles valeurs $\frac{u}{y}$.

On obtient finalement $A_0'' = \frac{A_0'}{u}$ et $A_1'' = \frac{A_1'}{u}$ (voir cette revue, p. 27) et l'équation de la droite résultée par la linéarisation de la partie de la courbe après le point d'équivalence, sera après la symétrisation $y = \frac{A_0'}{u} = \frac{A_1'}{u} x$.

On fait $A_0 + A_1 x = \frac{A_0'}{u} + \frac{A_1'}{u} x$ et on obtient le point d'intersection des deux droites $y = A_0 + A_1 x$ et $y = \frac{A_0'}{u} + \frac{A_1'}{u} x$, dont l'abscisse donne cette fois le point d'équivalence, respectivement le volume d'équivalence V_e. On obtient:

$$x = V_e = \frac{uA_0 - A_0'}{A_1' - uA_1} \tag{6}$$

A_0, A_1, A_0' et A_1' peuvent être calculés à l'aide des formules (1), (2), (3), et (4). Puisque A_1 est toujours négatif et u toujours positif,

$$u = \frac{|A_1'|}{A_1} \quad \text{(voir cette revue, p. 27)} \tag{6'}$$

après avoir remplacé, on obtient:

$$x = V_e = \frac{uA_0 - A_0'}{2A_1'} \tag{7}$$

Si on remplace dans les équations des deux droites non symétrisées l'x par le V_i (5) on obtient l'ordonnée du point d'inflexion y_i, donc:

$$y_i = A_0 + A_1V_i = A_0' + A_1'V_i, \tag{8}$$

puis

$$V_i = \frac{y_i - A_0}{A_1} = \frac{y_i - A_0'}{A_1'} \tag{9}$$

De la même manière, si dans l'équation de la droite $y = A_0 + A_1x$ on remplace x par V_e, on obtient l'ordonnée du point d'équivalence, donc:

$$y_e = A_0 + A_1V_e \tag{10}$$

d'où

$$V_e = \frac{y_e - A_0}{A_1} \tag{11}$$

Il en résulte des formules (9) et (11):

$$V_e = V_i = \frac{y_e - y_i}{A_1} \tag{12}$$

En examinant la figure no. 1, on remarque que le triangle ABC est isocèle, puisque $A_1 = \frac{A_1'}{u}$ et donc $\overline{\text{AN}} = \overline{\text{NB}}$.

Donc $y_e = \frac{y_i}{2} + \frac{y_i - \frac{y_i}{u}}{2} = \frac{uy_i + y_i}{2\mu}$ et en remplaçant dans (12) on obtient:

$$V_e - V_i = \frac{y_i(u - 1)}{2A_1'} \tag{13}$$

Puisque y_i et A_1' sont positifs, pour $u > 1$ la différence $V_e - V_i > 0$ et donc $V_e > V_i$, ce qui résulte aussi de la figure no. 1.

Pour $u < 1$, (fig. 2) $uy_e = y_i - \overline{\text{NB}}$ et $\overline{\text{NB}} = A_1' \cdot \overline{\text{NC}} = A_1'(V_i - V_e) = -A_1'(V_e - V_i)$. Puisque $A_1' = uA_1$ et comme toujours $A_1 < 0$, il en résulte que $\overline{\text{NB}} = uA_1(V_e - V_i)$. Donc

$$y_e = \frac{y_i - uA_1(V_e - V_i)}{u} \qquad \text{et en remplaçant dans} \quad (12)$$

on obtient

$$V_e - V_i = \frac{y_i - uy_i - uA_1(V_e - V_i),}{A_1}$$

respectivement

$$2(V_e - V_i) = \frac{y_i(1 - u)}{A_1} \qquad \text{et finalement}$$

$$V_e - V_i = \frac{y_i(u - 1)}{2A_1'} \tag{13}$$

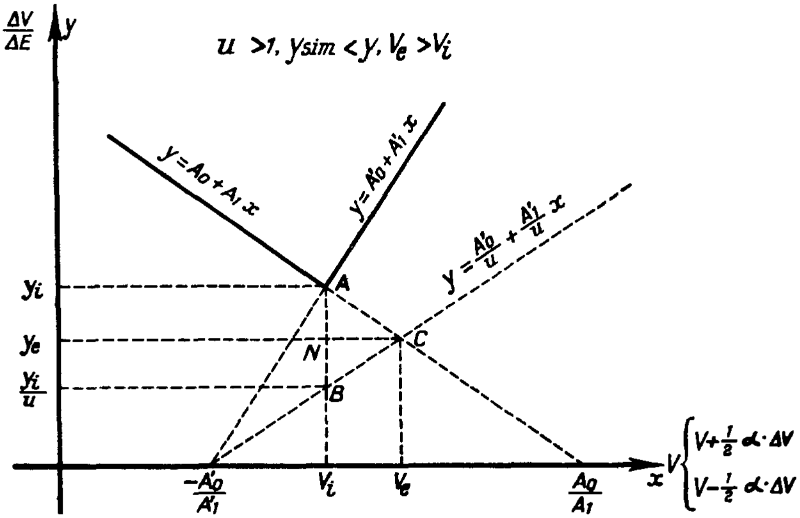

Fig. 1.

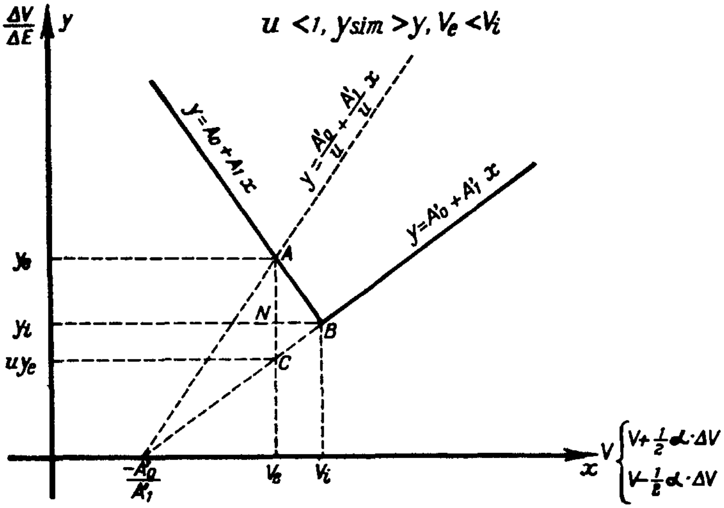

Fig. 2.

Puisque y_i et A_1' sont positifs, pour $u < 1$ la différence $V_e - V_i < 0$ et donc $V_e < V_i$, ce sui résulte aussi de la figure no. 2.

Si l'ordonnée y_i du point d'inflexion (calculée à l'aide de la formule (8) est négative, respectivement lorsque $\frac{A_0}{A_1} < \frac{A_0'}{A_1'}$, pour $u > 1$, on obtient à l'aide de la formule (6), $V_e' < V_i$ (fig. 3) et pour $u < 1$, on obtient $V_e' > V_i$ (fig. 4), ce qui naturellement ne correspond pas à la réalité (c'est à cause de cela qu'on désigne la valeur obtenue par V_e').

Si $y_i < 0$ et si $u > 1$, pour que $V_e > V_i$ et si $u < 1$ pour que $V_e < V_i$, il faut déplacer les deux courbes de sorte que l'ordonnée du point d'inflexion, y_i, ait une

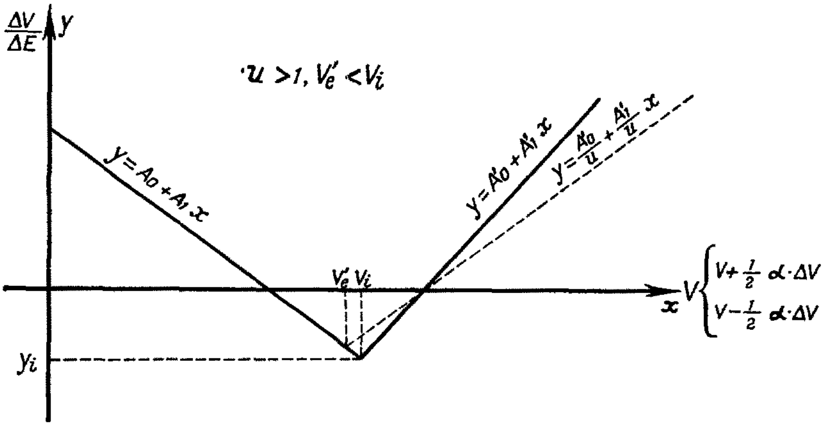

FIG. 3.

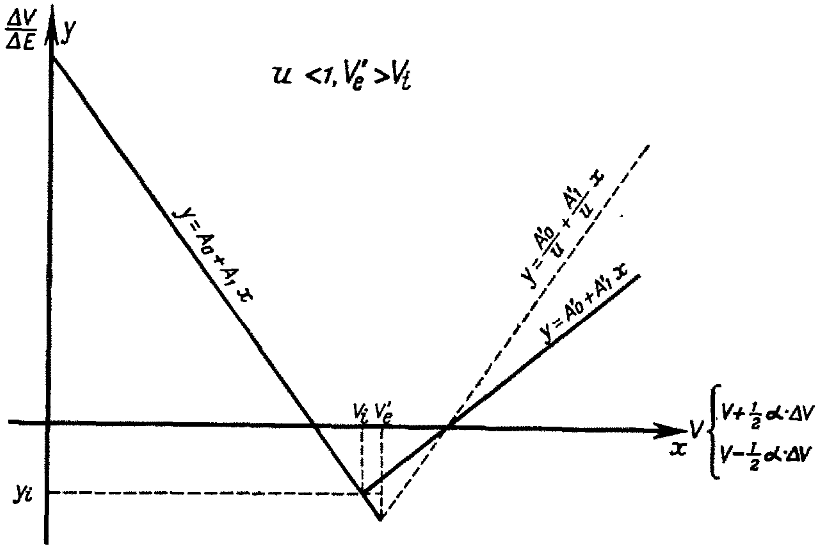

FIG. 4.

valeur positive égale à celle négative, c'est-à-dire $|y_i|$ dépl $= |y_i|$ non dépl. Il en résulte que l'ordonnée à l'origine de la droite $y = A_0 + A_1 x$ doit augmenter en valeur absolue à $2y_i$, et l'ordonnée à l'origine de la droite $y = A_0' + A_1' x$ doit diminuer en valeur absolue de $2y_i$ (fig. 5 et 6).

Puisque toujours $A_0 > 0$ et toujours $A_0' < 0$ et puisque $y_i < 0$, les équations des deux droites seront:

$$y_{\text{dépl.}} = (A_0 - 2y_i) + A_3 x \qquad \text{et}$$

$$y_{\text{dépl.}} = (A_0' - 2y_i) + A_1' x$$

L'équation de la droite symétrisée d'après le point d'équivalence sera:

$$y_{\text{symm. dépl.}} = \frac{A_0' - 2y_i}{u} + \frac{A_0'}{u} x$$

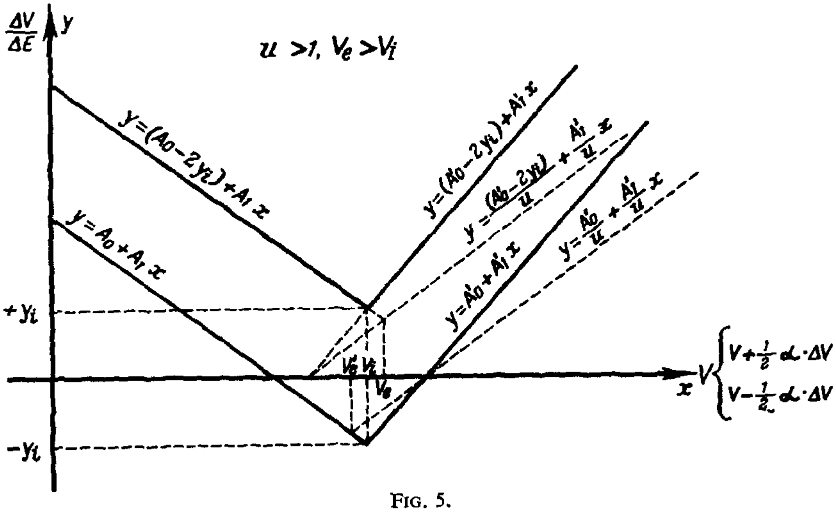

Fig. 5.

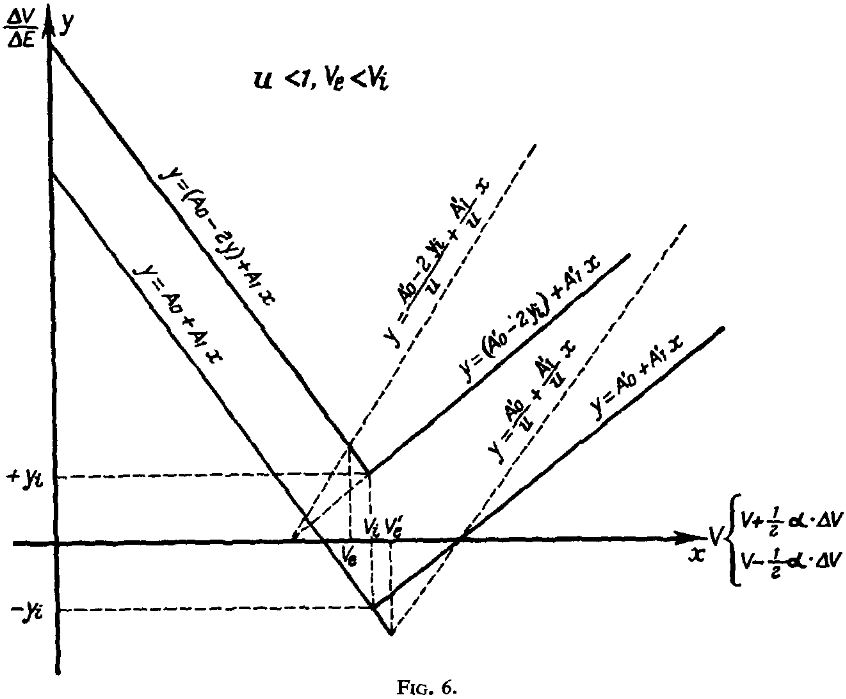

Fig. 6.

Le point d'intersection est maintenant facile à calculer par voie analytique, car il correspond évidemment au volume d'équivalence V_e.

$$(A_0 - 2y_i) + A_1 x = \frac{A_0' - 2y_i}{u} + \frac{A_0'}{u} x$$

Il en résulte que:

$$x = V_e = \frac{uA_0 - A_0'}{A_1' - uA_1} - 2\,\frac{y_i(u-1)}{A_1' - uA_1}$$

Puisque $u = \frac{|A_1'|}{|A_1|}$ et toujours $A_1' < 0$, on obtient finalement

$$V_e = \frac{uA_0 - A_0'}{2A_1'} - 2\frac{y_i(u-1)}{2A_1'} \tag{14}$$

Si on prend $y_i = A_0 + A_1V_i = A_0' + A_1'V_i$ et $u = \frac{|A_1'|}{|A_1|}$ et on remplace dans la formule (14), on obtient:

$$V_e = \frac{uA_0 - A_0' - 2uy_i + 2y_i}{A_1' - uA_1}$$

et puisque toujours $A_1 < 0$, on a:

$$V_e = \frac{u(A_0 - 2y_i) - A_0 + 2y_i}{2A_1'} = \frac{u(A_0 + 2A_1V_i) + A_0' + 2A_1'V}{2A_1'}$$

c'est-à-dire:

$$V_e = V_i - \frac{y_i(u-1)}{2A_1'} \tag{15}$$

respectivement

$$V_e - V_i = -\frac{y_i(u-1)}{2A_1'} \tag{13}$$

Puisque toujours $y_i < 0$, pour $u > 1$ la différence $V_e - V_i > 0$, donc $V_e > V_i$ (fig. 5).

Pour $u < 1$, la différence $V_e - V_i < 0$ et donc $V_e < V_i$ (fig. 6).

Dans tous les quatre cas possibles $\left(y_i > 0 \begin{cases} u > 1 \\ u < 1 \end{cases} \text{et } y_i < 0 \begin{cases} u > 1 \\ u < 1 \end{cases} \right)$ on a pour la différence $V_e - V_i$ la formule

$$V_e - V_i = \frac{y_i(u-1)}{2A_1'} \tag{16}$$

(On prend dans ce cas y_i toujours positifs).

Il en résulte que seulement pour $y_i = 0$, $V_e = V_i = \frac{A_0}{A_1}$, c'est-à-dire le titrage est symétrique ($u = 1$) et donc la méthode G. Gran[1] est valable seulement pour les titrages symétriques. Dans tous les autres cas $\frac{A_0}{A_1} \neq V_e$.

En vérité, la différence $y_{\text{sym}} - y = \frac{\Delta V}{u \cdot \Delta E} - \frac{\Delta V}{\Delta E} = \frac{\Delta V}{\Delta E}\left(\frac{1}{u} - 1\right)$ sera nulle pour $\frac{\Delta V}{\Delta E} = y = A_0' + A_1'x = 0$. Les deux droites concourent sur l'abscisse au même point (voir toutes les figures) et donc seulement pour cette valeur $\frac{A_0'}{A_1'}$ de l'abscisse, admettent le même point d'intersection $\frac{A_0}{A_1}$ avec la droite $y = A_0 + A_1x$.

Calculons maintenant le point d'équivalence au cas de quelques titrages potentiométriques.

(1) *Titrage de* 10 ml *de solution de l'acide gluconique* 7,687 · 10^{-2} N *par* NaOH 2,5 · 10^{-1} N[7].

Pour linéariser, on prend $v_i = 3{,}08$ ml (calculé d'après Hahn-Weiller)[2]; les résultats figurent dans le tableau no. II, cette revue, p. 29.

On obtient: $A_0 = 601{,}53$ (formule 4), $A_1 = -195{,}57$ (formule 2), $A_0 = -860{,}77$ (formule 3), $A_1' = 279{,}65$ (formule 4) et $u = 1{,}42$ (formule 6′).

TABLEAU I

NaOH, *ml*	1,50	2,00	2,60	2,75	3,00	3,06	3,12	3,18	3,25	3,50	4,00
E, *mV*	212	229	256	284	341	392	632	664	674	698	721

Avec ces valeurs on obtient: $V_i = 3{,}075$ ml (formule 5), $y_i = -0{,}77$ (formule 8) et enfin (à l'aide de la formule 13):

$$V_e - V_i = \frac{0{,}77(1{,}42 - 1)}{2 \times 279{,}65} = 0{,}0006$$

c'est-à-dire $V_e = 3{,}075 + 0{,}0006 = 3{,}0756 \approx 3{,}076$ ml.

(2) *Le titrage du sulfate ferreux par* $KMnO_4$ 10^{-1} N *en solution de* H_2SO_4 1 N[8].

TABLEAU II

$KMnO_4$ ml	20,00	20,60	20,95	21,05	21,10	21,15	21,18	21,21	21,25	21,31	21,60	27,80
ω, (ohms comp)	200	210	220	230	240	250	360	450	480	490	500	510

Pour linéariser, on prend $v_i = 21{,}175$ ml calculé d'après Hahn-Weiller (2); les résultats figurent dans le tableau no. 4 IV, cette revue, p. 30.

On obtient $A_0 = 12776{,}17$ (formule 1), $A_1 = -603{,}13$ (formule 2), $A_0' = -22 \cdot 348{,}75$ (formule 3), $A_1' = 1053{,}15$ (formule 4) et $u = 1{,}75$ (formule 6′).

Avec ces valeurs on obtient $V_i = 21{,}20$ ml (formule 5) $y_i = -20{,}28$ (formule 8) et finalement (en employant la formule 13):

$$V_e - V_i \frac{20{,}28(1{,}77 - 1)}{2 \times 1060{,}20} = 0{,}007$$

c'est-à-dire $V_i = 21{,}20 + 0{,}007 = 21{,}207 \approx 21{,}21$ ml.

CONCLUSIONS

On décrit une nouvelle méthode pour le calcul du point d'équivalence dans les titrages potentiométriques. Dans ce but on calcule les équations des deux droites obtenues par la linéarisation de la courbe potentiométrique, avant et après le point d'équivalence, en employant la méthode des moindres carrés. Puis on détermine analytiquement le point d'intersection des deux droites (formule 5), point qui correspond au volume d'infléxion de la courbe de titrage.

On calcule le coefficient réel d'asymétrie u (formule 6′) et finalement le volume d'équivalence V_e (formule 13).

Il est évident que le calcul du volume d'inflexion, par consequent du volume d'équivalence par toutes les méthodes décrites jusqu'ici dans la littérature et qui font usage seulement des données du voisinage immédiat de ce stade du titrage, est sujet à de fortes erreurs. En vérité, dans le voisinage immédiat du point d'équivalence il y a de fortes variations de potentiel; des erreurs même négligeables dans l'évaluation des volumes entraînent des erreurs considérables dans les valeurs de V_i et V_e.

Suivant la méthode décrite, on calcule le volume d'équivalence par la méthode des moindres carrés, en employant les données de titrage éloignées du point d'équivalence et même avec des adjonctions inégales de réactif. Il en résulte que la valeur du volume d'équivalence ainsi trouvée, a le caractère d'une moyenne arithmétique.

Summary—A new method is described for defining the point of equivalence in a potentiometric titration. The equivalence of the two straight lines obtained by linearising the titration curve, before and after the equivalence point, is calculated using the method of the least squares. Then the point of intersection of the two straight lines is determined, this corresponding to an inflection volume V_i of the titration curve. The real coefficient of asymmetry, u, and finally the equivalence volume V_e are then calculated.

Zusammenfassung—Eine neue Methode zur Auffindung des Äquivalentpunktes in potentiometrischen Titrationen wird beschrieben. Die Formel der beiden Gerade nach Linearisierung der Kurve vor und nach dem Endpunkte werden mittels der Methode der kleinsten Quadrate errechnet. Sodann wird der Schnittpunkt der beiden Geraden ermittelt. Dieser Punkt entspricht dem Wendepunktvolum V_i der Titrationskurve. Der Assymetriekoeffizient, u, sowie das dem Äquivalenzpunkte entsprechende Volum E werden schliesslich errechnet.

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THE FORMATION OF INTERHALOGENS

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Summary—The formation of interhalogen compounds has been investigated in the reactions between elementary bromine or iodine with mercury^{II} chloride, silver chloride, and silver chloride dissolved in saturated sodium chloride solution, and between elementary iodine and silver bromide, both alone and dissolved in concentrated potassium bromide solution. A new method has been evolved for the determination of the content of elementary bromine in bromine chloride.

WHEN investigating the halogen addition of unsaturated organic compounds, Hübl[1] used a standard reagent which was freshly prepared by combining a separately stored ethanolic iodine solution with an ethanolic solution of mercury^{II} chloride. This method was examined later by Schweissinger,[2] Ephraim[3] and Wijs.[4] Schweissinger presumed mercury^{II} chloride to react with elementary iodine under the given conditions. In the opinion of both Ephraim and Wijs, iodine chloride is the product of the reaction. They suggested the use of an iodine chloride solution for the determination of the iodine number. The use of a solution of bromine in glacial acetic acid was proposed by Winkler[5] for the determination of the iodine bromine number, and he recommended also the addition of a minute amount of mercury^{II} chloride to the reaction mixture. However, the possibility of formation of bromine chloride was not considered. Instead, the process was treated as a catalytic reaction. As pointed out in a recent paper,[6] the heterolytic dissociation of the elementary halogen ($Br_2 \rightleftharpoons Br^+ + Br^-$) is promoted by a mercury^{II} salt, *i.e.* the latter binds the bromide ion, formed during the reaction, as a poorly dissociating salt. In the titration suggested by Winkler, similarly bromine chloride formed according to the equation:

$$HgCl_2 + Br_2 \rightarrow HgBrCl + BrCl \qquad (1)$$

represents the active component.

The order of the degree of dissociation of the halides of mercury^{II} ($HgCl_2 > HgBr_2 > HgI_2$; the dissociation constants are K_{HgCl_2}: $2{\cdot}6 \times 10^{-15}$; K_{HgBr_2}: 8×10^{-20}; K_{HgI_2}: $3{\cdot}2 \times 10^{-29}$) explains reaction (1). In order to prove the suggested formation of bromine chloride, and of interhalogens in general, the following experiments were carried out.

Saturated bromine-water was diluted one hundred-fold, then about 0·30 g of mercury^{II} chloride was dissolved in a 50-ml portion of this solution in a 100-ml Erlenmeyer flask equipped with a glass stopper. The original brownish-orange colour of the solution turned slightly straw-yellow. The tint was compared to that of a similar 50-ml portion of the diluted bromine-water free from mercury. Subsequently, as much potassium iodide was dissolved in the straw-yellow liquid as was needed for the complete dissolution of the precipitated mercury^{II} iodide. An equal amount of potassium iodide was added to the reference solution as well. Both solutions exhibited the same colour.

The above experiment was repeated with 50-ml portions of saturated iodine-water, except that only 0·1 g of mercury$^{\text{II}}$ chloride was dissolved in one of the 50-ml aliquots. The brownish tint of iodine disappeared. On adding potassium iodide, both solutions showed the same colour. The latter experiment seems to support the following reaction:

$$HgCl_2 + I_2 \rightarrow HgClI + ICl \qquad (2)$$

Solutions of bromine and iodine, respectively, in glacial acetic acid behaved similarly with mercury$^{\text{II}}$ chloride, although to a smaller degree.*

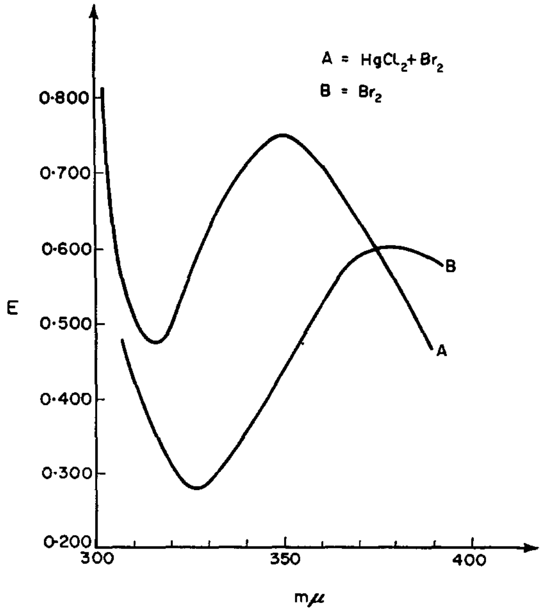

FIG. 1

With the aim of unambiguously clearing up the problem and of investigating the formation of bromine chloride, the ultraviolet absorption curve of a solution of bromine in hydrochloric acid, and also of a solution containing mercury$^{\text{II}}$ chloride (1*M* HCl, 0·1*M* $HgCl_2$, 0·01*M* Br_2) was established. As can be seen in Fig. 1, a curve characteristic of bromine chloride[7] was obtained, the shape differing markedly from the ultraviolet absorption spectrum of elementary bromine. (This curve shows a more elongated form than that of the chloride complex of bromine chloride established in a solution free from a mercury$^{\text{II}}$ salt; this can be ascribed to the fact that the major part of the chloride content of the solution is bound by mercury$^{\text{II}}$ ions as a chloromercurate complex.)

In our further investigations, the bromine chloride was separated from the mercury complex by distillation into a receiver filled with hydrochloric acid. The ultraviolet absorption curve of this distillate was also established. (The composition of the reaction mixture was: 3 g of mercury$^{\text{II}}$ chloride plus 2·2 ml of saturated bromine-water in 20 ml of 20% hydrochloric acid; the receiver contained 20 ml of 20% hydrochloric acid which was diluted to 100 ml with water after the distillation.)

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* Presumably the heterolytic dissociation of elementary iodine is markedly lower in acetic acid of low dielectric constant ($\varepsilon = 9{\cdot}7$) than in water ($\varepsilon = 80{\cdot}3$).

As can be seen in Fig. 2, a curve characteristic of the chloride complex of bromine chloride was obtained.

The ultraviolet absorption curve unambiguously proves that, under the given conditions, bromine chloride was definitely formed.

It was our intention to establish the amount of bromine chloride and elementary bromine in the distillate. A method for the determination of elementary bromine in bromine chloride has already been proposed,[8,9] but this method involves the removal, by boiling, of large amounts of hydrogen cyanide and cyanogen bromide. It seemed practical, therefore, to evolve a new method and this was done as follows. The total of bromine chloride plus elementary bromine is determined in an aliquot of the solution by iodometry. Then, the content of elementary bromine in another aliquot of the solution is oxidised by chlorine-water to bromine chloride and, on binding excess chlorine by cyanide, the amount of total bromine chloride (*i.e.* that of equivalent cyanogen bromide formed during the reaction with cyanide) measured by iodometry. The difference between the two measurements is equivalent to the content of elementary bromine in the reaction mixture.†

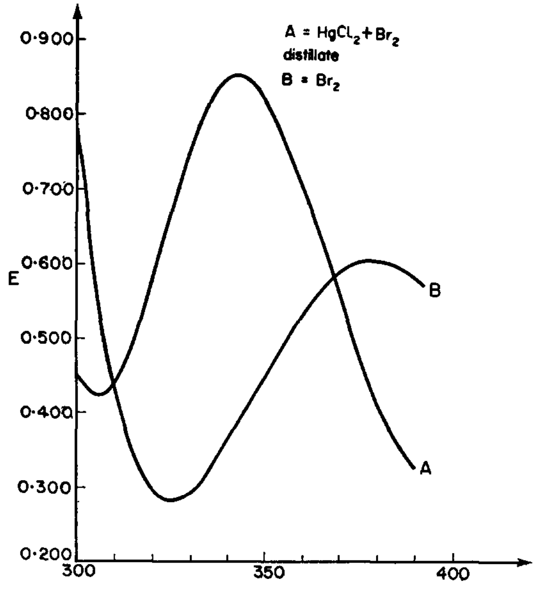

FIG. 2

With the use of this method, the composition was determined of the mixture of halogens which forms when mercury$^{\text{II}}$ chloride and elementary bromine react in a hydrochloric acid medium and the products are distilled into hydrochloric acid. Under optimum conditions, the distillate contained 85% of bromine chloride and 15% of elementary bromine. On replacing the hydrochloric acid in the reaction mixture, during distillation, by an equivalent amount of sodium chloride, the halogens in the

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† The amount of elementary bromine formed by the homolytic decomposition of bromine chloride ($2\,BrCl \rightleftharpoons Br_2 + Cl_2$) can be determined by the analysis of a bromine chloride solution prepared from equivalent amounts of bromine and chlorine. The equilibrium constant calculated from the results of measurements is around $K_{20^\circ} = 4 \times 10^{-4}$.

distillate were present mainly as bromine chloride (78%), the amount of bromine being 22%. On carrying out distillation from an aqueous solution of mercury^{II} chloride, 62% of the halogen content of the distillate was present as bromine chloride and 38% as bromine.

The reactions between elementary iodine and mercury^{II} chloride and mercury^{II} bromide, respectively, were also studied. Preparative experiments (iodination of antipyrine) proved that, analogous to bromine, the heterolytic dissociation of iodine ($I_2 \rightleftharpoons I^+ + I^-$) is promoted by a mercury^{II} salt. Thus, antipyrine could be iodinated in an acidic medium by elementary iodine in the presence of mercury^{II} ions, although antipyrine does not react in an acidic medium with elementary iodine alone.

It was not possible to isolate iodine chloride and iodine bromide, respectively, by distillation. It seems possible that iodine (I^+) quickly reacts[13] in a hot solution in the presence of mercury^{II}:

$$3I^+ + 3H_2O \rightleftharpoons IO_3^- + 2I^- + 6H^+ \qquad (3)$$

Iodide ions formed according to equation (3) are bound by mercury^{II} ions.

In our opinion, also the anomaly observed in the rates of the reactions between calomel (Hg_2Cl_2) and halogens can be interpreted on the basis of our investigations. It has been pointed out by Schulek[10] that the rates of the oxidation reactions of calomel by various halogens decrease in the order $I_2 > Br_2 \gg Cl_2$. This phenomenon can be interpreted as follows. The heterolytic dissociation of iodine and bromine is completed by calomel in that the latter binds the halogen ions, due to the following order of solubility products of mercury^{I} halides (the solubility products in decreasing order are Hg_2Cl_2: 2×10^{-18}; Hg_2Br_2: $1{\cdot}5 \times 10^{-21}$; Hg_2I_2: $1{\cdot}2 \times 10^{-29}$). Thus, oxidation is actually carried out by the electrophilic halogen ions formed (I^+ and Br^+, respectively). Elementary chlorine does not react with mercury^{I} chloride; no Cl^+ ions are thus formed, so that calomel is much more slowly oxidised by molecular chlorine.

Similarly the reactions between silver chloride and bromine, silver chloride and iodine, and of silver bromide and iodine were examined. During these experiments, extremely dilute bromine-water and iodine water were used. The colour changes observed in these reaction mixtures similarly pointed to the formation of bromine chloride, iodine chloride and iodine bromide, although interhalogens could only be formed in a surface reaction, due to the very poor solubilities of silver chloride and silver bromide (solubility of AgCl $\sim 10^{-5}$ mole/l., that of AgBr $\sim 10^{-6}$ mole/l., and that of AgI $\sim 10^{-8}$ mole/l.). In contrast, more intense colour changes were observed when silver chloride dissolved in a saturated solution of sodium chloride was treated with very dilute bromine-water and iodine-water, respectively, or silver bromide dissolved in a concentrated solution of potassium bromide was treated with very dilute iodine-water. Only bromine chloride could be isolated in these experiments since, owing to the above mentioned reaction (3), all attempts to isolate iodine chloride and iodine bromide failed.

EXPERIMENTAL

Determination of the content of elementary bromine in bromine chloride

Ten ml of an approximately 0·005*M* solution of bromine chloride were measured into 10 ml of a 2% solution of potassium iodide. The liberated iodine was titrated after standing for a few min with a 0·01*N* standard solution of sodium thiosulphate in the presence of starch as indicator. Subsequently, an identical volume of test solution was measured into a 100-ml Erlenmeyer flask with a ground-glass stopper, then treated dropwise with saturated chlorine-water until a pale straw-yellow tint appeared. In order to bind excess chlorine, about 1 ml of 5% potassium cyanide solution was added to the reaction mixture. On vigorously shaking and allowing the mixture to stand for 5 min, 0·20 g of potassium iodide was added to the solution and after the elapse of 20 min the liberated iodine was titrated with a 0·01*N* standard solution of sodium thiosulphate.

The difference between the consumption of standard thiosulphate solution in the two titrations indicates the content of elementary bromine of the reaction mixture (1 ml of 0·01*N* $Na_2S_2O_3 \equiv$ 0·79916 mg of Br).

Preparation of iodo-antipyrine

One hundred ml of saturated aqueous iodine (about 0·1*N* with respect to sulphuric acid) was treated with 2 ml of 1*N* mercury^{II} sulphate solution and 2 ml of a 1% solution of antipyrine. Iodo-antipyrine was extracted from the reaction mixture by shaking with chloroform, then isolated by a previously described method.[12] It was identified by its m.p. (167–168°) and the iodine content was determined (40·23%) (m.p. given in the literature for 4-iodo-antipyrine is 167–169°; its theoretical iodine content is 40·40%).

Distillation experiments

On dissolving 3 g of mercury^{II} chloride in 20 ml of 20% hydrochloric acid in the flask of the distillation apparatus evolved by Schulek, the solution was treated with 2·2 ml of freshly saturated bromine-water. The bromine chloride formed was distilled into 20 ml of 20% hydrochloric acid. On completing the distillation, the solution in the receiver was made up to a volume of 100 ml. Then the amount of bromine chloride and bromine was determined in the solution by the above method.

In establishing the ultraviolet absorption curves, a Beckman DU quartz spectrophotometer was employed with 1-cm quartz cuvettes, using a hydrogen lamp as the light source.

Zusammenfassung—Die Bildung von Interhalogenen wurde in den Reaktionen zwischen elementarem Brom bzw. Jod und Quecksilber(II)chlorid in wässriger Lösung, ferner in den Reaktionen zwischen elementarem Brom bzw. Jod und Silberchlorid in wässriger Suspension, sowie in einer Lösung desselben in gesättigter Natriumchloridlösung nachgewiesen. Die Reaktion zwischen elementarem Jod und Silberbromid wurde sowohl in einer wässrigen Suspension wie in einer konzentrierten wässrigen Kaliumbromidlösung des letzteren näher untersucht und die Bildung von Jodbrom festgestellt.

Eine neue Methode zur Bestimmung von elementarem Brom neben Bromchlor wurde angegeben.

Résumé—La formation de composés interhalogénés a été étudiée dans les réactions entre le brome ou l'iode élémentaire d'une part, le chlorure mercurique, le chlorure d'argent et le chlorure d'argent dissous dans une solution saturée de chlorure de sodium d'autre part, et entre l'iode élémentaire et le bromure d'argent, seuls et dissous dans une solution concentrée de bromure de potassium. Une nouvelle méthode a été élaborée pour la dosage de la teneur en brome élémentaire du chlorure de brome.

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THE USE OF BROMINE CHLORIDE IN ANALYTICAL CHEMISTRY

DETERMINATION OF UNSATURATED ALDEHYDES

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Summary—The standard solution of bromine chloride previously suggested by the authors readily lends itself to the determination of the double bond of unsaturated aldehydes. Bromine chloride, electrophilic in nature, reacts extremely quickly with unsaturated double bonds of nucleophilic nature, while it is not capable, under the selected conditions, of oxidising the similarly electrophilic aldehyde group.

IT has already been pointed out in our earlier studies[1,2] that bromine chloride, owing to its electrophilic nature, reacts with nucleophilic reaction partners such as aromatic compounds,[1] unsaturated double bonds,[2] *etc.* at a rate exceeding that of the less electrophilic elementary bromine. Also, the advantages due to the fact that bromine chloride has a redox potential[3] markedly exceeding that of elementary bromine ($E_{BrCl} = 1{\cdot}3$ V; $E_{Br_2} = 1{\cdot}07$ V), and that the redox potential of the hydrochloride complex of bromine chloride can be varied by changing the concentration of hydrochloric acid[4] were emphasised. On the basis of these properties, it was possible to utilise bromine chloride in solving a number of analytical problems.

The scope of the present paper is to point out the possibility of the selective use of bromine chloride. Thus, the Br^+ cation which forms during the heterolytic dissociation of bromine chloride reacts with a nucleophilic reaction partner more quickly than does elementary bromine, whilst with an electrophilic partner it reacts much more slowly. Because of this property, bromine chloride is suited to the selective determination of nucleophilic groups, *e.g.* unsaturated double bonds, in the presence of electrophilic groups of reductive character, *e.g.*, aldehyde groups. The standard solution of bromine chloride suggested by us was, therefore, successfully applied to the determination of the double bond of unsaturated aldehydes without any attack of the aldehyde group by the standard oxidising solution. This problem is of great importance from the point of view of the analytical control of the synthesis of certain organic drugs. For example, it is possible in this way to determine the degree of unsaturation (the degree of hydrogenation) of catalytically hydrogenated double bonds, even in the presence of an aldehyde group.[5]

In the present investigations, three readily available unsaturated aldehydes, acrolein, crotonic aldehyde and cinnamic aldehyde, were used, whilst a $0{\cdot}1N$ solution of potassium bromate served as a standard solution which contained, according to equation (1), an equivalent amount of bromide ions:[6]

$$BrO_3^- + 2Br^- + 3Cl^- + 6H^+ \rightarrow 3BrCl + 3H_2O \qquad (1)$$

The neutral standard solution was added in excess to the unsaturated aldehyde.

On acidifying with hydrochloric acid, bromine chloride, formed according to (1), participates in the addition reaction. Excess bromine chloride was measured by iodometric back titration. In certain investigations, a 0·1*N* solution of bromine chloride containing hydrochloric acid,[6] prepared according to (1), was used.

It was found that:

1. the bromine chloride addition takes place completely and almost instantaneously when only a small excess (5 to 10%) of bromine chloride is present (*cf.* Table 1);

TABLE I.—BROMINE CHLORIDE ADDITION TO UNSATURATED ALDEHYDES
DEPENDENCE ON THE EXCESS OF BrCl

Substance	Content present, %	BrCl excess, %	Content found, %	Deviation, %
Crotonic aldehyde	93·00	9·5	92·83	−0·17
		4·0	93·22	+0·22
		115·0	93·00	+0·0
Acrolein	86·00	6·0	86·23	+0·23
		21·0	86·07	+0·07
		29·0	85·91	−0·09
		35·0	85·74	−0·26
		170·0	85·64	−0·36

TABLE II.—BROMINE CHLORIDE ADDITION TO UNSATURATED ALDEHYDES
DEPENDENCE ON THE REACTION PERIOD

Substance	Content present, %	Reaction period, *min*	Content found, %	Deviation, %
Crotonic aldehyde	93·00	0·5	93·22	+0·22
		1·0	93·00	±0·0
		5·0	92·83	−0·17
		15·0	93·00	±0·0
Acrolein	86·00	0·5	86·07	+0·07
		1·0	86·23	+0·23
		5·0	85·91	−0·09
		15·0	85·91	−0·09

2. the experimental results showed no increases when the excess of bromine chloride was raised to 100% and the reaction period was simultaneously prolonged to 15 min; this proves that the aldehyde group is not oxidised under the given conditions (*cf.* Table II);
3. it is possible to determine unsaturated aldehydes on the basis of the rate of their bromine chloride addition with an error of ±0·5% (*cf.* Table III).

An attempt was made to determine the content of active substance in the unsaturated aldehyde solutions used in the present experiments, also on the basis of their aldehyde group. For measuring the aldehyde group, the method suggested by Schulek and Maros[7] was applied. In the case of cinnamic aldehyde, the aldehyde bisulphite was decomposed by hydroxylamine hydrochloride.[8] Subsequent to the addition of bromine chloride, the aldehyde group was again measured in the titrated solutions.

In the case of cinnamic aldehyde, identical results were obtained on the basis of both the addition of bromine chloride and the content of aldehyde. Thus, the content of aldehyde group was not affected by the addition of bromine chloride. (It must be noted that the aldehyde bisulphite of the addition product is less stable, which fact is responsible for the small scattering of the experimental results.)

In the case of acrolein and crotonic aldehyde, measurement on the basis of the aldehyde group gave lower results than those obtained on the basis of bromine chloride addition. When, however, the determination of aldehyde was carried out after the addition of bromine chloride, results on the basis of the aldehyde content were in accordance with those obtained with bromine chloride.

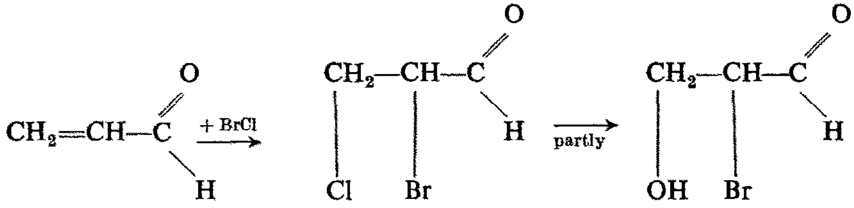
TABLE III. BROMINE CHLORIDE ADDITION OF UNSATURATED ALDEHYDES

Substance	Amount weighed, *mg*	Consumed 0·1*N* BrCl, *ml*	Amount found, *mg*	Content found, %	Deviation, %
Cinnamic aldehyde	43·44	6·49	42·88	98·71	−0·29
(Content: 99·00%)		6·51	43·01	99·01	+0·01
	85·50	12·86	84·97	99·38	+0·38
		12·86			
Crotonic aldehyde	17·86	4·74	16·61	93·00	+0·00
(Content: 93·00%)		4·73	16·58	92·83	−0·17
	35·15	9·31	32·63	92·83	−0·17
		9·31			
	35·15	9·35	32·77	93·22	+0·22
		9·35			
Acrolein	12·28	3·77	10·57	86·07	+0·07
(Content: 86·00%)		3·77			
	24·70	7·57	21·22	85·91	−0·09
		7·57			
	24·70	7·60	21·30	86·23	+0·23
		7·60			

These experimental results showed that in the aqueous solutions of acrolein and crotonic aldehyde, respectively, a portion of the aldehyde groups is bound to the double bonds (polymerisation) and thus cannot form aldehyde bisulphite. Bromine chloride, however, owing to its more positive character, saturates the double bonds and in this way liberates the aldehyde groups.

In order to clear up the course of the bromine chloride addition to unsaturated aldehydes, the reaction products were separated and analysed. The aldehyde content and the amount of bromine and chlorine falling to an aldehyde group were established. According to our measurements the ratio throughout was one atom of bromine and various amounts of chlorine (always below one atom) to each aldehyde group. From the analytical results, we calculated that the reaction product is the mixture of the corresponding bromine chloride derivative and one of its decomposition products where the chlorine atom was replaced by a hydroxyl group.

Thus, according to our investigations, the bromine chloride addition to acrolein takes place as follows:



The process is analogous with crotonic aldehyde and cinnamic aldehyde. The results are in fair accordance with the results obtained in research into the bromine chloride addition of other unsaturated compounds.[9]

EXPERIMENTAL

Determination of the Bromine Chloride Addition to Saturated Aldehydes

Reagents

0·1*N standard solution of bromate* (containing also bromide): prepared by dissolving 2·7835 g of potassium bromate and 3·9670 g of potassium bromide in water and diluting to 1000 ml.

0·1*N standard solution of bromine chloride*: prepared by dissolving 2·7835 g of potassium bromate and 3·9670 g of potassium bromide in about 300–400 ml of water, acidifying the reaction mixture with 365 ml of 20% hydrochloric acid, and diluting the solution after a few min to 1000 ml.

0·1*N standard solution of sodium thiosulphate*

Potassium iodide

Distilled hydrochloric acid: 20%.

1% *solution of potato starch*: decomposed and preserved by 0·1% salicylic acid.

All the reagents should be of analytical grade.

Procedure

An aliquot of the aqueous solution of the unsaturated aldehyde (acrolein, crotonic aldehyde), equivalent to about 3–20 ml of bromine chloride, is measured into a Schulek-type bromination flask. Standard bromate solution containing bromide is added in an amount such that the bromine chloride developed on acidifying with hydrochloric acid will be present in at least a 5% but not over 100% excess. Before acidification, the bromination flask is closed by means of its funnel-inserted stopper moistened with water, and a vacuum is produced in the flask by suction, using the funnel-inserted stopper equipped with a stop-cock. The amount of 20% hydrochloric acid required for acidification (5 to 10 ml) is poured into the cup-like broadened neck of the bromination flask or into the funnel-inserted stopper and allowed to flow into the reaction mixture by loosening the stopper or opening the stop-cock. After 5 min, 10 ml of a 5% solution of potassium iodide is introduced into the flask in a similar way, and the liberated iodine is titrated with 0·1*N* standard sodium thiosulphate solution in the presence of starch as indicator.

In the case of an unsaturated aldehyde insoluble in water, such as cinnamic aldehyde, the determination can be carried out in an ethanolic medium. As, however, ethanol is very slowly oxidised by bromine chloride, it is advisable to use as small excesses of bromine chloride and as short reaction periods as possible. The aliquot of the test solution is treated with 0·1*N* bromine chloride solution, added dropwise from a Winkler container-burette, until excess bromine chloride is indicated by a persistent yellow tint. Subsequently, in order to measure excess bromine chloride, about 0·20 g of potassium iodide is immediately added to the reaction mixture and the amount of liberated iodine is established by titration with 0·1*N* standard sodium thiosulphate solution in the presence of starch as indicator.* The titre of 0·1*N* bromine chloride solution should be checked iodometrically.

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* Conventional Erlenmeyer flasks with glass stoppers may also be used in this type of determination.

In the case of unsaturated aldehydes, the equivalent weight is equal to half of the molecular weight. Thus, 1 ml of 0·1*N* bromine chloride solution is equivalent to 2·803 mg of acrolein, 3·5045 mg of crotonic aldehyde, and 6·6075 mg of cinnamic aldehyde. The error of the determinations is ±0·5% (*cf.* Table III).

The samples of unsaturated aldehydes (cinnamic and crotonic aldehydes, acrolein) used in the present measurements were purified by distillation, and the purity was controlled according to Peters[10] by bromine addition at the temperature of melting ice and also by the hydroxylamine hydrochloride method,[11] on the basis of the content of aldehyde group.

In this way, cinnamic aldehyde proved to be 99·00% pure, while crotonic aldehyde was of 93·00% and acrolein of 86% purity.

Investigation of the Bromine Chloride Addition Product of Unsaturated Aldehydes

An aqueous (or ethanolic) solution, containing about 0·20 g of the substance to be analysed, was treated in a 150-ml separating funnel with 0·1*N* bromine chloride solution until the colour due to excess bromine chloride persisted. Then excess bromine chloride was reduced by the addition of sodium sulphite. On shaking the reaction product with three lots of 50 ml of ether, the ethereal phases were filtered through a cotton filter covered with anhydrous sodium sulphate into a flask of known weight. On removing the ether by distillation on a water bath, the weight of the residual oily layer was established (by measuring the weight increase of the flask), and it was dissolved in ethanol to a known volume. Subsequently, the content of aldehyde group and of halogen was determined in aliquots of this stock solution. Before the determination of the content of bromine and chlorine, mineralisation was carried out by the conventional potassium hydroxide method. Bromide was determined by the cyanogen bromide method suggested by Schulek, then the combined content of both halogens was established by argentimetry.

Zusammenfassung—Die von den Autoren empfohlene Bromchloridmasslösung ist geeignet zur Bestimmung von Doppelbindungen in ungesättigten Aldehyden. Das elektrophile Reagens reagiert sehr schnell mit der nukleophilen Doppelbindung, ist aber nicht imstande die ebenfalls elektrophile Aldehydgruppe zu oxydieren.

Résumé—La solution étalon de chlorure de brome recommandée par les auteurs se prête aisément au dosage de la double liasison des aldéhydes non saturées. Le réactif, qui est électrophile, réagit tres rapidement avec la double liaison non saturée, qui est nucléophile, mais il n'est pas capable dans les mêmes conditions, d'oxyder le groupe aldéhydique électrophile.

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FUNDAMENTAL PRINCIPLES OF TITRATIONS WITH POTASSIUM BROMATE

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Summary—Based on the results of researches into the chemistry and analytical uses of interhalogen compounds and of halogen ions of one positive charge, the fundamental principles of bromatometry are discussed by the authors.

It is pointed out that in redox titrations with potassium bromate, in place of bromate or bromic acid, actually elementary bromine, or bromine chloride, or bromine chloride and elementary chlorine act as agents. Thus, bromine and bromine chloride form a complex with the halide content (bromide and chloride, respectively) of the solution to be titrated. The redox potential and polarity (electrophilic nature) of this complex can be controlled by varying the halide concentration.

By clearing up the fundamental principles it has been possible to determine precisely the optimum experimental conditions of the various bromatometric procedures.

THE conventional form of the fundamental equation of bromatometry is as follows:

$$BrO_3^- + 6H^+ + 6e \rightarrow Br^- + 3H_2O \qquad (1)$$

This equation, however, only indicates the final state of bromate reduction. Bromatometric titrations are carried out in an acidic medium in the presence of halide ions, such as bromide or chloride. In this case, the following reactions occur, depending on the actual concentration of bromate, bromide and chloride:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (2)$$

$$BrO_3^- + 2Br^- + 3Cl^- + 6H^+ \rightarrow 3BrCl + 3H_2O \qquad (3)$$

$$BrO_3^- + 5Cl^- + 6H^+ \rightarrow BrCl + 2Cl_2 + 3H_2O \qquad (4)$$

Thus, in the presence of excess bromide, elementary bromine forms according to equation (2), while in the presence of a given minute amount of bromide (when the ratio of bromate to bromide is 1:2), bromine chloride develops according to equation (3). In the absence of bromide ions, when chloride is present, bromine chloride and elementary chlorine[2] form according to equation (4). Under the given conditions, therefore, either elementary bromine, or bromine chloride, or a mixture of bromine chloride and elementary chlorine act as oxidising agents in bromatometric oxidations. The direct oxidising effect of bromate only prevails in a medium free from chloride and bromide and also when the bromide ions developed during the reduction process are bound by mercury^{II} ions (as poorly dissociated mercury^{II} bromide), to prevent the formation of bromine.[3] Direct oxidations by bromate alone are extremely slow reactions which can only be utilised for analytical purposes in exceptional cases, in the presence of suitable catalysts and as a rule solely in hot solutions.* In the conventional bromatometric titrations (generally carried out in solutions containing bromide or hydrochloric acid) the course of the reaction is determined rather by that of the redox systems bromine/bromide or bromine chloride/bromide and chlorine/chloride instead of by the redox potential of the system bromate/bromide or of the system bromate/bromine (see Table I).

TABLE I

System	Redox potential, *V*
BrO_3^-/Br_2	1·52
BrO_3^-/Br^-	1·42
$Br_{2\,aq}/Br^-$	1·087
$BrCl_{complex}/Br^-$	1·3
$Cl_{2\,aq}/Cl^-$	1·36

One should also consider that in aqueous solutions containing halides, both elementary bromine and bromine chloride and, to a smaller degree, also elementary chlorine, are present as halide complexes. The redox potentials of halogen-halide and interhalogen-halide complexes are below those of the corresponding free halogens and interhalogens, and decrease with a rise in the halide concentration.[4]

Further, we must emphasise that in a great number of reactions which serve as a basis of bromatometric determinations, particularly in oxidation reactions of organic compounds, in halogen substitution reactions of aromatic molecules, in halogen addition reactions of unsaturated double bonds etc., the chemical process is not determined solely by the redox potential of the reaction partners, because their structure and chemical nature also play a decisive role. Thus, the bromine substitution[5] of aromatic compounds of nucleophilic nature and the halogen addition[6] of unsaturated double bonds of similarly nucleophilic nature take place with bromine chloride (electrophilic in nature) at rates markedly exceeding those of the reaction with less polar (*i.e.* less electrophilic) elementary bromine or with elementary chlorine of higher redox potential but similarly of less electrophilic nature.

However, the formation of halogen-halide and interhalogen-halide complexes (under the action of halide ions) also reduces the degree of polarity and thus the electrophilic nature of halogens and interhalogens in addition to the redox potential of the system proper.

It is possible in this way, by varying the concentration of bromide according to the nature of the substance to be determined and to the requirements to be met during the determination, to choose whether elementary bromine developed according to equation (2), or bromine chloride according to equation (3) or bromine chloride and elementary chlorine according to equation (4) should constitute the active agent. Further, the redox potential of the bromine-bromide complex and the polarity of the molecule will also be determined by the bromide concentration, while the redox potential and polarity, together with the electrophilic nature of the bromine chloride-chloride complex can be governed by varying the chloride concentration.

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* There is no possibility of oxidising even ascorbic acid to dehydro-ascorbic acid if the conditions exclude the formation of elementary bromide and bromine chloride. A bromine addition before oxidation was observed by Schulek, Kovács and Rózsa.[17]

Taking into account the above considerations, the phenomenon which was pointed out by Zöllner and Varga,[7] without an attempt at explanation, can be interpreted. Thus, in a great number of bromatometric procedures, an increase in the bromide concentration gives markedly lower (3 to 50%) results. In other cases, however (such as antipyrine[3]), more precise determinations are possible at higher bromide concentrations, while in the presence of too small an amount of bromide, the results are too high due to over-bromination. Finally, in certain cases (such as with hydrazine[8] or hydroxylamine[9]), the determinations must be carried out in a hydrochloric acid medium free from bromide.

On increasing the bromide content of a reaction mixture, according to the afore-mentioned considerations, complexes form and the dissociation of the complexes is suppressed. Thus, the redox potential, together with the polarity (electrophilic nature) of bromine are reduced. This is the reason why the rate of oxidation and, in certain cases, that of bromination, respectively, decrease and low results are obtained. In contrast, in the bromatometric determination of molecules which, on reacting with agents of higher redox potential and more electrophilic nature, may suffer an undesirable over-bromination or may lead to undesired side reactions, the presence of an agent of lower redox potential and lower reactivity can be attained by using excess bromide. Finally, bromine chloride (formed in a hydrochloric acid solution free from bromide or, alternatively, containing given amounts of bromide, *e.g.* 1:2 ratio of BrO_3^- : Br^-) is necessary in certain determinations where quantitative oxidation is to be conducted in a given manner. Also, in the halogen addition of unsaturated double bonds where the reactivity is hindered by negative substituents of the vicinal carbon atoms, bromine chloride should be used.

During the preparation and practical use of a standard solution of bromine chloride suitable for analytical purposes, we succeeded in proving completely the validity of the afore-mentioned presumptions. The standard solution of bromine chloride was prepared according to equation (3) in a hydrochloric acid medium from equivalent amounts of bromate and bromide.[1] Careful physical and chemical investigations (absorption spectra in the visible and ultraviolet regions, redox potentials, various chemical reactions, *etc.*) were carried out to prove that the solution obtained is, in all respects, identical to the bromine chloride solution containing hydrochloric acid which was prepared from elementary bromine and chlorine.

The bromine chloride substitution of a great number of aromatic compounds,[10] the addition of bromine chloride to unsaturated double bonds[6,11,16] and many oxidation reactions with bromine chloride[2,12,13,15] were subjected to a thorough examination. In all cases, as expected, a marked increase of reaction rates was observed.

The standard solution of bromine chloride suggested by us was applied with success to the determination of reducing substances which can be oxidised only extremely slowly or non-stochiometrically by elementary bromine. The bromatometric determination of these substances was previously only possible in media free from bromide, in solutions of high hydrochloric acid concentration. In contrast to that, we were able to determine hydrazine and its derivatives[13] in an aqueous solution directly, without acidification, by using bromine chloride, whilst the method suggested by Kurtenacker yields correct results only in solutions of hydrochloric acid content over 10%. Bromine chloride was similarly used with success in the determination of hypophosphite[12] and hydroxylamine.[2]

On using a standard solution of bromine chloride, it was possible to determine unsaturated compounds as well, *e.g.* maleic acid and fumaric acid,[6] which otherwise are practically incapable of taking up bromine in an addition reaction in an acidic medium, due to the hindering effect of the carboxylic groups on both carbon atoms in the vicinity of the double bond.

The investigation of aromatic substitution reactions by bromine chloride disclosed markedly higher reaction rates in these reactions than in the substitution reactions by elementary bromine. However, on applying bromination periods longer than the optimum values, as is usual in the Koppeschaar method, the obtained results were high, pointing to oxidative side reactions. Similar phenomena were observed when measurements were carried out in the presence of minute amounts of bromide (or in solutions free from bromide) according to Koppeschaar.

Considering the higher reaction rates of brominations carried out with bromine chloride and with Br^+ cations developed during the dissociation of this compound, respectively, it was possible to interpret the mechanism of action of mercury^{II} ions *i.e.* of the "catalyst" generally used in bromine addition reactions.[14]

Thus, it was assumed that the heterolytic dissociation of elementary halogen is completed by mercury^{II} ions, with the formation of poorly dissociated mercury^{II} halides:

$$Hg^{2+} + Br_2 \rightarrow HgBr^+ + Br^+ \tag{5}$$

The increase in reaction rate is due to the formation of Br^+ cations.

In order to prove the validity of this assumption, bromine water was treated with mercury^{II} chloride and, since HgBrCl is less dissociated than $HgCl_2$, bromine chloride should be formed[21] according to the equation:

$$HgCl_2 + Br_2 \rightarrow HgBrCl + BrCl.$$

Bromide chloride could, in fact, be distilled off, then identified by its ultraviolet spectrum and by chemical reactions.

In this way, researches into the chemistry and analytical use of interhalogen compounds and of halogen ions of one positive charge resulted in a clearing up of the fundamental principles of bromatometry. With a complete knowledge of the chemical processes occurring during the determination and of the ways of controlling them, it was possible to establish precisely the optimum conditions for the various bromatometric procedures.

Zusammenfassung—Die Grundlagen der Bromatometrie werden diskutiert. Es wird gezeigt, dass in Redoxtitrationen unter Verwendung von Kaliumbromat an Stelle von Bromsäure elementares Brom, Bromchlorid oder Bromchlorid und elementares Chlor die reagierenden Komponenten sind. Brom und Bromchlorid bilden einen Komplex mit dem Halogen (Bromid oder Chlorid) der zu titrierenden Lösung. Redoxpotential und Polarität (Elektrophilie) dieses Komplexes kann durch Regulierung der Halogenkonzentration geändert werden. Auswertung experimenteller Befunde machte es möglich die optimalen Bedingungen für verschiedene bromatometrische Bestimmungen zu ermitteln.

Résumé—Les principes de la bromatométrie sont discutés. Les auteurs font remarquer que, dans les titrages par oxydo-réduction utilisant le bromate de potassium au lieu de l'acide bromique, le brome élémentaire, ou le chlorure de brome, ou le chlorure de brôme et le chlore élémentaire agissent comme réactifs. Le brome et le chlorure de brome forment un complexe avec l'halogénure (bromure et chlorure) de la solution à titrer. Le potentiel d'oxydo-réduction et la polarité (nature électrophile) de

ce complexe peuvent être controlés en faisant varier la concentration d'halogénure. L'examen des conditions expérimentales a permis de déterminer les conditions expérimentales optimales pour les différentes techniques bromatométriques.

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A STUDY OF SOME SOLVENTS AS MEDIA FOR THE HIGH FREQUENCY TITRATION OF WEAK ACIDS*

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Summary—Six solvents, with different basicities and dielectric constants, were studied to determine their suitability as media for high frequency (HF) titrations of weak acids. There is no definite correlation between the slopes of the HF response and conductance curves and the two properties, dielectric constant or basicity, of the solvent. The apparent strength of the acid or base in these solvents is not due to any single solvent property but it is a combination of the properties of the solute and the solvent.

In general, from this and other papers, solvents with relatively high dielectric constants and very weakly basic properties are most likely to be successful solvents for non-aqueous HF and conductance titrations.

INTRODUCTION

MOST investigators of HF methods have studied specific titrations in a few specific solvents. Some weak bases have been titrated in glacial acetic acid[8,10,16,18] and benzene-methanol solutions.[6,12] Acidic compounds have been titrated in benzene-methanol solutions,[5,7] pyridine,[13] dimethylformamide,[3,14] and solvent mixtures of dimethylformamide, diethylamine, and triethylamine.[9] Conductance titrations have been carried out in dimethylformamide, methanol, and pyridine, and binary mixtures of these solvents.[14,15]

Although work has been done on acid-base titrations in non-aqueous solvents, no systematic study has been made with respect to the different solvents that might be suitable media for the titration of weak acids by means of HF methods. The purpose of this investigation was to study a selected series of solvents for the titration of weak organic acids by HF and conductance methods.

EXPERIMENTAL

Equipment

The basic equipment consisted of the Sargent Chemical Oscillometer, Model V, with accessories, and the Campbell-Shackelton Shielded Ratio Box with its accessories.[14] The conductance cell was stored before and after use in the same solvent in which measurements were made.

Reagents

All solvents were further purified as directed, then stored under dry nitrogen.

Benzene: shake with Drierite, then distil over phosphorus pentoxide.

Methanol: reflux with magnesium turnings, then distil.

Acetonitrile: distil several times from phosphorus pentoxide, then from freshly fused potassium carbonate, and finally distil with no drying agent present.

N:N-*Dimethylformamide:* distil from solid potassium hydroxide and calcium hydride.

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Ethylenediamine: reflux with solid potassium hydroxide, then further reflux with metallic sodium, and finally distil from metallic sodium.

Pyridine: reflux with solid potassium hydroxide and distil from potassium hydroxide and a small amount of calcium hydride.

n-Butylamine: allow to stand over solid potassium hydroxide for several days, then reflux, and finally distil from metallic sodium.

Piperidine: distil from solid potassium hydroxide with a small amount of calcium hydride present.

Benzoic acid: prepare a 0·01*N* standard solution by dissolving 0·0025 g equivalents in *N:N*-dimethylformamide, then dilute to 250 ml in a calibrated flask.

Ammonium iodide, 3:5-*dinitrobenzoic acid, and* o-*nitrobenzoic acid solutions:* prepare by dissolving 0·001 g equivalents of each acid in each of the pure solvents, then dilute to 0·01*N* in 100-ml calibrated flasks.

Potassium methoxide: prepare by dissolving about 0·025 g equivalents of potassium in 20 ml of cold methanol, then dilute to 250 ml with methanol and benzene so that the final ratio is a 12:1 benzene-methanol solution. Standardise this solution against standard benzoic acid solution, using thymol blue indicator, then dilute an aliquot of this stock solution to 0·01*N* with 12:1 benzene-methanol as solvent.

Tetrabutylammonium hydroxide: prepare by the method of Cundiff and Markunas.[2] Carry out the reaction in about 20 ml of dry methanol, then dilute the product to 250 ml with dry benzene. Standardise with benzoic acid, then dilute an aliquot to 0·01*N* with 12:1 benzene–methanol solvent.

Procedures

The experimental procedures and precautions were essentially the same as described by Ting, *et al.*[14] In addition, all solvents and solutions were kept under dry nitrogen, and all transfers of solutions were made by forcing the solution from the container to the desired vessel through an air-tight system with dry nitrogen under pressure.

All measurements were performed at 25° in a constant temperature room. All toxic materials were handled in an exhaust hood, and protective gloves were worn when necessary. When conditions were such that the room temperature could not be maintained with the exhaust hood in use, a protective mask was worn while measurements were being made.

The HF response curves and conductance curves were determined for the acidic materials, ammonium iodide, 3:5-dinitrobenzoic acid, and *o*-nitrobenzoic acid; also for the bases, potassium and tetrabutylammonium hydroxide. The two factors, relative basicity and dielectric constant influenced the selection of the six solvents.

DISCUSSION

A change in the dielectric property of a sample in the cell produces a corresponding change in the capacitance of the resonance circuit of the HF unit of which it is a part. Thus, the HF response curve is due to a change or a lack of change in the apparent capacitance of the solution in the cell. The instrument response curve for an acid represents the concentration of the protonated solvent ion, which has a capacitance effect; thus, it represents the degree of dissociation of the acidic substance in the solvent. In the same way, the slope of the conductance curve represents the degree of dissociation of the solute.

In the series equivalent circuit the series HF capacitance term may be represented as follows

$$C_s = \frac{1}{\dfrac{1}{C_1} + \dfrac{\omega^2 C_2 R^2}{R^2 C_2{}^2 \omega^2 + 1}}\,.$$

Then re-arranging to the more convenient form

$$C_s = \frac{C_1(R^2 C_2{}^2 \omega^2 + 1)}{R^2 \omega^2 C_2{}^2 + R^2 \omega^2 C_1 C_2 + 1},$$

since R = $1/k$, where k is the low frequency conductance of the solution,

then
$$C_s = \frac{C_1(C_2{}^2\omega^2 + k^2)}{\omega^2 C_2{}^2 + \omega^2 C_1 C_2 + k^2}.$$

At a given frequency ω is a constant, and for a given solvent in a cell C_1 and C_2 are also constants; thus C_s is a unique function of k.

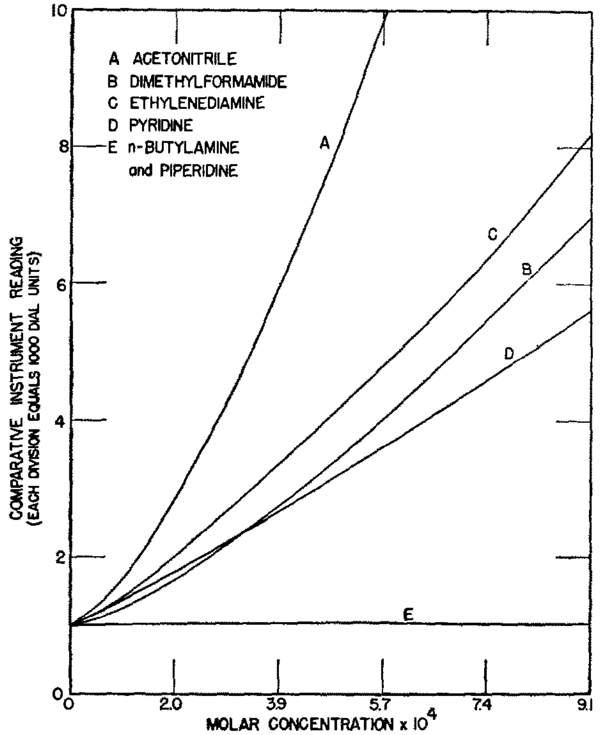

FIG. 1. HF response curves for ammonium iodide.

The response curves for ammonium iodide dissolved in the same solvent as contained in the cell (Fig. 1) and the conductance curves (Fig. 2) indicate that the ammonium ion is most acidic in acetonitrile and that ammonium iodide has a very low degree of ionisation in the strongly basic solvents, n-butylamine and piperidine, both of which have very low dielectric constants. The HF response curves in Figs. 1, 3, and 5 were plotted from a common starting point to show more clearly the relative change with concentration, though the initial instrument reading for acetonitrile was twice as great as that for ethylenediamine and six times as great as that for piperidine. The slopes for the conductance curves (Fig. 2) decrease in the same order but not in the same magnitude as the dielectric constant of the solvent. The difference in the slopes of the conductance curves for ammonium iodide in acetonitrile and in dimethylformamide is probably due to the difference in the viscosity of these two solvents. The difference in the slopes of the HF response curves for the ammonium iodide in acetonitrile and in dimethylformamide (Fig. 1) may also be attributed to the viscosity of these two solvents. However, on the basis of the dielectric constant and viscosity the slope of the response curve for ammonium iodide in ethylenediamine would be expected to be less than that for ammonium iodide in dimethylformamide. This difference between the slope of the HF response curve for ammonium iodide in acetonitrile and the slopes of the curves obtained in dimethylformamide, ethylenediamine, and pyridine cannot be attributed to the difference in the dissociation of the ammonium iodide due to any single property of the solvents. It may be that solvation of the ammonium ion by dimethylformamide, ethylenediamine or pyridine reduced the change in capacitance of the solution as the ammonium iodide was added.

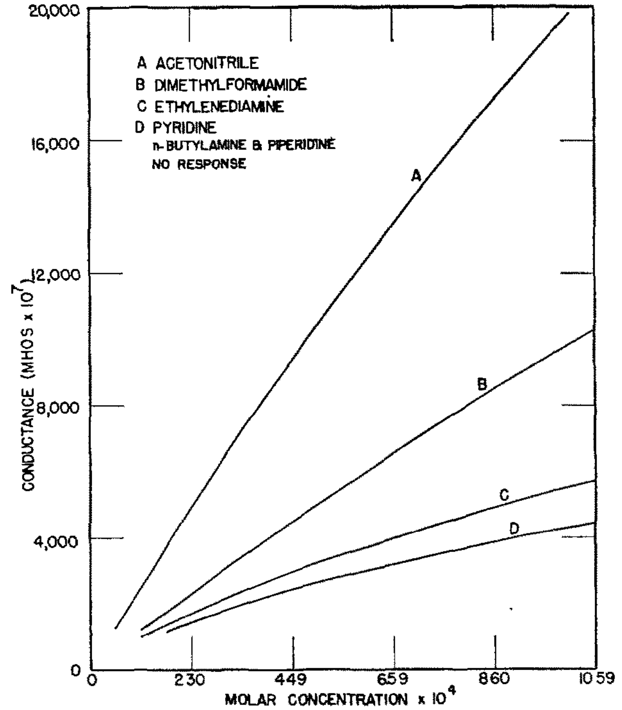

FIG. 2. Conductance curves for ammonium iodide.

The 3:5-dinitrobenzoic acid is indicated to be very weakly ionised in acetonitrile by both the response curves (Fig. 3) and the conductance curves, so that its dissociation also is not a function of the dielectric constant of the solvent.

The dissociation of the ammonium iodide in these solvents may be

$$NH_3 \text{---} H \text{---} I \rightleftharpoons NH_4^+ + I^- \rightleftharpoons NH_3 + H^+ + I^-.$$

The extent to which the equilibrium would lie to the right will depend on the dielectric constant of the solvent and on the success of the competition between the solvent, ammonia, and the iodide ion for the proton. Thus, each of the solutions could contain undissociated ammonium iodide, solvated ammonium ions, and solvated protons. A comparison of the equivalent conductance of a hydrated proton and hydrated ammonium ion with their response curves shows a definite correlation. Thus, the difference between pure conductance curves and HF response curves can be due to the difference in the capacitative effect from the different ratios of solvated protons to solvated ammonium ions, which is not measured by conductance. The difference in the response curves may also be due to the shielding of the charge on the ionic species by the solvating molecule, which would reduce the apparent capacitance of the solvated ion.

The lack of HF response (Fig. 3), as well as no measureable conductance change for the 3:5-dinitrobenzoic acid in pyridine, *n*-butylamine and piperidine, is probably due to the complete formation of the acid dimer which is favoured in solvents with low dielectric constants.[15] The lack of response of conductance when this acid was added to acetonitrile may be due to the formation of a strongly bound complex.

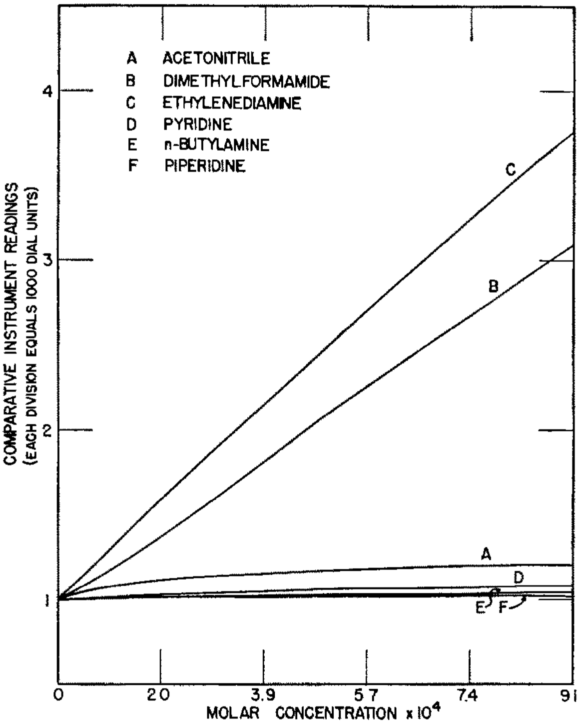

Fig. 3. HF response curves for 3:5-dinitrobenzoic acid.

In both the HF response and conductance curves the *o*-nitrobenzoic acid was found to be a weak to very weak acid and was weaker than the 3:5-dinitrobenzoic acid in these solvents (Fig. 4). This is in contrast to their K_a values in water, where the *o*-nitrobenzoic acid is the slightly stronger acid, and to the theoretical K_a values calculated for these acids in these solvents.[4]

In low dielectric constant solvents the internal hydrogen-bonded form of the *o*-nitrobenzoic acid predominates, while the dimer form of the 3:5-dinitrobenzoic acid predominates. However, the net result depends upon the degree of formation of the non-ionised form with the decrease in dielectric constant. Thus, the strength of the 3:5-dinitrobenzoic acid is less affected by the change from water to solvents with low dielectric constants, so that this acid behaves as the stronger acid.

The tetrabutylammonium hydroxide behaves as a strong base in acetonitrile, and little dissociation is indicated in n-butylamine and piperidine (Fig. 5). Potassium

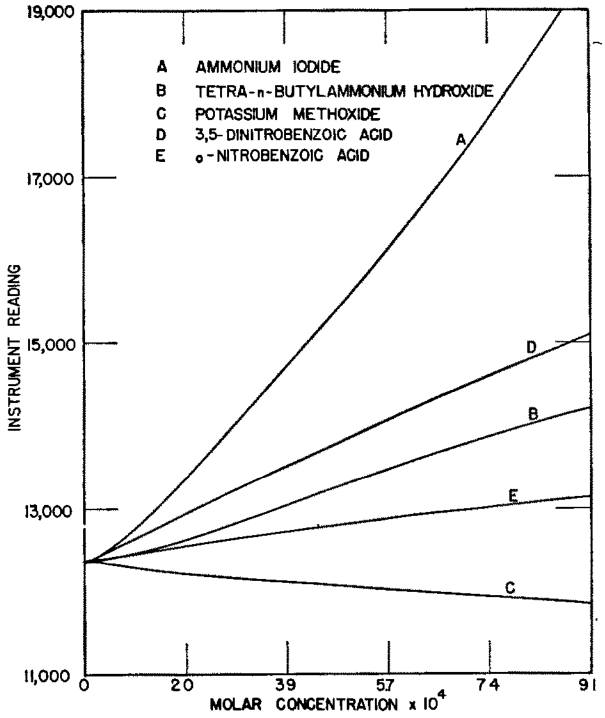

Fig. 4. HF response curves for the solutes in ethylenediamine.

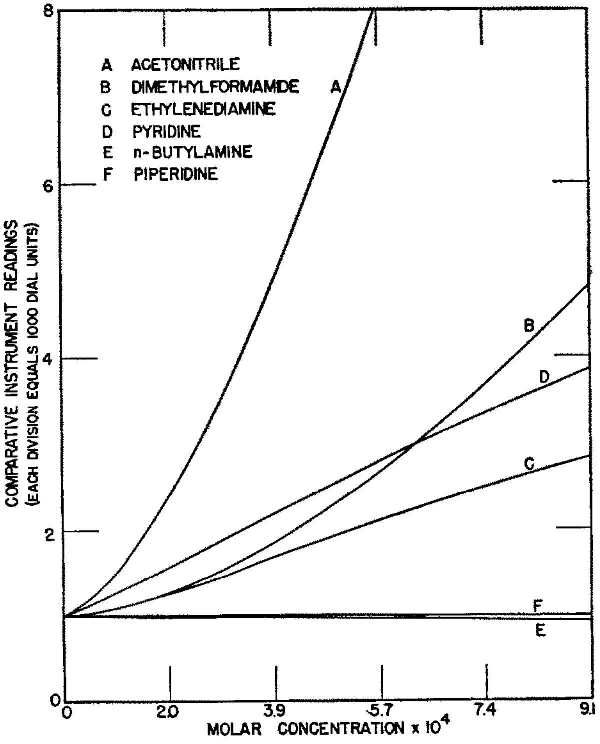

Fig. 5. HF response curves for tetrabutylammonium hydroxide.

methoxide behaves similarly to tetrabutylammonium hydroxide in these three solvents. The large difference in the strengths of these two bases is shown in ethylenediamine (Fig. 4). The degree of ionisation for the potassium methoxide is apparently very low as indicated by the HF response curve. The zero or negative response curves for the two bases indicate the formation of ion pairs or possibly higher neutral aggregates. This is particularly characteristic of the alkali metal bases used with solvents having low dielectric constants.[17] However, the negative slope for the potassium methoxide (Fig. 4) could be partly due to the lowering of the solvent dielectric constant caused by the addition of the 12:1 benzene-methanol to the ethylenediamine. From Fig. 5 and Table I it would appear that there is a closer relationship between the basic properties of the solvent and the dissociation of the two bases than between the dielectric constant of the solvent and the dissociation of the bases.

TABLE I.—A COMPARISON OF THE HIGH FREQUENCY RESPONSE CURVES AND CONDUCTANCE CURVES OF THE ACIDS AND BASES

Solvent	Solvent properties			Approximate slopes for the acid and base curves									
				Ammonium iodide		3:5-Dinitrobenzoic acid		o-Nitrobenzoic acid		Tetrabutylammonium acid		Potassium methoxide	
	ρ	pKb	ε	HF	Cond.	HF	Cond.	HF	Cond.	HF	Cond.	HF	Cond.
Acetonitrile	0·345	18·3	38·8	1·5	1·3	<0·1	<0·1	<0·1	<0·1	1·2	1·2	1·0	0·9
Dimethylformamide	0·796	14·0	26·6	0·7	0·7	0·2	0·3	0·1	0·2	0·5	0·5	0·3	0·4
Ethylenediamine	1·54	4·0	16·0	0·8	0·4	0·3	0·3	0·1	<0·1	0·2	0·2	−0·1	0
Pyridine	0·878	8·8	12·5	0·5	0·3	<0·1	0	<0·1	0	0·3	0·2	−0·1	0
n-Butylamine	0·681	3·4	5·3	<0·1	0	<0·1	0	<0·1	0	−0·05	0	−0·05	0
Piperidine	1·36	2·8	5·8	<0·1	0	<0·1	0	<0·1	0	−0·05	0	−0·05	0

0—No resistance readings could be obtained.

Both the acids and bases in this study are indicated to be only slightly ionised in n-butylamine and piperidine, the solvents with very low dielectric constants and with strong basic properties. The relative strengths or degrees of dissociation are summarised in Table I, where an average slope of 0·8 or greater may be considered to be highly dissociated or strongly acidic or basic, 0·5 to 0·8 as relatively strong, and 0·1 or less as very weak. There is no definite correlation between the slopes of the HF response or conductance curves and a single property of the solvent such as the dielectric constant or the basicity.

The HF titration curves for the acids in dimethylformamide are shown in Fig. 6. No angle is formed at the equivalence point in the titration of *o*-nitrobenzoic acid. No titrations were possible in n-butylamine and piperidine. In pyridine only the HF titration of 3:5-dinitrobenzoic acid with tetrabutylammonium hydroxide produced an angle that could be used to indicate the end-point. This titration curve passes through a maximum before the end-point, similar to that observed by Bruss and Harlow[1] in their work with phenols, and Maryott[11] in his work with carboxylic acids, which indicates that an acid-anion complex was being formed during the titration.

The solutions of 3:5-dinitrobenzoic acid changed gradually from red to a deep purple during the titrations; thus, the use of a colour indicator was impractical. The

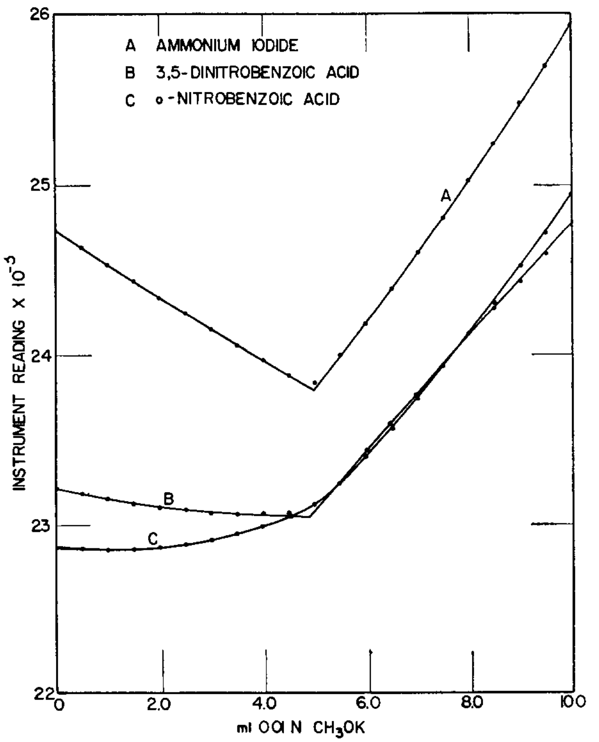

FIG. 6. HF titrations in dimethylformamide.

quinonoid form for the resonance structures of the potassium salt is the predominant form in alkaline solutions and is the structure responsible for the deep purple colour.

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Zusammenfassung—Sechs Lösungsmittel mit verschiedener Basizität und Dielektrizitätskonstante wurden im Hinblick auf ihre Eignung als medium für die Hochfrequenztitration von schwachen Säuren studiert. Es wurde kein definierter Zusammenhang zwischen der Steigung der Hochfrequenz- und Leitfähigkeitskurven und den beiden genannten Eigenschaften gefunden. Die scheinbare Stärke einer Säure oder Base in diesen Lösemitteln ist keineswegs von einer einzigen Eigenschaft der Solvens abhängig, sondern ist eine Kombination der Eigenschaften von sowohl Solut als auch Solvens.

Allgemein kann gesagt werden, (nach diesen Untersuchungen und denen anderer Autoren), dass Lösemittel mit einer relativ hohen Dielektrizitätskonstante und sehr schwach ausgeprägten basischen Eigenschaften am wahrscheinlichsten die beste Eignung für Hochfrequenz- und Leitfähigkeitstitrationen zeigen werden.

Résumé—Les auteurs ont étudié six solvants, de basicités et de constantes diélectriques différentes, afin de déterminer leur intérêt comme milieux pour les titrages HF d'acides faibles. Il n'y a pas de relation définie entre les pentes de la réponse HF et des courbes de conductances, et les propriétés du solvant—constante diélectrique et basicité. La force apparente de l'acide ou de la base dans ces solvants n'est pas due à toute propriété du solvant seul, mais est une combinaison des propriétés du soluté et du solvant.

En général, d'après ce mémoire et d'autres, les solvants qui ont des constantes diélectriques relativement élevées et des propriétés très faiblement basiques doivent très probablement réussir pour des titrages en milieu non aqueux par haute fréquence et conductance.

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MICRODETERMINATION OF CHLORIDE IN WATER

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Summary—An indirect colorimetric method for the determination of chloride has been developed. This method is based on the decrease in the absorption of the mercury-diphenylcarbazone complex caused by chloride ions. The influence of pH and of temperature on the determination have been thoroughly investigated and experimental conditions derived which make possible the determination of 10 to 60 μg of chloride in the presence of an excess of copper, nickel, cobalt, zinc, cadmium and lead, which are removed by chloroform extraction as diphenylcarbazonates.

AMONG the few colorimetric methods for the determination of small amounts of chloride ion, one of the best known and most used is an indirect method based on the decrease in colour of the mercury-diphenylcarbazone complex caused by chloride ions.[1-6] This method involves the following fundamental reactions:

$$Hg^{2+} + H_2DcO \rightarrow HgHDcO^+ + H^+$$

$$HgHDcO^+ + 2Cl^- \rightarrow HgCl_2 + HDcO^-$$

where H_2DcO and $HDcO^-$ represent, respectively, the molecule and the anion of diphenylcarbazone, and $HgHDcO^+$ the coloured complex cation with mercury.[2-7] In the presence of an excess of diphenylcarbazone, an inner complex salt of the type $Hg(HDcO)_2$ can undoubtedly be formed and at higher concentrations precipitated.

The high absorption of the blue-violet complex is influenced by many factors and this method suffers, therefore, from many difficulties. First, it is very sensitive to changes of pH of the solution. Afterwards, when the mercury complex concentration increases, the precipitate is formed and the stability of the coloured solution is small. Another disadvantage of the method consists in the interference of other metals which also form coloured complexes with diphenylcarbazone. This can be partly avoided when the pH is low, but the absorption of the mercury complex is then smaller and it is virtually impossible to determine trace amounts of chloride ion. Most authors accept a pH of 3·3 as the best compromise; nevertheless, in the presence of some other ions, especially copper, cobalt, nickel, and zinc, the determination can be disturbed. Some of these metals also occur in tap water and their influence should, therefore, be eliminated before chloride determination. Previously[3] we have eliminated the influence of copper in a concentration of less than $10^{-3}\%$ by the addition of triethanolamine as a masking agent. This is not very convenient, however, because other remaining metals can interfere and high concentrations of triethanolamine disturb the determination. The best results would be expected when the solution is devoid of other ions and the possibility of their removal is investigated in this paper.

This is accomplished by means of an extraction of metal ions with a chloroform solution of diphenylcarbazone before the colorimetric determination of chloride ion.

EXPERIMENTAL

In the course of the investigation the influence of those factors which are of importance from the point of view of the colorimetric determination alone, as well as the factors which influence the removal of interfering ions by extraction, have been studied.

Effect of pH. The light absorption of the mercury-diphenylcarbazone complex depends on the pH of the solution. For a pH of less than 3·3–3·5 any decrease in the dissociation of the diphenylcarbazone strongly diminishes the absorption. In the range from about pH 3·5 to 6·0 it is nearly constant while above 6·0 it increases slightly. The decrease of light absorption when chloride ions are added varies for different pH values. By increasing the pH, the effect of the chloride becomes smaller, and even above 4·0 no significant decrease of light absorption after the addition of chloride was noted, when the added amount did not exceed 25 μg (Fig. 1).

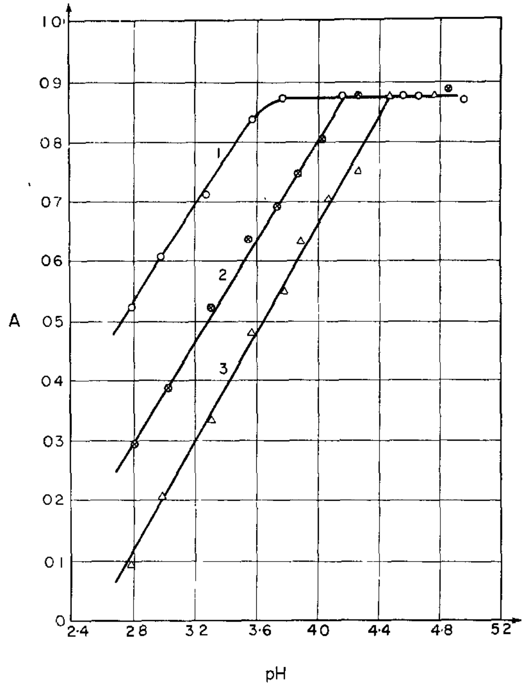

FIG. 1.—Change of absorption with pH for solutions of mercury-diphenylcarbazone complex: 1—in the absence of Cl^-; 2—in the presence of 25 μg Cl^-; 3—in the presence of 50 μg Cl^-.

From the above results it follows that the useful pH range for chloride determination is very narrow —the optimum lies between 3·3 and 3·5. For a lower pH the decrease is proportional to the light absorption, but the drop in absolute light absorption of the mercury-diphenylcarbazone complex makes the method much less sensitive to trace amounts of chloride.

To prevent small changes of pH we found it satisfactory to buffer the solution with an appropriate buffer reagent. This was more convenient than adding a measured volume of acid as was previously practised. A suitable buffer, which neither complexes mercury nor contains chloride ions, was formate-formic acid.

Effect of temperature. In most colorimetric methods the influence of temperature is rather small.[8] In our case the measured solution is not, in fact, a true solution, but a suspension. Its formation is very sensitive to temperature changes. Therefore, it was necessary to control the temperature of the measured solution carefully, as well as to study the effect of temperature changes. The light absorption of solutions containing the mercury-diphenylcarbazone complex and 0, 10, 20, 30, and 40 μg of chloride ion was measured at various temperatures. In Table I values for 24° and 33° are given.

Effect of time. In all previous methods of chloride determination the period of time between the

TABLE I. THE INFLUENCE OF TEMPERATURE ON THE ABSORPTION MEASUREMENTS

Chloride ion present, μg	Absorption	
	24°	33°
0	0·310	0·237
10	0·284	0·208
20	0·260	0·167
30	0·222	0·125
40	0·180	0·097

preparation of the solution and the measurement proved to be rather important. Generally, it should be very short. To overcome this disadvantage we started to use a protective (stabilising) colloid. Good results have been obtained with gum arabic. This improved the results greatly, so that over a period of 2 hr no essential changes were observed. After 4 hr, the change in absorption was less than 10%.

Removal of interfering ions. When the diphenylcarbazone complex is formed at higher pH values, the percentage of bound metals obviously increases. It is advantageous, therefore, to remove any interfering ions by extraction at a higher pH than is used in the proper colorimetric determination. Thus, the extraction was carried out in a solution of sodium formate, approximately 0·02*F*. After the separation of the non-aqueous solvent layer, the pH of the aqueous solution was made about 3·4 by the addition of nitric acid. A fixed volume of mercury^{II} nitrate solution and of diphenylcarbazone solution were added and the absorption of the resulting solution measured.

Benzene, diethyl ether, n-amyl acetate and carbon tetrachloride were tested as solvents but the results were not satisfactory. Good results were obtained with chloroform if it was sufficiently pure. Any contamination from phosgene and chloride must be avoided.

To separate the layers after the extraction it seemed advantageous to filter the water phase through filter paper or cotton to remove small droplets of chloroform. In this case special care should be taken to use materials purified from chloride, which usually contaminates these substances.

Reagents

Mercury^{II} nitrate, 0·01*F*: Dissolve 1·083 g of pure mercury^{II} oxide in 3 ml of concentrated nitric acid and dilute to 1 litre with water. This solution is 0·01*N*, and for direct use should be diluted ten times with water.

Diphenylcarbazone for colorimetry, 0·02%: Dissolve 200 mg of pure diphenylcarbazone in 100 ml of 95% ethyl alcohol. This solution is diluted 1 : 10 with water.

Diphenylcarbazone for extraction, 0·25%: Dissolve 250 mg of pure diphenylcarbazone in 100 ml of freshly distilled chloroform.

Sodium formate, 0·1*F*: Dissolve 5·2 g of sodium formate in 1 litre of water.

Formate buffer, 0·1*F*: Dissolve 5·2 g of sodium formate in 700 ml of water, and adjust with 1·0*F* nitric acid to a pH of 3·4. Dilute to 1 litre with water.

Nitric acid, 0·05*F*: Dilute 3·2 ml of the concentrated acid with water to 1 litre.

Gum arabic, 2%: Dissolve 2 g of arabic gum in 100 ml of hot water. If the solution is turbid, filter through a sintered-glass filter.

All reagents should be prepared with double distilled (from alkaline solution) water.

Apparatus

A Jouan photoelectric colorimeter (Bonet-Maury) was used for most of the experiments. The measurements were performed at 520 mμ. Some measurements were carried out with a Lange colorimeter using a green filter and 1-cm cells.

Procedure

In the absence of interfering ions. In a 50-ml calibrated flask place an aliquot of the test solution containing from 10 to 60 μg of chloride ion. To this flask add 5 ml of formate buffer, 10 ml of 0·02%

diphenylcarbazone solution and 1 ml of gum arabic solution. Dilute with water to about 45 ml, mix thoroughly, then add 2 ml of 0·001*N* mercury^{II} nitrate solution. After dilution to 50 ml, bring the solution to a constant temperature (*e.g.* 20°) and measure its absorption at 520 mμ. Calculate the result from a calibration curve which is obtained in the same manner, using solutions of known chloride content *e.g.* 0, 10, 20, 40, and 60 μg of chloride ion. The calibration curve is linear within the range 0 to 60 μg of chloride ion.

TABLE II. THE DETERMINATION OF CHLORIDE ION IN THE ABSENCE OF INTERFERING IONS

Chloride ion, added, μg	Chloride ion found, μg	Standard deviation, μg	Coefficient of variation, %	Accuracy, μg
10	10	0·90	9·0	0
20	19	1·45	7·3	−1·0
30	30·5	1·20	4·0	+0·5
40	39·4	1·50	3·8	−0·6
50	49·7	1·18	2·4	−0·3
60	59·8	1·00	1·7	−0·2

TABLE III. THE DETERMINATION OF CHLORIDE ION IN THE PRESENCE OF INTERFERING IONS

Chloride ion present, μg	Chloride ion found, μg	Difference, μg	Remarks
10	12·0	+2·0	50 μg Cu^{II} added
25	28·5	+3·5	
50	50·3	+0·3	
10	8·5	−1·5	200 μg Cu^{II} added
25	23·5	−1·5	
50	45·0	−5·0	
10	8·5	−1·5	100 μg Ni^{II} added
25	24·2	−0·8	
50	49·5	−0·5	
10	8·8	−1·2	100 μg Cd^{II} added
25	25·0	0	
50	46·5	−3·5	
10	8·5	−1·5	100 μg Co^{II} added
25	26·3	+1·3	
50	51·5	+1·5	
10	10·0	0	100 μg Pb^{II} added
25	27·5	+2·5	
50	54·0	+4·0	
10	10·0	0	100 μg Zn^{II} added
25	27·5	+2·5	
50	49·5	−0·5	
14	15	+1·0	Tap-water sample
21	24	+3·0	
35	40	+5·0	

In the presence of interfering ions. The presence of interfering ions can be inferred if the addition of the diphenylcarbazone solution produces a colour in the absence of mercury^{II} ions. In this case the interfering cations must be removed. The aliquot of test solution is placed in a separatory funnel, 5 ml of sodium formate solution added and two extractions carried out with 5-ml portions of the chloroform solution of diphenylcarbazone. The water phase, after extraction, is washed with pure chloroform. The remaining solution (if necessary filtered from chloroform droplets) is placed in the 50-ml calibrated flask, about 7 ml of 0·05*F* nitric acid added (the pH of the resulting solution should be 3·4) and the procedure continued as in the absence of interfering ions.

RESULTS

The method described is a useful colorimetric procedure for the quantitative determination of micro amounts of chloride ion. Good results can be obtained provided the experimental conditions are carefully controlled. The precision is good, the accuracy being ± 1·0 μg (Table II). Greater errors are obtained in the presence of interfering cations (Table III). In this case an error of 5·0 μg can sometimes occur, but no systematic error was observed, and the low precision is rather connected with the more complicated operations and handling of samples necessary under such conditions. An average error of accuracy in this case is equal to 1·6 μg of chloride ion.

Zusammenfassung—Eine indirekte kolorimetrische Methode der Bestimmung von Chloridionen war bearbeitet. Die Methode besteht auf der Schwächung der Absorption von Quecksilber-Diphenylkarbazon Komplex. Der Einfluss von pH und Temperatur auf die Bestimmung war untersucht und die experimentale Bedingungen für die Bestimmung von 10 bis 60 μg Cl^- waren gegeben. Bei Anwesenheit des Überschusses von Kupfer, Nickel, Kobalt, Zink, Kadmium und Blei soll man diese Kationen durch $CHCl_3$-Extraktion als Diphenylkarbazonaten beseitigen.

Résumé—Une méthode indirecte pour la determination des ions de chlorure est présenteé: on exploit la diminution de la densité optique du complexe de mercure avec diphénylcarbazone en présence des ions du chlorure. On a étudié l'influence de pH et de la température, en precisant les conditions dans lesquelles il est possible de determiner de 10 à 60 μg de Cl^-. Cuivre, nickel, cobalt, zinc, cadmium et plomb peuvent être extraits sous la forme des diphénylcarbazonates.

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APPLICATIONS OF INFRARED SPECTROSCOPY—II*

OBSERVATIONS ON SOME ASPECTS OF THE ZEISEL ALKOXYL DETERMINATION

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Summary—A sensitive infrared method for quantitative determination of vapours has been used to study some of the reaction variables in the Zeisel alkoxyl determination. Several conflicting reports in the literature have been clarified. Reaction conditions giving rapid and accurate determinations on solids and volatile liquids, even in presence of large sulphur concentrations, are described: for determinations on vanillin the standard deviation is 0·16%. Interaction between alkyl iodides and sulphuretted hydrogen has been found to occur only in aqueous solutions; the use of soda-asbestos as a solid scrubber therefore has fundamental advantages over aqueous solutions, and gives excellent results.

ALTHOUGH the determination of alkoxyl groups is still based on Zeisel's classical method,[1] an iodometric procedure[2] has largely superseded the original gravimetric technique. In addition, an almost continuous catalogue of modifications to procedure, reagents, scrubber composition and apparatus design has been published. (See, for instance, references 3, 4, 5, 6, 7, 8, 9 and 10.) Since conflicting recommendations and statements still exist in the literature, an attempt to clarify the present position seemed desirable.

METHOD OF INVESTIGATION

A sensitive infrared technique,[11,12] developed recently for the quantitative determination of substances in the vapour phase, has been used to study certain stages of the alkoxyl determination. Milligram-quantities of the lower alkyl iodides can be trapped quantitatively in liquid nitrogen[11] and can subsequently be determined by referring the heights of selected characteristic peaks in their infrared spectrum to a carefully constructed calibration curve. This is previously obtained under carefully standardised spectroscopic conditions by quantitatively volatilising weighed amounts of purified alkyl iodides into the infrared gas-cell. (Experimental details of the procedures involved will be given in a subsequent paper[35] describing an infrared method for the simultaneous determination of methoxyl and ethoxyl groups.) Other vapours, *e.g.* hydrogen sulphide, hydrogen iodide and iodine, do not interfere with the determination since there is (*a*) no reaction between these and alkyl iodides in the vapour phase, and (*b*) no overlapping of peaks in their infrared spectra.

Since it is necessary in infrared spectroscopy to exclude water-vapour, the volatile reaction products are trapped after passage through Anhydrone; an Anhydrone guard-tube must be fitted to the trap, as shown in Fig. 1. Careful preliminary tests showed that, of the normal volatile reaction products, Anhydrone retained only water-vapour.

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* Part I: D. M. W. Anderson, *Analyst*, 1959, **84**, 50.

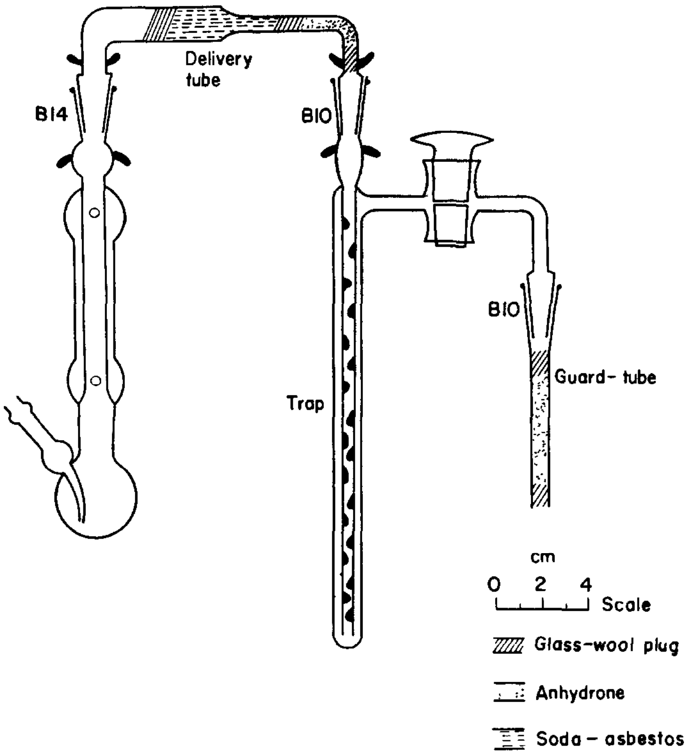

Fig. 1. Assembled apparatus.

The reaction products could therefore be trapped either before or after passage through scrubbers or absorbers of the type normally used in Zeisel determinations. The subsequent spectroscopic examination not only revealed which alkyl iodide had been produced and permitted simultaneous measurement of its concentration, but also revealed if any other volatile product affecting the validity of the result had been produced. The high sensitivity and adequate accuracy of this infrared technique conveniently gave information on (*a*) efficiency of removal of hydrogen sulphide by scrubbers (*b*) sources of loss of alkyl iodide, and (*c*) anomalous reaction of certain compounds.

EXPERIMENTAL

Reagents

Hydriodic acid: M.A.R., sp. gr. 1·7 (6-ml ampoules).

Phenol: AnalaR.

Anhydrone: M.A.R., 14–22 mesh.

Soda-asbestos: M.A.R.

Alkyl iodides: for calibration purposes, the reagent grade was re-distilled three times; the still-head was packed with Anhydrone and the middle fraction collected each time.

Standard compounds

*α-Methyl-*D*-glucoside*

Vanillin
Phenacetin organic analytical standards.

In addition, *vanillin* (microanalytical standard grade) purified by zone-melting was used.

Apparatus

This was assembled as shown in Fig. 1, and consisted of:

(*a*) the combined reaction-flask and condenser described in B.S. 1428: part C 1:9154 (type-2 apparatus).

(*b*) a delivery-tube, which could be packed with Anhydrone and soda-asbestos. Ground-glass joints were lightly coated with silicone grease.

(*c*) a trap, similar to that previously described.[11] Recent traps have been made with Vigreux-type indentations in the inner absorption tube, as shown in Fig. 1.

(*d*) the design of scrubber described in B.S. 1428: part C 1:1954 was used to investigate the efficiency of aqueous scrubbing solutions.

Calibration curves

Fig. 2 shows a typical calibration curve, constructed by making about 5 different measurements per 5-mg range of alkyl iodide using a Hilger double-beam infrared spectrometer. The gas-cells described in references 11 and 12 were used: gas-cells "A" (length 12·5 cm) and "B" (length 31·5 cm) respectively permitted determination of 4–10 mg and 1–4 mg quantities of methyl iodide.

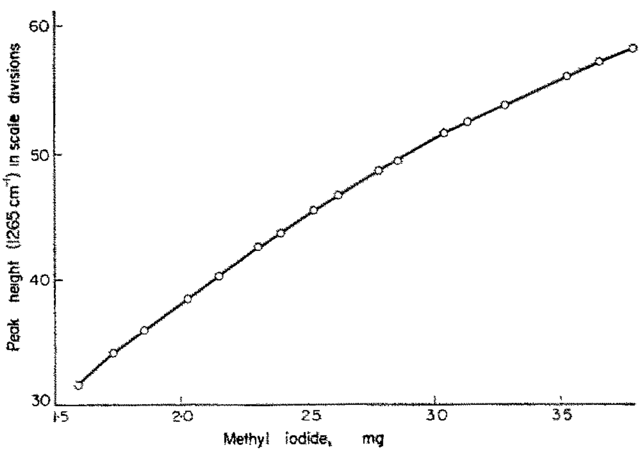

FIG. 2. Calibration curve for determination of methyl iodide.

Weighing of samples

For solids, a long-handled weighing-spoon[10] was used. Volatile liquids were conveniently weighed in a long-handled micro weighing-bottle[10] fitted with a leak-proof ground-glass stopper.

Flow-gas

The infrared technique required nitrogen to be used. Nitrogen ("N.O.F." grade) was passed through soda-asbestos, silica gel and Anhydrone. The flow-rate, stabilised by needle-valves and passage through a large reservoir fitted with capillary outlet, was adjusted by a Rotameter, Type 704, calibrated over the range 4–25 ml per min.

Heating of reaction-flask

An electrothermal flexible heating mantle, Type MBJ 1822, gave very steady ebullition. Recent papers[13] still report difficulty with "bumping", although electrical heating was earlier reported to be advantageous.[14]

Preliminary determinations using standards

(*a*) *Conditioning of acid and apparatus:* The contents of one 6-ml ampoule of hydriodic acid was added to the reaction flask and refluxed for 30 min under a steady flow of nitrogen (6–8 ml per min).

This procedure is advisable: it conditions the apparatus, ensures that the acid is constant-boiling, and decomposes any excess hypophosphorous acid which may have been added. (In any infrared investigations, all traces of phosphine must be removed, since its absorption peaks overlap the particular alkyl iodide peaks used for determination).

(*b*) *Determination of reaction-times and optimum flow-rate:* Recommended flow-rates have varied between 4[7,15] and 25[8] ml per min. For 2–5 mg samples and a flow-rate of 6–8 ml per min, we obtained quantitative recovery of methyl iodide from vanillin in 10–15 min and of ethyl iodide from phenacetin in 15–20 min from start of reflux. These times vary little from those found by Kirsten[8] (25 ml per min) and by Inglis[9] (12–15 ml per min). Since some compounds could possibly react more slowly than these standards, a reflux period of 30 min was adopted for methoxyl and ethoxyl compounds, and has since proved adequate for many organic compounds containing a wide range of other functional groups and analysed as "unknowns" by one of us (J. L. D.)

Although Inglis used carbon dioxide flow-gas at 12–15 ml per min with one scrubber (to minimise the tendency for methyl iodide to dissolve in aqueous solution), it had earlier been established[10] that a flow-rate of 6 ml per min caused high results if a second scrubber was not used. Pending investigation of these conflicting reports of scrubber efficiency, we considered that, since the reaction-times quoted above were sufficiently short for routine analyses, and were not in any case decreased appreciably by using faster flow-rates, the use of a slow flow-rate was fundamentally correct experimentally in minimising tendencies towards (*a*) inadequate gas scrubbing, and (*b*) incomplete alkyl iodide retention in the final stage. Any scrubber solution in which alkyl iodides react or are appreciably soluble at low flow-rates is unsatisfactory in any event. A flow-rate of 6–8 ml per min was therefore adopted as standard.

(*c*) *Results:* Table I shows the results obtained for standard compounds. This gives a true representation of the poorest results that may be expected, since none of the results obtained was rejected; the standard deviation is also shown.

TABLE I. RESULTS OF ALKOXYL DETERMINATIONS ON STANDARD COMPOUNDS

Compound	Range of sample weights taken, *mg*	No. of detns.	Alkoxyl content		Stand. Devn., %	Max. divergence from theory	
			Theory, %	Av. found, %		+	−
Vanillin	1·84–3·39	15	20·40	20·39	0·16	0·28	0·28
α-Methyl-D-glucoside	2·38–4·36	5	15·99	15·99	0·08*	0·11	0·07
Phenacetin	2·82–3·67	6	25·15	25·18	0·17*	0·20	0·23

* Calculated by the range method.

Having established that the reaction conditions described and the spectroscopic method of determining alkyl iodides gave satisfactory analyses of pure reference compounds, the following investigations were made.

INVESTIGATIONS

1. *Concentration and colour of hydriodic acid*

Most analysts have found constant-boiling hydriodic acid adequate, but the use of more concentrated acid (sp. gr. 1·96) has been proposed,[16] and the addition of a few drops of this concentration to the constant-boiling acid suggested.[5] Reflux for 30 min over red phosphorus before use has been recommended.[6,17] We have found the M.A.R. constant-boiling acid, conditioned as already described, to be satisfactory; tests showed that, at 6–8 ml per min, only trace amounts, if any, of hydriodic acid vapour were volatilised. The use of more concentrated acid would give increased amounts of distilling acid vapour, so introducing a possible source of error.

Furter[4] stated that the use of fresh colourless acid was essential. Steyermark,[18] however, found that the colour was not critical if the acid was refluxed before use: more recently it was observed[19] that the presence of free iodine in the hydriodic acid was in fact advantageous. Belcher[7] obtained acceptable results titrimetrically in the presence of 20 mg added iodine, although an increased blank was observed. Our experiments confirm that the acid colour has no effect on the yield of alkyl iodide. Appreciable volatilisation of iodine does, however, occur from very dark mixtures, particularly if the compound under analysis contains sulphur or strong reducing groups, or, as can occur with carbohydrate materials, is readily decomposed to give carbon. As Kirsten pointed out,[8] this may impose an additional test on the scrubber efficiency, although much of the iodine condenses out before reaching the scrubber.

2. *Repeated use of acid in routine analyses*

In routine analyses when compounds are known to decompose quantitatively in the normal reaction-time, one charge of acid can safely be used for 8 determinations (av. sample weight = 5 mg) if the mixture is refluxed between each determination: to allow a safety margin, we have always used a reflux period of 30 min, but a shorter period may be found adequate. In one series of experiments, 14 successive determinations were satisfactorily made without change of acid. Care must always be exercised, however: we have found certain compounds[20] which liberate alkyl iodides continuously for several hours.

3. *Determinations on volatile liquids*

Earlier investigations found double distillation[9,18,21] or the use of modified apparatus[8] necessary for quantitative results. Double distillation is not essential when the following procedure is used:—

Weigh the sample as already described. Transfer to a reaction flask charged with a mixture of hydriodic acid (6 ml) + phenol (approximately 0·25 g) which has been conditioned as described for 30 min, *then allowed to cool completely*. The small stoppered weighing-bottle must submerge completely in the phenol-hydriodic acid mixture. Shake the reaction flask to loosen the weighing-bottle stopper. Using a nitrogen flow-rate of 2–4 ml per min, heat gently so that reflux begins after 8 to 10 min, then increase the flow-rate to 6 to 8 ml per minute and reflux for 30 minutes.

Compounds such as methanol, anisole, 1:1- and 1:2-dimethoxyethanes, and ethyl orthoformate have been analysed without difficulty in this way. Infrared experiments with anisole revealed that no detectable traces of unreacted anisole were volatilised together with the methyl iodide unless the flow-rate was increased to >15 ml per min.

4. *Effect of presence of sulphur*

The presence of sulphur has long been known to complicate alkoxyl analyses, causing low results. Sulphur present in organic functional groups is usually reduced to hydrogen sulphide by reflux with hydriodic acid; inorganic sulphate reacts similarly. Commonly only 1 sulphur atom is present, but the ratio of sulphur atoms to alkoxyl groups in compounds can exceed 1:1. It is of importance that the analysis of compounds mixed with relatively large amounts of inorganic sulphate has caused particular difficulty.[22,23]

An interaction between hydrogen sulphide and alkyl iodides, resulting in mercaptan formation,[1,24] is considered to cause the low results; Bethge and Carlson[25] suggested that this reaction is favoured in alkaline solution. The infrared technique has shown that *no* reaction between hydrogen sulphide and alkyl iodides occurs in the vapour phase: alkoxyl compounds containing sulphur, or to which had been added sodium sulphate, gave theoretical yields of alkyl iodide in presence of the evolved hydrogen sulphide. The undesired interaction must therefore occur only *in aqueous solution.*

Mere absorption of hydrogen sulphide by scrubbing solutions is therefore insufficient; quantitative removal of sulphide ions from solution in a rapid reaction is essential. Scrubbers must also effectively remove iodine and hydrogen iodide vapours: although the use of (*a*) low flow-rates, and (*b*) pre-conditioning of the hydriodic acid should ensure that the amounts of these involved are normally very small, there will be a tendency for increased volatilisation of iodine when much hydrogen sulphide is released. Thus any scrubber able to remove satisfactorily the large amounts of hydrogen sulphide liberated when excess inorganic sulphate is present will have a safety-factor when sulphur-containing organic compounds are analysed. The following investigation of scrubber efficiency was made from this viewpoint.

5. *The efficiency of aqueous scrubbing solutions*

The functional efficiency of the design of scrubber used must also be considered here; the volume of scrubbing solution and the flow-rate used will be contributing factors. The efficiencies of some scrubbing solutions were therefore initially compared at a flow-rate of 6–8 ml per min, 4 ml of the solution being used in the B.S. (1954) design spiral scrubber.

Our results confirmed[10] that aqueous sodium thiosulphate is unsatisfactory because of reaction with methyl iodide.[26,27] Table II summarises the other results obtained. For each solution tested, several determinations were made under the conditions shown; the range of recoveries obtained is quoted, since averaged results at the 100% level can be misleading.

(*a*) *In absence of sulphur*, all the solutions listed were satisfactory. Water itself, however, gave slightly low results; this is in agreement with Heron *et al.*,[10] who reported 94–98% recovery. These negative errors are undoubtedly due to the solubility of methyl iodide in water; the effect can be minimised by keeping the scrubber temperature at 42° ± 1°, but this adds a complicating factor to the scrubber design. Moreover, whilst heated scrubbing solutions have been recommended,[1,6,28] Colson[21] has pointed out that the increased possibility of hydrolysis of methyl iodide may lead to low results. As shown in Table II, the negative error was dependent on the volume of water used, and large errors were introduced when sulphur was present (*cf.* the results obtained with water saturated with hydrogen sulphide).

(*b*) *In presence of* 3–4 *mg of added sodium sulphate* (equivalent to 1 sulphur atom per methoxyl group for 3 mg samples of vanillin) only sodium acetate and sodium bicarbonate of the solutions tested were clearly unsatisfactory (*cf.* ref. 25).

(*c*) *In presence of larger amounts of sulphur*, both sodium antimonyl tartrate and the sodium thiosulphate + cadmium sulphate mixture began to give low results. This finding explains the differing opinions expressed regarding their efficiency (*cf.* 7 and 25, 8, 10 and 27). In agreement with earlier investigators,[23,29] cadmium sulphate gave good results; it was the only satisfactory solution when a large excess of sulphur was present. The formation of heavy cadmium sulphide precipitates did not influence its efficiency, as has been suggested.[30]

TABLE II. EFFICIENCY OF SOME SCRUBBING SOLUTIONS* IN METHOXYL DETERMINATIONS IN THE PRESENCE AND ABSENCE OF SULPHUR

Range of weight of vanillin, 2·92–3·39 mg, ∴ methoxyl present approx 0·2 mEquivs.

Composition of scrubbing liquid†		Wt. of sodium sulphate added, *mg*	∴ Sulphur present, *mEquivs*	Range of methoxyl recovery, %
5% aq. sodium bicarbonate		0	0	99·4–100·4
		3	0·2	95·1–95·3
		10	0·7	92·5–92·7
		27	1·9	90·0–90·4
25% aq. sodium acetate		0	0	100·0–100·5
		4	0·3	98·1–98·5
		30	2·1	91·1–91·2
10% aq. sodium antimonyl tartrate		0	0	99·5–100·2
		3	0·2	99·6–100·0
		10	0·7	95·1–95·3
		15	1·0	94·1–94·2
5% aq. sodium thiosulphate + 5% aq. cadmium sulphate (1 + 1 V/V)		0	0	100·0–100·5
		3	0·2	100·0–100·1
		10	0·7	99·1–99·5
		18	1·3	97·7–98·0
5% aq. cadmium sulphate		0	0	99·8–100·6
		3	0·2	
		10	0·7	
		15	1·0	
		32	2·2	99·0–99·2
Water	2 ml	0	0	99·5–99·7
	4 ml	0	0	98·8–99·2
	2 ml	4	0·3	97·5–97·9
	4 ml	4	0·3	96·8–97·1
Water satd. with hydrogen sulphide	2 ml	0	0	95·2
	3 ml	0	0	94·0
	4 ml	0	0	91·3
	5 ml	0	0	90·7

* Used in the spiral scrubber described in BS1428 : C 1 : 1954. Flow-rate = 6–8 ml per min. Temp. of solutions = 20° ± 1°.

† Volume used = 4 ml, unless otherwise stated.

With high concentrations of hydrogen sulphide, the decreased efficiency of sodium antimonyl tartrate may be caused by complex thio-anion formation from the original Sb_2S_3 precipitate, and subsequent interaction between the thio-anion and alkyl iodide.* For cadmium sulphate the concentration of hydrogen sulphide is apparently not so critical since cadmium sulphide does not form complex sulphides.

In earlier experiments, Gran[30] found a preliminary water scrubber essential (to remove hydrogen iodide vapour), since otherwise the scrubber acidity increased

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* We are grateful to one of the referees for this suggestion.

sufficiently to cause some dissolution of the cadmium sulphide precipitate. This effect, however, resulted from his use of acid more concentrated than the azeotrope. Although the introduction of a water scrubber removed one source of error, another was simultaneously introduced, as already described; Gran found that this in turn could be minimised by increasing the flow-rate to 40 ml per min. Experiments at this very high flow-rate revealed that the absorption of hydrogen sulphide by water is indeed much less than at 6–8 ml per min; the high flow-rate either decreases the efficiency of scrubbing, or creates a superior competitive "degassing" effect.

In solutions containing sodium thiosulphate + cadmium sulphate, complexing of thiosulphate ions by cadmium will undoubtedly occur. The decreased efficiency of this scrubbing mixture at high sulphur concentrations (at which cadmium sulphate itself remains efficient) is probably due to removal from solution of cadmium as cadmium sulphide. Some of the previously complexed thiosulphate is therefore liberated, so increasing its possibility of reaction with alkyl iodide.[26,27]

Many other aqueous scrubbers have been proposed, *e.g.* red phosphorus suspensions,[1,2,4,28] solutions of organic compounds,[27] acetic acid[8] and hydrochloric acid.[25] The efficiency of these was not investigated.

The B.S. design spiral scrubber gives adequate scrubbing efficiency under the experimental conditions described, but not at greatly increased flow-rates. When aqueous cadmium sulphate was used in two spiral scrubbers joined in series, no detectable leakage of hydrogen sulphide to the second scrubber occurred at a flow-rate of 10 ml per min; slight leakage occurred at 15–20 ml per min. This supports the earlier warning by Heron *et al.*[10] regarding scrubbing efficiency.

6. *The use of a solid scrubber*

Having established that reaction between hydrogen sulphide and alkyl iodides occurred only in aqueous solution, it appeared that the use of a suitable solid scrubber would eliminate several possible sources of error. The use of solid scrubbers was apparently first suggested by Fierz-David *et al.*,[31] but their use in alkoxyl determinations attracted little attention until recently.[13,32,33,34]

We have found soda-asbestos (M.A.R.) to be a very efficient solid scrubber, although Večeřa and Spěvák[34] apparently rejected it after trial experiments. It quantitatively absorbs and firmly retains hydrogen iodide, iodine, hydrogen sulphide

TABLE III. EFFICIENCY OF A SODA-ASBESTOS SOLID SCRUBBER
Flow-rate = 6–8 ml/min

Compound	Range of weights taken, *mg*	∴ Alkoxyl present, *mEquivs*	Wt. of sodium sulphate added, *mg*	∴ Sulphur present, *mEquivs*	Range of alkoxyl recovery, %
Vanillin	2·736–3·01	approx. 0·2	0	0	99·6–100·5
			10	0·7	99·7–100·5
			30	2·1	99·7–100·5
			60	4·2	99·7–100·1
Phenacetin	2·98–3·61	approx. 0·2	0	0	99·5–100·4
			30	2·1	99·8–100·6
			60	4·2	100·0–100·6

and carbon dioxide; even when quantities of these vapours have been absorbed there is no retention of alkyl iodides. Table III shows its high efficiency under testing conditions. In addition, when 40 mg of sodium sulphate was refluxed for 3 hr, using a flow-rate of 40 ml per min, no hydrogen sulphide passed the scrubber.

Experimentally, the use of a solid scrubber simplifies the apparatus and procedure. The use of nitrogen as flow-gas is, of course, essential. The spiral liquid scrubber is replaced by a straight connecting tube, as shown in Fig. 1; a packing of soda-asbestos 2 inches long is adequate, and is renewed for each analysis.

The reaction conditions described in this paper and the results presented on scrubbers are totally applicable to alkoxyl determinations in which the standard gravimetric or iodometric finish is employed.

Details of the investigation of reaction conditions for determination of propoxyl and butoxyl groups, of the differentiation of ester from ether groups, and of the infrared method for analysis of compounds containing methoxyl and ethoxyl groups will be given shortly in further parts of this series.

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Zusammenfassung—Eine empfindliche Infrarotmethode zur quantitativen Bestimmung von Dämpfen wurde verwendet um die Reakationsvariablen der Alkoxylbestimmung nach Zeisel zu studieren. Verschiedene Widersprüche in der Literatur wurden klargestellt. Die Raktionsbedingungen zur raschen Erzielung genauer Resultate bei der Analyse von festen Körpern und verdampfbaren Flüssigkeiten, selbst in Gegenwart grosser Mengen an Schwefel, werden beschrieben. Es wurde gefunden, dass die Reaktion zwischen Alkyljodid und Schwefelwasserstoff nur in wässriger Lösung stattfindet; die Anwendung von Soda-Asbest als festes Absorptionsmittel hat daher fundamentalen Vorteil gegenüber einer wassrigen Lösung und gibt exellente Resultate. Mit Vanillin ausgeführte Testbestimmungen zeigen eine Standardabweichung von 0·16%.

Résumé—Une méthode infra-rouge sensible pour la détermination quantitative des vapeurs a été utilisée pour l'étude des variables de la réaction dans le dosage des alkoxyl de Zeisel. Différents rapports contradictoires dans la littérature ont été clarifiés. Les conditions de réaction, donnant des dosages rapides et précis pour des solides et des liquides volatils, même en présence d'une grande concentration de soufre, sont décrites; pour des dosages de vanilline, l'écart standard est 0,16%. Les auteurs ont trouvé que l'interaction entre les iodures d'alkyl et l'hydrogène sulfuré se produisait seulement en solutions aqueuses; l'utilisation d'amiante sodée comme laveur solide a cependant des avantages fondamentaux sur les solutions aqueuses, et donne d'excellents résultats.

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COLORIMETRIC DETERMINATION OF TRACE AMOUNTS OF ALUMINIUM IN STEEL

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Summary—The method for the determination of aluminium in steel consists of a preliminary separation of iron, together with nickel, chromium, copper and molybdenum, by mercury cathode electrolysis. The electrolysed solution is made up to a known volume, and from an aliquot, the residual iron, together with any titanium and vanadium, is removed by extraction of the cupferrate with chloroform.

After destruction of the excess cupferron, the solution is neutralised, a measured excess of acid is added, and the aluminium-nitrated Solochrome Cyanine R complex is formed under optimum conditions.

IT is often necessary in the case of mild steels to establish the method of manufacture (*e.g.* Bessemer or open-hearth process), nitriding and other treatments. In some cases it is important to know whether ferro-silicon or aluminium has been used to "kill" the steel. In the case of aluminium, it is known that the presence of this metal can influence brittleness, austenitic grain size and ageing characteristics, to mention only the more important effects.

As the amount of aluminium to be determined is in the range 0·005–0·5 %, normal gravimetric and titrimetric methods are inapplicable. A survey of polarographic methods is given by Perkins and Reynolds,[1] and an examination of the one most used is described in associated papers.[2–4] Colorimetric procedures have been described by Sandell[7] and current methods are surveyed in a review article.[8]

Separation of aluminium

One of the main difficulties in most methods is the separation of the aluminium from interfering metals. In all methods, iron constitutes a serious interference and it must be either masked or removed. Because of the relatively large ratio of iron to aluminium in a steel—it can be as high as 20,000 : 1—complete removal is preferable. This is generally accomplished in a two-stage procedure, the first removing the bulk of the iron, the second removing residual traces of iron.

Various methods are quoted for the removal of the bulk of the iron and they can be classified under the following headings:

(1) Precipitation,
(2) Solvent extraction,
(3) Chromatography,
(4) Mercury cathode electrolysis.

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All four types of method were examined and the following points were noted.

(1) *Precipitation:* Various improvements on the classical separation of iron using sodium hydroxide have been proposed[9,10] in an attempt to reduce the adsorption of aluminium on ferric hydroxide, which can account for a loss of up to 25% of the aluminium content.[11] The most recent of these methods[10] has been examined, but some difficulty was encountered in obtaining stable coloured solutions free from suspended solid matter.

(2) *Solvent extraction:* The methods listed include extraction of the iron from hydrochloric acid solution with isopropyl ether[12–14] or isobutyl acetate,[15] extraction of ferric thiocyanate with amyl alcohol-ether,[16] extraction of the iron-sodium diethyldithiocarbamate complex with chloroform[15] and selective extraction of aluminium oxinate in the presence of EDTA after first converting the iron to ferrocyanide.[17]

In those methods using organic complexing agents, it was found that the aluminium added as an impurity by the reagents was often more than that being determined. Also, the solvent-acid type of extraction removed iron only, leaving elements such as nickel, vanadium and titanium, which would cause interference unless removed at a later stage.

(3) *Chromatography:* As an alternative to the classical separation technique, a separation on a cellulose column was attempted following Bishop's procedure.[18] Using this procedure Rooney[15] found that small amounts of titanium, vanadium, zirconium, chromium, nickel and cobalt were either not separated or only partly separated from iron.

Experiments have shown that cadmium, antimony, tin, copper, iron, cobalt, manganese and zinc were not retained on the column, whereas aluminium, nickel, chromium, titanium and some zirconium were retained.

Any subsequent procedure must include provision for the removal of nickel and zirconium, both of which cause interference with the final aluminium determination. This, coupled with the fact that the preparation of the column *etc.*, is a time-consuming procedure[19] when compared with other methods, led to the discontinuation of further work on these lines.

(4) *Mercury cathode electrolysis:* One of the simplest techniques, which has been used for the removal of iron from aluminium for nearly seventy years,[20] is electrolysis at a mercury cathode. Numerous methods for the determination of aluminium in steels and related materials, using this technique, have been described in the intervening years.[19,20–32] After a preliminary investigation, it was decided that this method would be the most suitable one for the separation of iron together with nickel, copper, chromium and molybdenum.

The removal of residual amounts of iron is generally accomplished by precipitation with sodium hydroxide,[19] by extraction with an organic solvent of the iron cupferrate,[13–16,25] the oxinate[10] or the 8-hydroxyquinaldinate,[31] or by fusion with sodium carbonate.[24]

Using the method of Scholes and Smith,[19] which employs a preliminary separation by mercury cathode followed by precipitation with sodium hydroxide (10*N*), complete removal of iron was achieved, but there were several reasons for not adopting this procedure as a whole. Thus:—

(*a*) the mercury cathode electrolysis was not always successful using the prescribed conditions, (*b*) the reduction in the volume of the sample solution after electrolysis (about 80 ml) to 5 ml was tedious and needed careful supervision to avoid any loss by "spitting", and

(*c*) the filtration of the ferric hydroxide plus floc was time-consuming and its efficiency was dependent on the success of the previous electrolysis stage.

Instead, a procedure resembling, in principle, that of Rosotte,[29] Jean,[28] and Fogelson *et al.*[25] was preferred for the removal of traces of iron. This consisted of a cupferron extraction, any titanium or vanadium present in the solution being removed at the same time.

Determination of aluminium in the iron-free solution

When the aluminium has been separated from gross amounts of interfering elements, a number of methods are available for the final determination.

Of the polarographic methods, the earlier ones attempted to measure the straightforward step due to aluminium at $-1{\cdot}7$ V (vs. S.C.E).[33] Unfortunately, this half-wave potential is close to the discharge potentials of sodium, potassium and barium ions. In addition, hydrogen, whose reduction wave precedes that of aluminium, will also interfere unless the pH of the solution is kept above 3. Willard and Dean[34] introduced a method in which the step due to a complex formed by aluminium with a di-*o*-hydroxyazo dye, Solochrome Violet RS, is measured. This method was most successful and it was applied to the determination of aluminium in steel and also in other materials.[1–4,15,18,19,35,36]

The method suffers from the disadvantage that the insolubility of the dyestuff limits the final concentration to 0·35 mg per 50 ml of solution. Recently the work of Ishibashi *et al.*[37] and others [5,6,38,39] has shown that it is possible to obtain direct aluminium waves at a pH value of 4 in lithium hydroxide solution. The Willard and Dean technique was applied following a preliminary separation of iron according to Rooney's method.[15] The polarograph used was a Tinsley MK.15 model with the following centre settings:—

sensitivity	4 μA F.S.D.,
damping	1,
counter current	0.

Under these conditions it became obvious that the smallest concentration of aluminium that could be determined was approximately 30 μg, based on a 1-g sample. This corresponds to 0·03%; and doubling the sample weight would only give a lower limit of 0·015% of aluminium and would need increased amounts of organic reagents for the removal of iron *etc.*, thus increasing the blank value. Increasing the sensitivity setting of the polarograph did not solve the problem, because at sensitivities greater than 4 μA F.S.D., the steps on the polarograms became so distorted that measurement of the step height became virtually impossible. In view of the limitations set by the polarograph, the various colorimetric procedures were reviewed. A variety of reagents have been used by various workers including aluminon,[12,13,16,32,40–46] alizarin S,[47–50] morin,[51,52] quercetin,[53] haematoxylin[54,55] Eriochrome Cyanine R,[10,14,51,56–62] oxine,[17,24,27,63] cupferron,[29] quinizarin sulphonic acid,[64] stilbazo[28] and arsenazo.[65]

In addition, two other reagents which, like Eriochrome Cyanine R are hydroxytriphenylmethane dyes, have been proposed[66] as suitable colorimetric reagents for aluminium.

Of the above reagents, the most promising one appeared to be Solochrome Cyanine R, or Eriochrome Cyanine R as it is referred to in American nomenclature.

The use of Solochrome Cyanine R as a colorimetric reagent for aluminium was first suggested by Eegriwe.[51] It forms a red-violet complex in an acetate buffer solution, and has been shown to be superior to aluminon,[11] especially with respect to complex formation at room temperature and stability to temperature change. Richter[59] has made a study of interferences in the method and concludes that a pH value of 3·8 is the most suitable for colour development. Other workers[10,14,19,56,57,61,62] are convinced that a pH value nearer to 6 is the optimum for colour development.

Hill[10] states that nitration of the dyestuff increases the stability of its aqueous solution.

EXPERIMENTAL

Mercury cathode electrolysis

As a starting point for the investigation, the method employed was that described by Scholes and Smith.[19]

A cell similar to the one described by Center *et al.*[67] was used, in which both the solution and mercury are stirred counter-current fashion by a stationary magnet, and the temperature is maintained below 40° by a water-cooled coil immersed in the solution.

Although many methods quote lengthy deposition times, it was found that when electrolysing the solution in a cell containing 30 ml of mercury, a time of 40 min was required to remove all but the last traces of iron from a 0·5-g sample of pure iron. A current of 15 A was used, and this gave a current density of 0·37 A/cm^2.

The use of sulphuric acid, as advocated by Scholes and Smith, is rather a slow method of sample dissolution, a much more efficient method being to use 5 ml of nitric acid and 5 ml of hydrochloric acid (1 + 1), followed by 10 ml of sulphuric acid. The solution was then heated until fumes of sulphur trioxide were evolved, so as to expel all volatile acids.

Some difficulty was experienced with the removal of iron in the presence of chromium, the formation of a black deposit on the surface of the mercury giving rise to a barrier to the deposition of the iron. Investigations were carried out, therefore, to determine the optimum electrolysis conditions.

Nearly all of the separations described using a mercury cathode[19,24,27–30,48,67,68] employ an electrolyte containing sulphuric acid, and observe special precautions for the satisfactory deposition of chromium. Hynek and Wrangell[31] state that a perchloric acid medium is to be preferred, because volatile acids can be smoothly expelled before electrolysis; and during electrolysis the fuming is only slight. Tests using perchloric acid showed that it is superior to sulphuric acid for these same reasons, and also because the use of perchloric acid precludes the formation of difficulty soluble metal salts at the forming stage, as often occurs with sulphuric acid.

It was found that the formation of the black film on the mercury surface was not a function of the acidity of the solution since neutralisation with sodium carbonate and re-acidification with a few drops of perchloric acid frequently did not prevent its formation.

It was also found that, for a series of electrolyses with a particular steel containing chromium, some of the separations were successful whilst with others there were considerable amounts of iron remaining in the solution and the mercury surface became covered with the familiar black film. Further work showed that if hydrochloric acid was omitted from the dissolution procedure, no difficulty was experienced with the deposition of iron or chromium, the mercury surface remaining clean and bright.

It has also been shown that if nitric and perchloric acids only were used for the dissolution, and two drops of hydrochloric acid (1 + 1) were added immediately before the electrolysis, the removal of iron was incomplete and the mercury surface became black.

The steels listed in Table I have been successfully electrolysed using the modified procedure. In all cases, the residual iron was removed by one extraction of the cupferrate with chloroform and at the end of the electrolysis period the mercury remained clean and bright in appearance.

TABLE 1

B.C.S. Code	Silicon	Manganese	Nickel	Chromium	Vanadium	Molybdenum	Tungsten	Titanium	Copper	Lead
271	0·32	0·46	0·01	0·04	<0·002	0·19	0·01	0·005	0·01	0·002
276	0·23	0·48	0·18	0·10	0·05	<0·01	0·20	0·005	0·12	—
152/1	0·035	1·11	—	—	—	—	—	—	—	—
224	0·30	0·695	0·10	1·46	0·24	<0·02	—	—	0·07	—
253	0·18	0·35	2·92	0·35	0·22	0·94	—	—	0·49	—
255	0·62	1·11	0·56	0·96	0·26	1·41	—	—	0·24	—
212	0·13	0·73	0·04	0·02	—	—	—	—	0·10	0·28
235	0·82	0·46	8·73	19·01	0·02	0·04	0·68	0·62	0·98	—
211/1	0·275	0·32	0·24	12·80	—	—	—	—	—	—
206	3·40	0·375	0·04	0·08	0·14	nil	—	0·16	—	—

With highly alloyed steels, for example B.C.S. 235 and 211/1, which are insoluble in nitric acid, the addition of hydrochloric acid is unavoidable and all traces must be removed by repeated fuming with perchloric acid after dilution with water.

Removal of traces of iron

Short[13] states that complete separation of iron from aluminium by extraction of the cupferrate with chloroform is achieved only when the pH of the solution is less than 0·4.

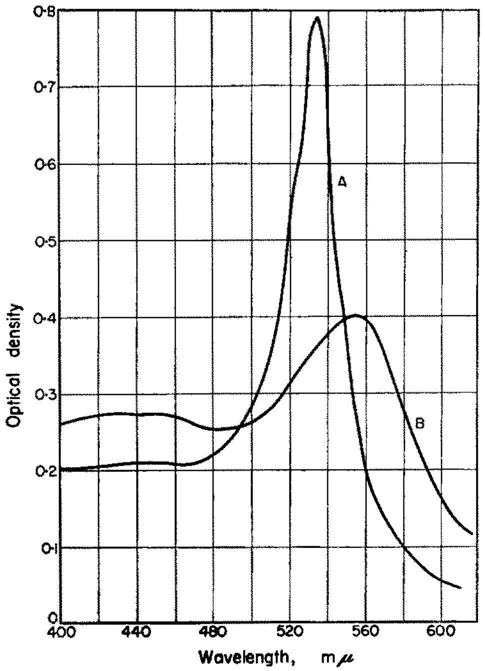

FIG. 1. Absorption spectra for nitrated Solochrome R complexes.
Curve A. Test solution containing 50 μg of aluminium measured against water.
Curve B. Test solution containing 200 μg of iron measured against water.

Using the Scholes and Smith procedure, including neutralisation before electrolysis and making the solution from electrolysis up to 100 ml, the pH of the solution was between 0·7 and 0·9. This necessitated the addition of 2·5 ml of perchloric acid to a 20-ml aliquot to lower the pH to 0·3. Using this method, the blank value rose to the equivalent of 9 μg of aluminium in the final solution. This was undesirable and a method of reducing this figure had to be found.

Fortunately, the use of the modified dissolution procedure, which obviated the need for a neutralisation stage provided the answer. After electrolysis the solution had a pH of 0·3–0·4 and the cupferron could be added to the aliquot without any adjustment of the acidity being necessary.

Colour development

The only modification to the Scholes and Smith procedure was the nitration of the Solochrome Cyanine R. This was intended to increase the stability of its aqueous solution; solutions of the nitrated reagent have been kept for many weeks without any sign of deterioration.

An absorption spectrum of the dye-aluminium complex confirmed that the maximum absorption is identical with the un-nitrated complex, *viz.*, 535 mμ. In addition, the absorption spectrum of the corresponding iron complex was plotted over the same range and showed a maximum absorption as 556 mμ. The two curves are shown in Fig. 1. They also show that the sensitivity of the iron complex is much less than that of the aluminium complex, but that iron does contribute a major interference if present.

"Blank" values

One of the principal limiting factors to the lower limits of the method is the magnitude of the blank value, which arises due to the colour of the reagent and pick-up of aluminium from apparatus and reagents. Methods which employ precipitation with strong alkali are particularly susceptible to contamination from glassware, and special precautions, such as the use of stainless steel or polythene apparatus, must be taken.[10,16,19] One of the advantages of the proposed method is that, apart from a rapid neutralisation stage before the colour development, the solution is at all times moderately or strongly acid and no special apparatus is required.

Rooney[15] found that there was little pick-up during the electrolysis stage. This has been confirmed and this stage is therefore omitted from the "blank" procedure.

The major part of the blank value, apart from the colour of the reagent, 5 ml of which gives an optical density of 0·138 units, probably arises from the presence of aluminium in the reagents.

With reasonable care in the fuming and evaporation stages to avoid adventitious contamination and using normal analytical grade reagents where available, the "blank" solution in the proposed method has an optical density of 0·170 units against water, or 0·032 units against a colour reagent "blank".

This is equivalent to 3 μg of aluminium in the final solution, which on the basis of a 0·5-g sample represents 0·003%. If it is desired to reduce this figure, it can be accomplished by (*a*) using a larger sample weight, and (*b*) using high-purity reagents stored in polythene bottles on receipt.

Reagents

All solutions should be prepared from reagents of the highest purity obtainable, and they should be stored in polythene bottles.

Nitric acid, (1 + 1): Dilute 500 ml of nitric acid (sp.gr. 1·42, AnalaR grade) to 1 litre with water.

Perchloric acid, 60%: AnalaR grade.

Hydrogen peroxide, 5%: (v/v).

Cupferron, 1% (w/v): Dissolve 0·5 g of cupferron, recrystallised from alcohol-ether (1 + 1), in 50 ml of water. Keep well stoppered and prepare fresh daily.

Phenolphthalein indicator solution: Dissolve 0·1 g of phenolphthalein in 50 ml of methylated spirits and dilute to 100 ml with water.

Hydrochloric acid, 0·2*N:* Dilute 20 ml of AnalaR grade hydrochloric acid (sp.gr. 1·16) to 1 litre with water.

Sodium hydroxide, 2*N:* Transfer 80 g of sodium hydroxide pellets to a 1-litre polythene bottle. Dissolve in water and fill to the neck.

Nitrated Solochrome Cyanine R solution, 0·1% (w/v): To 0·5 g of Solochrome Cyanine R add 2·9 ml of nitric acid (sp.gr. 1·42). Swirl for 2 min (till orange-red), add 100 ml of water and 0·36 g of urea. Dissolve and dilute to 500 ml.

Buffer solution: Dissolve 275 g of ammonium acetate and 110 g of hydrated sodium acetate in water and dilute to 1 litre. Add 10 ml of glacial acetic acid and mix thoroughly. Dilute 167 ml of this stock buffer solution to 1 litre with water. Adjust the pH of the diluted solution to 6·1 by adding either acetic acid or sodium hydroxide solution.

Standard aluminium solution: Dissolve 1·7556 g of AnalaR aluminium potassium sulphate in water and dilute to 1 litre in a graduated flask:

1 ml of this solution ≡ 10 μg of aluminium.

Procedure

Dissolution of sample: Transfer 0·5 g of the sample to a 150-ml beaker and dissolve in 10 ml of nitric acid (1 + 1), warming if necessary (*Note* 1). Add 5 ml of perchloric acid and evaporate, with the beaker covered, to fumes of perchloric acid. Uncover the beaker and fume for 1 min. Cool, dissolve in 10 ml of water and filter through a pad of filter pulp, using suction if necessary. Wash the pad with water and reserve the filtrate, (A), which contains acid-soluble aluminium. Ignite the pad in a platinum crucible, add 3 or 4 drops of dilute sulphuric acid and 2 ml of hydrofluoric acid, and evaporate to fumes of sulphur trioxide. Continue heating until dry, then ignite at 800° for a few min. Fuse the residue with 0·5 g of sodium hydrogen sulphate, cool and dissolve in 10 ml of water. If only the total aluminium is required, add this extract to (A) and continue with the electrolysis procedure.

If separate results are required for the acid-soluble and acid-insoluble aluminium, then the latter is obtained by treating the extract with 1 ml of perchloric acid, transferring to a separatory funnel and following the solvent extraction and colour development procedure.

Electrolysis: Transfer the solution to the electrolysis cell containing 30 ml of mercury. Adjust the volume of solution such that the cooling coil is half immersed. Electrolyse at 15 A for 40 min, washing down the sides of the beaker after 30 min. Reduce the current to 5 A, then transfer the solution to a 100-ml graduated flask. Wash out the cell, with the current still switched on, make up to volume with water and mix well.

Solvent extraction: Pipette a 20-ml aliquot (*Note* 2) into a 200-ml separatory funnel. Add 2 ml of 1 % cupferron solution, shake well and allow to stand for 5 min. Add 30 ml of chloroform, shake and discard the lower organic layer. Wash with 15 ml of chloroform, separate, and transfer the aqueous layer to a 150-ml beaker. Evaporate to 3 ml on a water bath, then transfer to a hot plate and heat to fumes of perchloric acid. Add 1 ml of nitric acid (1 + 1) dropwise and evaporate to fumes of perchloric acid. Repeat the addition of nitric acid and fuming procedure. Cool, add 10 ml of water and transfer to a 100-ml graduated flask. Add 5 ml of 5 % hydrogen peroxide and 2 drops of phenolphthalein indicator. Neutralise to a faint pink colour with 2*N* sodium hydroxide from a polythene wash bottle. Titrate until colourless with 0·2*N* hydrochloric acid and add exactly 1 ml in excess.

Colour development: Add 5 ml of nitrated Solochrome Cyanine R solution and 50 ml of the diluted buffer solution. Mix well, make up to volume and allow to stand for 30 min.

Measurement: Measure the optical density of the solution at a wavelength of 535 mμ, using 5-mm cells, against a reagent blank obtained by the full procedure but omitting the electrolysis (*Note* 3). The time required for the maximum development of colour is rather critical[19] and it is necessary to restrict the number of samples in a batch to six, including the reagent blank, to avoid a wide variation in time. It is also recommended that the spectrophotometer should be set against the reagent blank before each test solution is measured.

Note 1. In the case of highly alloyed steels, the addition of hydrochloric acid is sometimes necessary to effect dissolution. Five ml of hydrochloric acid (sp. gr. 1·16) should be used, and care taken that this is removed by repeated fuming with perchloric acid after dilution with water.

Note 2. The aliquot for colour development should contain not more than 70 μg of aluminium. For steels containing up to 0·07 % of aluminium a 20-ml aliquot is used, whilst for steels containing from 0·07 to 0·14 % of aluminium a 10-ml aliquot should be taken. The range of the method can be further extended by using a 5-ml aliquot or by reducing the sample weight.

Note 3. The aliquot of the blank solution should always be equal in volume to that of the sample.

Calibration

Prepare seven solutions, each containing 0·5 g of aluminium-free iron dissolved in 10 ml of nitric acid (1 + 1) and 5 ml of perchloric acid. To these solutions add, respectively, 0, 1, 2, 3, 4, 5 and 6 ml of standard aluminium solution. Carry out the full procedure on each, and measure the optical density of each solution against the solution containing no aluminium.

TABLE II.—RECOVERY OF ALUMINIUM FROM SYNTHETIC IRON-ALUMINIUM SOLUTIONS

Aluminium added, μg	Optical density	Aluminium found, μg*
10	0·115 0·122	9·5 10·0
20	0·259 0·262	20·0 20·0
30	0·380 0·380	29·0 29·0
40	0·540 0·530	41·0 40·0
50	0·656 0·660	50·0 50·0
60	0·800 0·795	60·5 60·0

* Results given to nearest 0·5μg.

TABLE III

Sample No. (B.C.S. Code)	Aluminium found (B.C.S. value), %	Aluminium found %
255	0·057	0·048 0·047
271	0·008	0·008 0·009
272	0·064	0·062 0·062
273	0·06(0)	0·058 0·059
274	0·029	0·029 0·029
275	0·02(0)	0·021 0·021
276	0·02(5)	0·024 0·023
277	0·01(5)	0·017 0·018

RESULTS

Due to the unavailability of B.C.S. steels standardised for aluminium content, trials were carried out by the proposed method using synthetic aluminium-iron solutions. The original solutions contained 0·5 g of iron, and 20-ml aliquots were used for the colour development. Table II shows the results obtained.

Various B.C.S. steels were then analysed, and the results obtained are shown in Table III.

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Zusammenfassung—Eine Methode fur Bestimmung von Aluminium in Stahl beruht auf einer vorhergehenden Trennung von Eisen zusammen mit Nickel, Chrom, Kupfer und Molybdän durch Elektrolyse an einer Quecksilberkathode. Die elektrolysierte Lösung wird auf definiertes volum gebracht und aus einem Aliquot wird das verbliebene Eisen, zusammen mit Vanadin und Titan durch Extraktion als Kupferronat entfernt. Nach Zerstörung des uberschussigen Kupferrons wird die Lösung neutralisiert und ein Säureuberschuss zugegeben. Sodann wird der Aluminiumkomplex des nitrierten Solochrom Cyanin R unter optimalen Bedingungen gebildet.

Résumé—La méthode consiste en une séparation préliminaire du fer conjointement au nickel, au chrome, au cuivre et au molybdène, par électrolyse sur cathode de mercure. La solution électrolysée est amenée à un volume connu, et à partir d'une partie aliquote le fer résiduel, conjointement à du titane et du vanadium est séparé par extraction des cupferrates par le chloroforme. Après destruction de l'excès de cupferron, la solution est neutralisée, on ajoute un excès connu d'acide, et le complexe de l'aluminium avec le solochrome cyanine R nitré est formé dans les meilleures conditions.

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APPLICATIONS OF COMPLEMENTARY TRI-STIMULUS COLORIMETRY—I

ANALYSIS OF BINARY AND TERNARY COLORANT SYSTEMS

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Summary—Complementary tri-stimulus colorimetry can be applied to the analysis of binary and ternary colorant mixtures. It is shown that for this purpose relation to the human eye is unnecessary, and that only the designation of the various parameters and the mode of calculation need be retained. The binary system of the EDTA complexes of copper and nickel and the ternary system of the EDTA complexes of copper, nickel, and cobalt are treated in detail as illustrative examples of the new approach. Results can be calculated graphically, in a purely algebraic manner, or in a combined graphical and algebraic manner. The relation of the new approach to classical photometric analysis of multicomponent systems is shown.

The author and his colleagues[1] have attempted to apply conventional tri-stimulus colorimetry to the objective description, characterisation, and evaluation of colour changes at the end-point in visual titrations. During the investigation some very useful extensions were made of the existing theory. The most important modification was the use of absorbance values, in place of transmittance values, in the calculation of the trichromatic co-ordinates. The mathematical derivations are of no moment for the problems to be considered in the present paper; hence, it suffices to present the final and basic formula derived for complementary tri-stimulus colorimetry:

$$P_r = G_r - J(Q_r - G_r) - J^2(Q_r - G_r - Q_r^{d}) \qquad (1)$$

The meaning and implications of the variables in this formula require brief comment so that the further considerations of this paper may be fully appreciated.

P_r represents the true colour point, that is the point plotted in a chromaticity diagram applying conventional tri-stimulus colorimetry. Using the ten selected ordinate method, this point is calculated as follows: Three sets of ten wavelength values are selected on the transmission curve. The transmittance readings of each of the three sets (also known as ranges) are summed, and each sum is multiplied by a factor which takes into account the spectral distribution of energy of the illuminant under which the colour is observed and the distribution of spectral sensitivity of the average (normal) human eye. The tri-stimulus values thus obtained, X, Y, and Z, can now be used to describe the colour objectively. The result can be expressed graphically by calculating the trichromatic coefficients (also known as the trichromatic co-ordinates) according to the following formulae

$$x = X/(X + Y + Z) \qquad (2a)$$

$$y = Y/(X + Y + Z) \qquad (2b)$$

$$z = Z/(X + Y + Z) \qquad (2c)$$

P_r is expressed in terms of these co-ordinates, and with the subscript r equal to 1, 2, and

3 corresponds, respectively, to the x, y, and z values of the point. For a more extended presentation of this approach, the reader is referred to relevant monographs.[2,3]

Q_r represents the complementary colour point. The numerical values of its co-ordinates are obtained in the same manner as described for the true colour point, P_r, but employing absorbance values instead of transmittance values. In other words, instead of considering the light reaching the eye as receptor, the light absorbed (and hence *not* reaching the eye) is considered. The absorbance readings at the ten ordinates in each range are summed, and each sum is multiplied by the same factors employed in the calculation of the true colour point. Thus, the three complementary tri-stimulus values are obtained, which may be denoted by U, V, and W (to distinguish from X, Y, and Z of conventional tri-stimulus colorimetry). Then the complementary colour coefficients (also known as complementary colour co-ordinates) are calculated according to the formulae

$$u = U/(U + V + W) \tag{3a}$$

$$v = V/(U + V + W) \tag{3b}$$

$$w = W/(U + V + W) \tag{3c}$$

Similarly Q_r is expressed in terms of these complementary colour co-ordinates and with the subscript r equal to 1, 2, and 3 corresponds respectively to the u, v, and w values of the point.

It is of utmost importance to appreciate that Q_r is *independent* of the concentration of the colorant and has a value which is a characteristic of the particular colorant. Any change in the concentration of the colorant will be expressed mathematically by a factor by which U, V, and W are all multiplied; this factor will cancel out in the operation performed in equation (3).

G_r in conventional tri-stimulus colorimetry is called the illuminant point, that is, it represents the colour co-ordinates of the illuminant. In complementary tri-stimulus colorimetry, it is called the "grey point". For a particular illuminant, the point has the same location (*i.e.* the same numerical values of the co-ordinates) in both systems.

J is the optical concentration of the colorant and is defined by the following equation:

$$J = E\,.\,C\,.\,l \tag{4}$$

where C is the analytical concentration of the colorant in the absorbing solution, expressed in a suitable unit and l is the length of the light path through the absorbing solution. The similiarity of equation (4) to the Lambert-Beer law can be recognised by realising that J is the sum of all the absorbance readings in the three ranges (each multiplied by the appropriate factor), and hence can be expressed as

$$J = (U + V + W) \times \kappa. \tag{5}$$

κ is constant, having the numerical value $2{\cdot}303/3{\cdot}1616 = 0{\cdot}72843$ when the ten selected ordinates and illuminant C are employed. The manner in which this value is ascertained is of no moment for the present study and is described elsewhere.[1] Then the coefficient E, which may be called the overall absorptivity, is related to the equivalent parameter ε (extinction coefficient) in the Lambert-Beer law by the relationship $\Sigma K_r\,.\,\varepsilon_i = E$, where i becomes all of the wavelengths at which readings are taken, and K_r is the factor by which the values for each range are weighted.

Q_r^d takes care of the dichromatistic tendency of the absorbing solution, that is, of the change in hue when the concentration of the colorant and/or the length of the light path through the solution are changed. This parameter is obtained by a similar calculation scheme as for Q_r but employing the square of the absorbance readings. In the consideration of colorant solutions that are optically very dilute, the value of J is small, and therefore the term $J^2 . Q_r^d$ in equation (1) has also a very small numerical value and can be neglected. For the applications of complementary tri-stimulus colorimetry presented in the present paper, this term is of no significance, and hence is not further discussed.

The achievements of the extended theory of tri-stimulus colorimetry can briefly be summarised: In complementary tri-stimulus colorimetry, only three parameters are needed for a full description of a dilute solution of a colorant, namely the complementary colour point Q_r, which is a concentration-independent characteristic of the colorant; G_r, the grey point, which is only related to the illuminant; and E the overall absorptivity. From the latter and the analytical concentration of the colorant, the optical concentration J can be calculated. In many applications, the knowledge of J suffices, and the analytical concentration of the colorant, C, need not be known, since J can readily be obtained from an absorbance curve. With the numerical values of the parameters at hand, the true colour point of any dilute solution of a particular colorant can be calculated.

The application of complementary tri-stimulus colorimetry to multicolorant systems offers distinct advantages not only for the description of colour, but also for the practical analysis of coloured solutions.

In subsequent considerations, it is assumed (*a*) that each colorant present obeys the Lambert-Beer law, and (*b*) that absorbances are additive (which amounts to the fact that the colorants do not react with each other).

Since absorbance readings are made at many wavelengths, it is not sufficient to assure the validity of Beer's law at a single wavelength only (for example, at an absorbance peak); rather the validity must be assured through all ranges of measurements.

When a single colorant is present in a solution, it is represented (regardless of its concentration) by a discrete point in the colour diagram, that is a rectangular plot of u and v. (Two co-ordinates are sufficient because the third co-ordinate is not independent since from the set of equations (3) it follows that $u + v + w = 1$; of course, where it is more convenient the pairs u–w or v–w can be plotted). A second colorant will, in general, be presented by a second point in this plot. If the colorants be called a and b and a line is drawn between their complementary colour points ($Q_{r,a}$ and $Q_{r,b}$), then any mixture of these two colorants is represented by a point on this line; provided of course that the assumptions made above are fulfilled (*i.e.* validity of Beer's law and additivity of absorbances).

These considerations have been used as the basis for the characterisation of colour changes of indicators (1) but are by no means restricted to that application. Complementary tri-stimulus colorimetry may be applied advantageously to a variety of problems in chemical analysis and in physical chemistry. In the present paper such colorimetry is extended to a point where the human eye is no longer considered as the receptor and where the receptor and illuminant are assumed to have hypothetical properties appropriate to the particular study. The only aspects of tri-stimulus colorimetry that are retained are the mode of calculation and the form of relationship between the various parameters. This extension is conveniently developed and explained by a stepwise argument. A binary colorant system is described, first using two ranges only; then extension is made to three ranges; then the effect of an added colorant impurity is considered, and finally the impurity is treated as a third component, thus arriving at the application of the theory to a ternary colorant system. Paralleling the theoretical development, the binary system consisting of the ethylenediaminetetra-acetate (EDTA) complexes of copper$^{\text{II}}$ and nickel$^{\text{II}}$ is considered as an instructive example. Finally, this example is extended to the ternary system containing these two complexes and the EDTA complex of cobalt$^{\text{II}}$.

THE BINARY SYSTEM Cu-EDTA AND Ni-EDTA EMPLOYING THREE RANGES

The absorbance curves of the copper-EDTA and nickel-EDTA complexes in aqueous medium at pH 7 are shown in Fig. 1 as curves I and II respectively. Only cursory inspection of these curves is required to appreciate that the binary system of these two EDTA complexes is a rather poor one for a conventional photometric determination of the two components. However, this difficulty can be largely circumvented by the new approach.

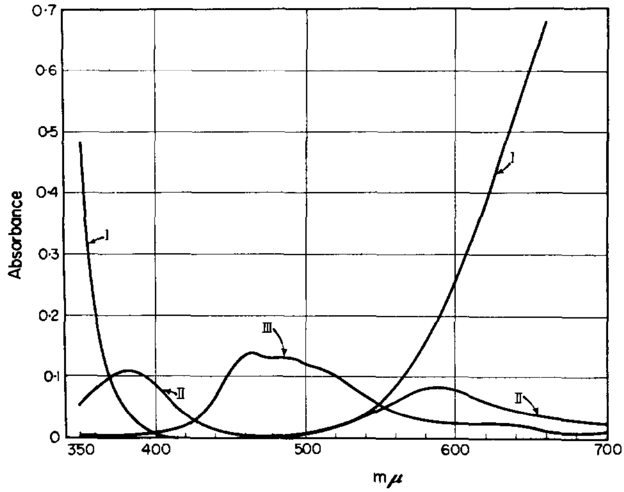

FIG. 1. Absorbance curves of the EDTA-complexes of I, Cu: II, Ni: III, Co.

By employing the ten selected ordinate method, the complementary colour points, Q_r, for the two (pure) colorants can be calculated from the absorbance curves in Fig. 1. For the copper-EDTA complex under the prevailing conditions, $u = 0{\cdot}616$ and $v = 0{\cdot}377$, and for the nickel complex $u = 0{\cdot}465$ and $v = 0{\cdot}429$. These two points are not very far apart in the colour diagram (that is, the u–v plot). This is not surprising since the solution colours of the two colorants are not very different. The colour of a copper-EDTA solution is bright blue-green and that of a nickel-EDTA solution dull blue.

In the present paper, where the approach is applied to the *analysis* of colorant mixtures rather than to characterise "true" colours, there is no need to relate colour to the human eye. Instead, colours can be considered in relation to a hypothetical eye having convenient properties which may be assumed. Thus in place of the ten selected ordinates used in conventional and complementary tri-stimulus colorimetry related to the human eye, ten or any other appropriate number of ordinates may be selected and at the most convenient wavelengths. Of course under such conditions wavelengths may even be selected outside the visible portion of the spectrum.

All calculations involved can be simplified by assuming that the hypothetical eye (in relation to a hypothetical illuminant) has such properties that all the factors which are applied as multipliers in conventional and complementary tri-stimulus colorimetry have a value of unity. In order to show the relation of the present treatment to tri-stimulus colorimetry in the simplest terms, it can be further assumed that the hypothetical eye is partially colour-blind and in such a way that instead of three ranges of wavelengths only two are needed. Then in terms of the binary system copper-EDTA and nickel-EDTA the treatment takes the following form.

For the u-range, the following wavelengths were selected: 370, 380, 390, 580 and 590 mμ and for the v-range, 580, 590, 600, 610, and 620 mμ. Only five ordinates were selected because in the particular example they gave a satisfactory average. (In general a greater number may be appropriate or necessary in order to secure satisfactory results). The selection of wavelengths may not have been optimum for the particular binary system under consideration, but the treatment in this paper is eventually extended to a ternary system containing cobalt-EDTA in addition and the selection is appropriate to this extension. The separation of the u-range into a long and short wavelength region is advantageous as this accentuates the influence of the nickel-EDTA complex which has a much smaller overall absorptivity, E, than does the copper complex. The absorbance readings at the five wavelengths selected for the two ranges are presented in Table I. (The Table also gives the values for a w-range; these values are considered in a further section and are not relevant to the treatment at this point.) The arithmetic sum of the absorbance readings for the copper curve in the u-range is $U = 0{\cdot}511$ and that for the v-range, $V = 1{\cdot}325$. According to the definition of complementary tri-stimulus colorimetry and equation (5) with $W = 0$, the sum of the

TABLE 1.

Ordinate number	u-range	v-range	w-range
1	0·093	0·158	0·000
2	0·039	0·205	0·001
3	0·016	0·257	0·001
4	0·158	0·318	0·002
5	0·205	0·385	0·003
	$U = 0{\cdot}511$	$V = 1{\cdot}323$	$W = 0{\cdot}007$

$J = U + V + W = 1{\cdot}841$

$u = U/J = 0{\cdot}2776$ Check $u + v + w = 1$

$v = V/J = 0{\cdot}7184$ $E = J/Cl = 1{\cdot}841/10 = 0{\cdot}1841$

$w = W/J = 0{\cdot}0040$

C = 10.0 ml of 0.1M Cu-EDTA per 100 ml of buffered solution. $l = 1$ cm.

parameters U and V is related to the optical concentration J. According to this relation

$$J = (U + V)\kappa = 0{\cdot}511 + 1{\cdot}325 = 1{\cdot}834.$$

The constant κ has been set equal to 1. This simplification is permitted because no relation to the human eye is maintained and, moreover, in all formulae further derived the J-values will appear in quotients so that it will cancel out.*

To keep the calculations as simple as possible in this illustrative example, the concentration of the copper-EDTA complex solution can be expressed in ml of 0·1*M* copper-EDTA solution per 100 ml of buffered solution. Then by substituting the value of J in equation (4), setting the cell length, according to the experimental conditions, to 1 cm and inserting the value of C employed, namely 10 ml per 100 ml of buffered solution, it is found that $E_{Cu} = J/C = 1{\cdot}834/10 = 0{\cdot}1834$ litre/mole. cm.

By proceeding in an analogous manner, the corresponding values can be secured for nickel.

For both components the values of the tri-chromatic co-ordinates (actually "dichromatic" in the present case since $w = 0$) can be readily calculated. For copper-EDTA, $u = U/J = 0{\cdot}511/1{\cdot}834 = 0{\cdot}2786$ and $v = V/J = 1{\cdot}325/1{\cdot}834 = 0{\cdot}7214$. Since by assumption $w = 0$, the sum of u and v should equal unity, which serves as a check of the calculation. In general it is advantageous to carry one more significant figure through the calculation than justified by the experimental results and to round the end results to the proper number of significant figures.

To this point in the discussion of this example, the approach parallels, to a certain degree, the classical photometric method of analysing a mixture of two colorants: the use of only two wavelengths is replaced by the selection of two sets of wavelengths, and in place of the extinction coefficients at two wavelengths, the overall absorptivities, E, are employed.

When the absorbance curve of a mixture of the EDTA complexes of copper and nickel is determined, it is possible to calculate the values of u, v and E for the mixture. By combining these values with the corresponding values for the two pure colorants, it is possible to set up two equations containing the concentrations of the two components in the mixture as the only unknowns and to solve for these concentrations.

Instead of this algebraic approach, which parallels the classical procedure and represents a type of averaging over a number of wavelengths, a graphical approach can be applied.

The u and v co-ordinates of each colorant, that is Q_r, are independent of concentration and are constants characteristic of each colorant; hence they are fixed points in the u–v plot. The complementary colour point of any mixture of the two colorants will be located on a straight line connecting these fixed points. From the results for the solutions of the pure colorants, it is possible to calculate the values of the u and v co-ordinates for any mixture of the two colorants. Thus we may calibrate the line connecting the complementary colour points of the two colorants for the position of this point, for any mixture, by expressing its composition in mole fraction (or any other convenient fraction). Thus it is simple to read the mole fraction from the line, when the co-ordinates of the mixture have been determined by experiment and without

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* The numerical value of κ in the present case (when related to the hypothetical eye) would be $2{\cdot}303/15 = 0{\cdot}15353$ because the weighting factors applied to derive Q_r have been assumed to be 1 and only five ordinates are used in each range.

knowledge of the actual concentration of the colorants in the mixture. (The individual concentrations can be calculated from results obtained graphically as will be shown for the case where three ranges are employed).

It is of interest to enquire what happens to the co-ordinates of the complementary colour point of a mixture when impurities are present in the solution that affect the absorbances at any of the selected wavelengths. The answer is that the co-ordinates will be changed; however, as only two ranges have been used, the point will still be on the line connecting the complementary colour points of the two pure colorants (system line). This is a simple mathematical consequence: when operating with only two ranges any "real" point has to be located on a straight line connecting the point (1, 0) on the abscissa of the u, v plot with the point (0, 1) on the ordinate. Thus "di-stimulus" colorimetry, that is operating with only two ranges, is restricted to a single line in a two-dimensional plot for an infinite number of systems. In other words, each system will operate on the same line although with different calibration and different points for the pure colorants.

THE BINARY SYSTEM Cu-EDTA AND Ni-EDTA EMPLOYING THREE RANGES

There is a distinct advantage to the use of three ranges, that is, three sets of wavelengths in the analysis of a binary colorant system. To extend the above considerations from two ranges to three ranges it need only be assumed that the hypothetical eye is *not* colour blind (*i.e.*, $w \neq 0$). The other properties assumed for that eye are retained, namely, that the factors involved as multipliers in the calculation of the tri-stimulus values have a value of unity. Even when three ranges are employed, only a u-v plot is necessary in the utilisation of the graphical approach because $u + v + w = 1$ according to the set of equations (3); hence w is not independent. However, unlike the situation when $w = 0$, an infinite number of lines will represent an infinite number of binary systems. [It should be appreciated that all Q_r points and consequently also all system lines will be located in the u–v plot within the triangular area bounded by the line connecting the points (0, 0), (1, 0) and (0, 1)]. One of that infinite number of lines will represent the binary system of the EDTA complexes of copper and nickel. Unlike the case in which $w = 0$, if a coloured impurity is introduced or a false measurement or a calculation error is made, the colour point Q_r, will *not* fall on the system line but will be displaced from it. Hence a non-concordant value will be signalled. Erratic influences may, of course, compensate, but this is highly improbable.

A case of *reductio ad absurdum* may be mentioned: The ranges might be selected in such a way that two colour co-ordinates vanish, that is, for one colorant $u = v = 0$ and for the other $v = w = 0$. However, the possibility of such a selection is equivalent to stating that each component can be determined photometrically, without interference due to the presence of the other, at a particular wavelength or wavelength range.

For the system under consideration the following wavelengths for the added w range were selected: 550, 560, 570, 580 and 590 mμ. The results thus obtained and the values calculated for the different parameters are presented in Table I. It can be readily appreciated that the displacement of a Q_r point from a system line in the u–v plot because of a given erratic influence will be smaller, the smaller the magnitude of the w-value. (The displacement becomes zero as w approaches zero.) From this point of view, the selection of the wavelengths in the three ranges may not be optimum for the determination of copper and nickel. However, the selection is appropriate for the extension of the example to the ternary system containing cobalt-EDTA complex (see below).

The u–v plot for the system Cu-EDTA and Ni-EDTA employing three ranges is presented in Fig. 2. From the results secured from the absorbance curves of solutions of the pure colorants, their colour points can be calculated. These Q_r points can be placed on a u–v plot and the system line connecting these points can be drawn. The system line can then be readily calibrated according to any desired fraction (*e.g.*, mole fraction). For a given mixture of the two colorants, the absorbance curve can be determined, and the complementary colour point of the mixture calculated and placed on the u–v plot. From the position of this point on the calibrated system line, the fraction of the components in the mixture can be read. (As noted above, the complementary colour point of the mixture will fall on the system line unless erratic influences are present).

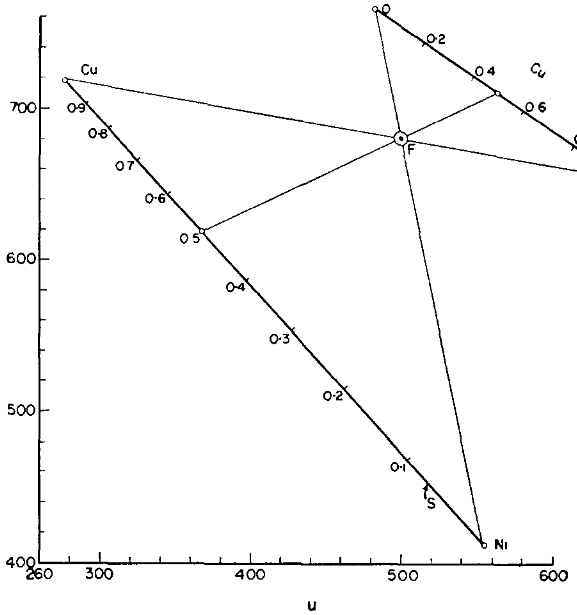

FIG. 2. u–v Plot containing the linear and non-linear calibration for the binary system Cu-Ni.

To prepare such a calibrated system line, all that is required are the colour co-ordinates and the value of E derived from the absorbance curves of the solution of the two pure colorants. The necessary formulae may be derived simply. The subscript m for the various parameters may be adopted to designate values for a mixture, and the subscripts a and b to designate values for the two pure colorants. Then for a mixture the sum of absorbances for the ordinates in the u range, U, is given by

$$U_m = C_a \cdot U_{a,1} + C_b \cdot U_{b,1} \tag{6}$$

where C is the concentration of the colorant, and $U_{a,1}$ and $U_{b,1}$ are the sum of the absorbances for the u range of the colorants a and b, respectively, and at unit concentration (subscript 1). In the illustrative example, the concentrations are expressed in ml of a 0·1M metal-EDTA solution per 100 ml of buffered solution. The U values naturally need not be obtained from an absorbance curve of a solution actually having unit concentration. The value can be secured from any solution by simply calculating $U_1 = U/C$, where U and C are the values for that particular solution.

Formulae analogous to (6) can be written for V_m and W_m. By dividing both sides of (6) by $(C_a + C_b)$ the following equation is obtained:

$$U_m/(C_a + C_b) = q \,.\, U_{a,1} + (1 - q) \,.\, U_{b,1} \tag{7}$$

where q is the mole fraction (or any other fraction depending on the concentration units selected for C) as defined by

$$q = C_a/(C_a + C_b) \tag{8}$$

Formulae analogous to (7) can also be written in terms of V_m and W_m.

For unit concentration the following formula is valid

$$U_{a,1} = u_a \,.\, E_a \tag{9}$$

Analogous expressions can be obtained for all other corresponding terms of both colorants.

By combining formulae (3a), (6) and (9) and applying the fact that $u + v + w = 1$, the following is obtained:

$$u_m = \frac{q \,.\, u_a \,.\, E_a + (1 - q) \,.\, u_b \,.\, E_b}{q \,.\, E_a + (1 - q) \,.\, E_b} \tag{10}$$

Analogous formulae may be similarly derived for v_m and w_m. The three equations can be generalised to the following formula by employing the complementary colour points

$$Q_{r,m} = \frac{q \,.\, Q_{r,a} \,.\, E_a + (1 - q) \,.\, Q_{r,b} \,.\, E_b}{Q \,.\, E_a + (1 - q) \,.\, E_b} \tag{11}$$

For use in some later applications of this formula, it may be mentioned that writing the expression for $Q_{r,m}$ in this form is equivalent to stating that the co-ordinates of the illuminant are located at the origin of the u–v plot.

The value of q determined from a graph calibrated by the procedure just described is insufficient for the calculation of the *concentrations* of the two components. However, by adding a known amount of one of the colorants to the mixture and proceeding similarly, a second q value is obtained. From consideration of these two q values, it is then possible to calculate the concentrations of the colorants in the original mixture. This addition need not be made in reality; rather the addition of an appropriate amount of either a or b can be assumed and the result obtained by calculation. From the equation

$$U_a = C_a \,.\, u_a \,.\, E_a \tag{12}$$

the value of U can be calculated for an addition of a. Analogous equations exist for V_a and W_a, and for U_b, V_b and W_b. If the portion of a tri-stimulus value associated with the added amount of either a or b is denoted by a prime mark, each tri-stimulus value for the solution after the addition has been made is, of course, the sum of the value for the original solution plus that for the addition: $U_m + U_m'$. If a prime mark is also used to denote the colour co-ordinates of the mixture after the addition has been made, the following equation is obtained by applying equation (3)

$$u_m' = (U_m + U_m')/(U_m + V_m + W_m + U_m' + V_m' + W_m') \tag{13}$$

Similar equations may be written for v_m' and w_m'.

Using the co-ordinates u_m' and v_m' another point is obtained on the u–v plot, which should also be located on the calibrated system line unless erratic influences are present. Then the value of q', that is the mole fraction (or other fraction) in the solution after the addition has been made, is obtained. The following two equations allow the calculation of the concentrations of the two colorants in the original mixture

$$q = C_a/(C_a + C_b) \tag{14}$$

$$q' = (C_a + C_a')/(C_a + C_b + C_a' + C_b') \tag{14a}$$

where C_a' and C_b' denote the addition of a and b, respectively made to the solution. The values of q and q' are read from the calibrated system line. C_a' or C_b' is known because they represent the addition assumed. (Of course only one colorant is assumed to be added, hence either C_a' or C_b' will be zero). Thus C_a and C_b, the concentrations of the two colorants in the original solution can be determined by solution of the two equations. The colorant to be assumed for the addition and in what amount will depend on the value of q. In order to obtain highest accuracy, these values should be selected so that q' will be located near the midpoint of the system line.

In the above treatment reference has been made to calibrating the system line for q values. This presents some difficulty as the calibration does not involve an equally spaced argument except when E_a equals E_b. This means that, for example, the distance on the system line between the points $q = 0{\cdot}1$ and $q = 0{\cdot}2$ will *not* equal in general the distance between $q = 0{\cdot}8$ and $q = 0{\cdot}9$. Thus, accurate interpolation when reading the q values will only be possible when many points have tediously been calculated. It is possible to calculate only a few points, and using them, to obtain more points by graphical interpolation, but this approach is also time-consuming. It would be equally inconvenient to try to make the selection of the wavelengths in the three ranges in such a way that the E values for the two colorants become numerically equal.

There is, however, a mathematical approach which in effect will make E_a equal to E_b. For solutions containing the colorants at unit concentration the following two equations hold

$$\left.\begin{aligned} E_a &= U_a + V_a + W_a \quad (15)\\ E_b &= U_b + V_b + W_b \quad (16)\end{aligned}\right\} (C_a = C_b = 1)$$

To one of the tri-stimulus values in each of the two equations a factor p may be applied as a multiplier and its value chosen in such a way that E_a becomes equal to E_b. Then from the following equation the numerical value of this multiplier can be evaluated

$$p \,.\, U_a + V_a + W_a = p \,.\, U_b + V_b + W_b \tag{17}$$

This operation in relation to the hypothetical eye implies that one of its three receptors has a sensitivity in one particular spectral region differing from that of the other two.

Caution must be exercised, however, in applying this method. The value of p may be numerically rather large; hence, in the later calculation of the trichromatic co-ordinates, the values for one of the ranges may predominate unduly, thus reducing the effectiveness of the averaging process considerably. From simple mathematical reasoning, it can be deduced that when operating with a factor p one or two of the co-ordinates will assume a negative sign. This, however, is no serious drawback because when plotting the colour diagram only the region showing the system line will be drawn, and the zero point will in any case be suppressed. It is, of course, not necessary to apply the multiplier to the U term as in equation (17); in some cases more convenient results may be obtained when p is applied to either V or W.

Probably the most satisfactory approach to obtaining a linearly calibrated line is based on constructing a nomogram directly on the u–v plot (and not employing the multiplier approach in the original calculations). For geometrical reasons, there exists somewhere external to the system line, S, in the u–v plot a focal point, F, and a linearly calibrated line (auxiliary line L), located in such a way that all straight lines connecting points representing the same q values on lines S and L pass through point F. The location of point F and line L can be established by applying analytical geometry, but this is an extremely tedious approach. The desired construction can be readily effected by the following trial-and-error method (*cf.* Fig. 2). Assume a focal point, F, somewhere on the u–v plot and draw lines through this point and the points $q = 0$, $q = 0{\cdot}5$ and $q = 1$ on the system line (it should be appreciated that only the point $q = 0{\cdot}5$ has now to be calculated). Cut a strip of graph paper of suitable length and mark off on one edge a scale of q between $q = 0$ and $q = 1$ in an equally spaced argument. Now place this paper on the u–v plot and move about its edge, which represents the auxiliary line L, until the three lines intersect with the corresponding points. Affix the slip of paper to the plot in this position either with paste or cellulose tape. To read a q value of a mixture proceed in the following way. Locate the complementary colour point by applying the u and v values to the u–v plot. When no erratic influences are present the resulting point will be on the system line S. Now draw a straight line from this point through the focal point, F. This line will intersect the linearly calibrated auxiliary line L. The q value is now read at this intersection point. This construction and its use is illustrated in Fig. 2 for the binary system Cu-EDTA and Ni-EDTA.

Only a little experience and a few trials are necessary in order to establish a satisfactory position for F and L. In general, care should be taken that both are located in relation to the system line in such a way that lines S and L are nearly parallel and that F is not too close to either of the two lines.

The graphical approach described above is especially appropriate when a given analysis must be effected repeatedly. For an occasional determination, the construction of a nomogram may be tedious, and an algebraic approach may be applied, for the calculation of either the q values or the concentrations of the colorants. The concentrations can be calculated in the following manner.

From equation (11) and its analogues for V and W, as applied to both colorants, the following set of equations can be derived:

$$U_m = C_a \, . \, u_a \, . \, E_a + C_b \, . \, u_b \, . \, E_b \tag{18a}$$

$$V_m = C_a \, . \, v_a \, . \, E_a + C_b \, . \, v_b \, . \, E_b \tag{18b}$$

$$W_m = C_a \, . \, w_a \, . \, E_a + C_b \, . \, w_b \, . \, E_b \tag{18c}$$

This set can be written in summation notation:

$$R_{i,m} = \sum_j C_j \, . \, r_{ij} \, . \, E_j \tag{19}$$

where $R_{i,m}$ becomes the sum of the absorbance readings for the mixture in the u, v and w ranges when i is 1, 2 and 3 respectively, and j becomes 1, 2, 3 . . . , thus denoting the various components. This summation suggests that the method is not restricted to a binary colorant system and with the necessary number of ranges can be applied to the resolution of any multicomponent system as long as the condition is fulfilled that $i \geqslant j$. Plotting the results is clearly no longer feasible when $j > 3$, because a multi-dimensional plot would be needed. The generalised case will be considered in a subsequent paper.

Since there are only two unknowns, C_a and C_b, and three equations in the set of (18), any pair of equations may be selected for the calculation. The choice of a pair will depend not only on the mathematical reasoning but also on the judgment as to which ranges may be subject to fewer erratic influences, including the effect of possible impurities, inconsistencies in the base line of the spectral measurement, and irregularities in the absorbance curve. Mathematically, the best pair is that for which the coefficients of the unknowns are as large as possible and differ as much as possible. It is often good practice to calculate the concentrations by all three of the possible pairs and to average the values obtained (after rejecting any value which is obviously too divergent). This reasoning and calculation approach parallels the classic approach to the photometric analysis of a binary system with ranges being employed instead of individual wavelengths; however, an averaging process is implicit that affords a more reliable basis for calculations.

Of course, the algebraic approach will not reveal any erratic influence except in so far as the result of the calculations from one pair of equations may differ markedly from those from the other two pairs. It is often advisable, therefore, to combine the algebraic and graphical approaches. The system line may be quickly plotted without calibration by merely connecting the complementary colour points of the two colorants by a straight line. Then the complementary colour point of any mixture to be analysed can be determined and plotted. Its location on or off the system line will reveal the reliability of that particular measurement, as it is improbable that erratic influences will compensate. If the measurements are thus found to be concordant, the algebraic calculation may be undertaken as described above.

THE TERNARY SYSTEM Cu-EDTA, Ni-EDTA, Co-EDTA

As discussed in the previous section, the presence of a coloured impurity will displace the complementary colour point of a binary mixture from the system line. The extent of the displacement will depend upon the concentration of the impurity and on the position of the system line in the u–v plot. Further, the smaller the value of w, the smaller will be the influence of the impurity. This latter statement can be appreciated from the earlier considerations of the study of a binary system employing two ranges, that is, when $w = 0$.

It is easily appreciated how an increase in the concentration of an impurity will influence the location of the complementary colour point of a binary mixture. Any point on the system line represents a mixture of the two colorants of a definite mole fraction. This mole fraction will not be changed by addition of an impurity (or in general terms of a third colorant). Hence the particular binary mixture, as far as its colour point is concerned, can be treated as a single colorant and with the added impurity (or third colorant) can be considered as forming a second binary mixture. The system line of this further mixture will be a straight line drawn between the point representing the original mixture on its system line and the complementary colour point of the impurity (third colorant). Hence, as increasing amounts of impurity (or third colorant) are added, the observed colour point will move progressively further from the original system line and along the secondary system line. This further line can, of course, be calibrated with regard to the mole fraction (or any other fraction) of the mixture between the original components a, b, and the third component, c.

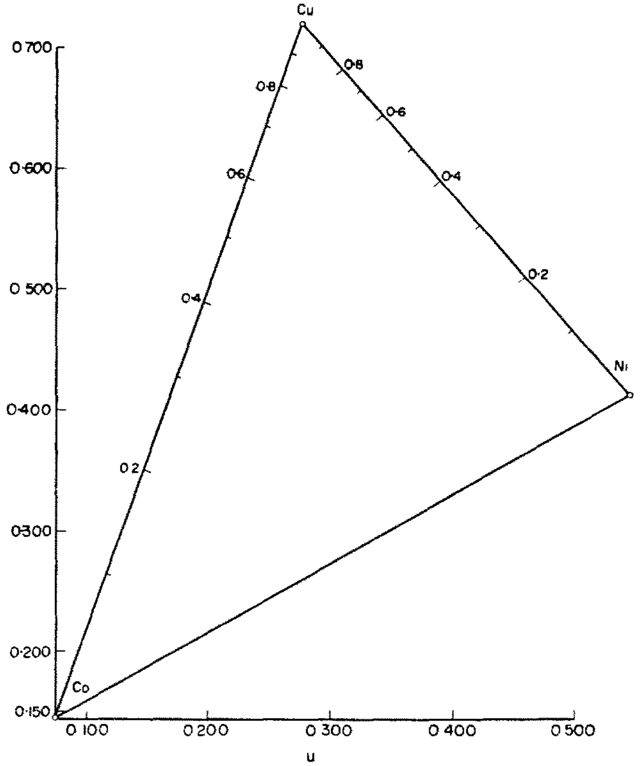

FIG. 3. u–v Plot containing the calibration triangle for the ternary system Cu-Ni-Co.

With this background consider the ternary system formed by colorants a, b and c. Using appropriate ranges, the complementary colour points of the three colorants, A, B, and C can be determined and placed on the u–v plot. (Fig. 3.) Any complementary colour point of a mixture of the three colorants will be located within the triangle formed by connecting these three points with straight lines. If M be the colour point of the mixture, then a straight line drawn from C through M will intersect the line between A and B at a certain point, thus giving the mole fraction in terms of a and b. Similarly a straight line from B through M will intersect the line between A and C at a certain point, thus giving the mole fraction in terms of a and c. From those values the mole fraction in terms of b and c can readily be calculated.

The three system lines may be calibrated by the approaches described for a binary system. Only two lines need be thus calibrated since the third fraction can be calculated from the values of the other two fractions. Further, the concentrations of the three components can be calculated in a manner analogous to that employed with a binary system. Thus, an addition of one of the colorants, say of a, is made (by calculation) and a new point is thus obtained and placed on the u–v plot, and a value is read for one mole fraction. This permits the calculation of the concentrations of two of the colorants in the mixture. Proceeding analogously, an addition of another component, say b, is made, and from the fraction obtained, the concentration of the third component may be calculated.

Alternatively, the purely algebraic approach may be utilised by extending the set of equations (18) by adding the corresponding terms for the third component, namely $C_c \, . \, u_c \, . \, E_c$, $C_c \, . \, v_c \, . \, E_c$ and $C_c \, . \, w_c \, . \, E_c$, to the three equations in the set. Then the three unknown concentrations can be determined by solving the three equations. This can be facilitated by utilising determinants and applying Cramer's rule.

The solution for the three concentrations then takes the following form

$$C_a = \frac{\begin{vmatrix} U_m & u_b & u_c \\ V_m & v_b & v_c \\ W_m & w_b & w_c \end{vmatrix}}{\Delta \times E_a} \, . \quad (20a) \qquad C_b = \frac{\begin{vmatrix} u_a & U_m & u_c \\ v_a & V_m & v_c \\ w_a & W_m & w_c \end{vmatrix}}{\Delta \times E_b} \, . \quad (20b)$$

$$C_c = \frac{\begin{vmatrix} u_a & u_b & U_c \\ v_a & v_b & V_c \\ w_a & w_b & W_c \end{vmatrix}}{\Delta \times E_c} \, . \quad (20c)$$

where

$$\Delta = \begin{vmatrix} u_a & u_b & u_c \\ v_a & v_b & v_c \\ w_a & w_b & w_c \end{vmatrix} \, . \quad (21)$$

It should be appreciated that the ternary system unlike the binary system is not over-determined. Hence, erratic influences cannot be detected by inspection of the location of the complementary colour point of the mixture (except in the extreme case where the point falls outside of the system triangle). Thus, the purely algebraic approach to the calculation of the concentration will in general be the most useful. The graphic approach, however, will be advantageous in problems where the ratio of the three components is required.

One case, however, may be mentioned for which the graphic approach is important. Consider a binary system, which always has present the same impurity or a third component, but in amounts which may vary from analysis to analysis. Only the components of the binary system need be determined and the impurity or third component is of no interest. Then the two colorants can be determined by the graphical approach from a plot which contains the system line of the two components and the complementary colour point of the additional colorant. The complementary colour point of any mixture is plotted, and a straight line is drawn through it and the complementary colour point of the third component; the fraction of the binary system is read at the intersection of this line with the system line of the binary mixture. Thus the binary mixture can be analysed with attention to the influence of any interfering third component, but without going into more extended calculations than necessary. It should, however, be emphasised that this approach is only possible if the same impurity is always present, although in amounts which may vary from analysis to analysis.

TABLE II. RESULTS OF ANALYSIS OF VARIOUS BINARY AND TERNARY MIXTURES

0·1*M* metal-EDTA solution per 100 ml of buffered solution					
Given, *ml*			Found, *ml*		
Cu	Ni	Co	Cu	Ni	Co
10·00	—	10·00	10·03	—	10·03
10·00	—	10·00	9·96	—	10·03
10·00	—	20·00	9·86	—	20·00
10·00	—	20·00	9·82	—	20·36
20·00	—	10·00	19·98	—	10·05
20·00	—	10·00	20·17	—	9·98
—	10·00	10·00	—	9·93	10·62
—	10·00	20·00	—	9·93	10·03
—	20·00	10·00	—	20·04	9·85
10·00	10·00	—	9·99	10·13	—
13·33	3·33	—	13·54	3·28	—
10·00	20·00	—	9·97	20·62	—
10·00	3·33	—	10·00	3·30	—
10·00	10·00	—	19·75	10·30	—
10·00	10·00	10·00	9·92	10·00	10·08
10·00	5·00	5·00	9·94	5·16	5·02
5·00	12·50	5·00	5·03	12·33	4·99
5·00	5·00	15·00	5·01	4·92	15·00
10·00	10·00	5·00	10·00	9·95	5·00

RESULTS

The results obtained by applying the complementary colour point approach to binary mixtures of the EDTA complexes of copper and nickel and also the ternary system containing in addition the cobalt-EDTA complex are presented in Table II. It is not claimed that the ranges selected (especially for the binary system) are the best possible. Further, it is not claimed that the procedure used is superior to any known method for the analysis of these mixtures. The sole purpose of this example is to provide an illustration of how complementary colorimetry can be applied to an analytical problem. To simplify the calculations, the concentrations have been expressed in ml of a 0·10*M* metal-EDTA solution per 100 ml of a buffered solution. The results in Table II were calculated by the graphical approach as well as by the purely algebraic approach. The accuracy and precision are quite satisfactory.

EXPERIMENTAL

The solutions employed in securing the results reported in the Tables and Figures of this paper were prepared as follows: Solutions 0·10M in copper^{II}, nickel^{II} and cobalt^{II} were prepared by weighing the calculated amount of an appropriate salt and dissolving it in water to give the proper volume of solution. Various volumes of these stock solutions were pipetted into 100-ml volumetric flasks; then 25 ml of a solution 0·4M in disodium ethylenediaminetetraacetate and 0·3M in ammonium acetate were added, and the mixture diluted to the mark with water. As a blank, a mixture of 25 ml of the EDTA-ammonium acetate solution and 75 ml of water was used. The absorbance curves were obtained by the use of a Cary recording spectrophotometer. It should be appreciated that the metal ion stock solutions were not standardised, and hence were most probably not exactly 0·1M However, this is without moment since the concentrations employed in expressing the results were expressed in ml of these stock solutions.

DISCUSSION

In several ways the application of complementary tri-stimulus colorimetry to the analysis of binary and ternary colorant systems parallels the classical photometric analysis of multicomponent systems. However, by the use of sets of wavelengths (ranges rather than single wavelengths) a process of averaging is involved. This averaging is implicit in the calculation of the complementary colour points of the pure components and of their mixtures. When a knowledge of the mole fractions of the component is sufficient, the graphical approach permits their rapid determination. In the case of a binary mixture the system is over-determined, if three ranges are employed, and the results calculated by different pairs of equations may be averaged, thus reducing erratic influences; further, such influences are signalled by the displacement of the complementary colour point of the mixture from the system line.

Admittedly many measurements are necessary in order to obtain the results required for the calculation. However, such measurements are facilitated by the use of recording spectrophotometers, which are becoming progressively available in analytical laboratories. It should be appreciated that a manually operated spectrophotometer may be applied, and indeed by its use a better averaging process may be secured. The pen of a recording instrument may not be set exactly on the initial wavelength; hence, the absorbance curve may be shifted, and wavelength readings will all deviate in one direction. This deviation will be especially serious on a steep portion of the absorbance curve. In the manual setting of the wavelengths, the deviations will probably be random.

As mentioned in the introduction to this paper, the validity of Beer's law must be established in order to apply this new approach, not at a particular wavelength but at all wavelengths employed. Fortunately the tedious construction of an absorbance-concentration plot is unnecessary. The complementary colour points serve as a criterion of the validity of Beer's law: If they are concentration-independent, Beer's law is obeyed. In practice, only two solutions of different concentrations of each pure colorant need be prepared and the absorbance curves measured; from these the complementary colour points may be calculated. If the two points are identical Beer's law is valid. One of the concentrations selected for this test should be near the upper limit of the concentration range to be employed in the subsequent analyses.

It is equally simple to establish whether additivity of the absorbances of the two colorants in binary systems exists. With additivity, the complementary colour point of a mixture will fall on the system line. It is possible, but highly improbable, that the two colorants might interact to yield a product that behaves so as to compensate for any dislocation of the complementary colour point.

Proper selection of the wavelengths in the various ranges is an important factor in securing a satisfactory analysis by complementary tri-stimulus colorimetry. The selection should be made in such a way that at least two of the three colour co-ordinates of each of the two components differ as much as possible from each other. In the calculation of the fraction or concentrations of the colorants, the quotients of differences are involved. Hence the numerical values of the differences should be kept large; otherwise, only a small deviation in a single value will cause a large deviation in the value of the difference and consequently of the quotient.

None of the co-ordinates should be too small in numerical value, otherwise the influence of one of the ranges is too limited and the averaging process is less effective. Further, the selection of the ranges should be made in such a way that the overall absorptivity values, E, do not differ markedly, otherwise, the results derived concerning the colorant with the smaller value will be strongly affected by small deviations in the parameters for the other colorant. Where a highly reliable result is sought for only *one* of the colorants, inverse criteria should of course be employed in the selection of ranges.

With these factors in mind, only little experience is necessary in order to establish readily the optimum conditions. Admittedly the new approach is more time consuming than classical photometric analysis, but results of greater reliability can be obtained.

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Zusammenfassung—Complementäre Tristimulus-Colorimetrie kann auf die Analyse binärer und ternärer Mischungen angewendet werden. Es wird gezeigt, dass Bezug auf das menschliche Auge unnötig ist. Nur die Designation der einzelnen Parameter und die Art der Berechnungen werden beibehalten. Binäre Gemische der ÄDTA-Komplexe von Kupfer und Nickel, sowie ternäre Gemisch der ÄDTA-Komplex von Kupfer, Nickel und Cobalt werden als Musterbeispie behandelt. Die Resultate können entweder auf graphischem Wege, durch reine Rechnung oder durch eine Mischung graphisch-rechnerisch erhalten werden. Die Beziehungen des neuen Weges zur klassischen photometrischen Analyse von Mehrstoffsystemen werden aufgezeigt.

Résumé—La colorimétrie trichrome peut être appliquée à l'analyse des mélanges colorés binaires et ternaires. On peut montrer que, pour cet usage, l'utilisation de l'oeil n'est pas nécessaire, et que seuls la désignation des différents paramètres et le mode de calcul doivent être retenus.

Le système binaire des complexes de l'EDTA avec le cuivre et le nickel, et le système ternaire des complexes de l'EDTA avec le cuivre, le nickel et le cobalt sont traités en détail comme exemples illustrés de cette nouvelle méthode.

Les résultats peuvent être calculés graphiquement, d'une façon purement algébrique ou d'une manière combinée graphique-algébrique. Le rapport entre cette nouvelle méthode et l'analyse photométrique classique des systèmes à plusieurs constituants est montré.

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SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE^{II} WITH BENZOHYDROXAMIC ACID

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Summary—Manganese^{II} reacts with benzohydroxamic acid in ammoniacal solution to form a stable reddish-brown complex (λ_{max} 500 mμ). The reagent does not absorb at this wavelength and the concentration of ammonium hydroxide is not critical above pH 10. The sensitivity is 0·015 μg of manganese per cm^2 for log I_0/I = 0·001; the spot-plate sensitivity is 0·2 μg of manganese per 0·05 ml. Beer's law is obeyed up to a manganese concentration of 10 ppm in 1-cm absorption cells. The colour reaction takes place in non-aqueous solvents; optimum conditions for the reaction in dimethylformamide have been established. Interference by iron, cobalt and copper is avoided by the separation of manganese from these ions by ion-exchange. Development of the method included a study of the effect of temperature, pH, reagent:manganese ratio, stability of the complex and the rate of colour formation.

The spectrophotometric method has been successfully applied to the determination of manganese in steel, bronze and magnesium alloy.

THIS paper describes a new spectrophotometric method for the determination of manganese, based on a sensitive colour reaction of benzohydroxamic acid with manganese^{II} in ammonical solution. The rate of complex formation is dependent upon the concentration of ammonia; however, maximum absorbance is unaffected by variations of the ammonia concentration from 0·07*M* to 7*M*. In solutions exceeding 0·5*M* in ammonium hydroxide the reaction proceeds rapidly and the maximum absorbance is reached in 2 to 3 minutes. The colour reaction has several advantages: it is independent of temperature, few ions interfere, the ammonia concentration is not critical and the ionic strength of the solution has a negligible effect on the system. Interference by iron, cobalt and copper is avoided by separation of these ions from manganese using an ion-exchange technique developed by Kraus and Moore.[5] The separation is accomplished by adsorption on Dowex-1,8X anion-exchange resin from 12*M* hydrochloric acid and selective elution with decreasing concentrations of hydrochloric acid.

Complex formation is accompanied by a change of the oxidation state of the manganese from +2 to +3. The oxidation is accomplished by the oxygen dissolved in the solution. Boiling the solutions of reagent and manganese before the addition of ammonia will prevent the appearance of the complex colour, provided that air is excluded. Common reducing agents, such as stannous chloride, do not prevent air-oxidation of the manganese^{II}.

Hydroxamic acids, in general, have received little attention as reagents for

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metallic ions, but in organic analysis fairly wide use is made of the characteristic reddish-violet complex formed by the reaction of iron$^{\text{III}}$ with these acids in dilute hydrochloric acid[2]. Benzohydroxamic acid has been used by Wise and Brandt[8] for the determination of quinquevalent vanadium.

EXPERIMENTAL

Apparatus

Spectrophotometers: Beckman Spectrophotometers, Models DU and DK-2. Matched 1-cm and 10-cm Corex cells and matched 1-cm quartz cells.

pH Meter: Beckman Model G, with Beckman general purpose glass electrode.

Ion-exchange columns. The ion-exchange columns were made from 7-mm (o.d.) Pyrex tubing, sealed to a capillary stopcock on one end and to 20 cm of 15-mm (o.d.) Pyrex tubing on the other end. The columns were packed with Dowex-1,8X, 50- to 100-mesh resin, and each end was stoppered with a glass-wool plug. The resin bed was 18 cm in length.

Reagents

Benzohydroxamic acid: Prepare a 2% (w/v) solution by dissolving the acid in triply-distilled water.

Manganese$^{\text{II}}$*:* Prepare a standard stock solution by dissolving Matthey's "Specpure" Mn_3O_4 in hydrochloric acid and diluting to volume. Alternatively, prepare a stock solution from electrolytic manganese metal of high purity (>99·9%).

Ammonium hydroxide: Use reagent-grade ammonium hydroxide or dissolve pure ammonia in triply-distilled water.

GENERAL CHARACTERISTICS OF THE MANGANESE COMPLEX

The manganese complex is reddish-brown and has a fairly wide absorption band at 500 mμ. At this wavelength the complex obeys Beer's law over a manganese concentration range from 0·4 to 10 ppm. The optimum concentration range is 3 to 10 ppm.

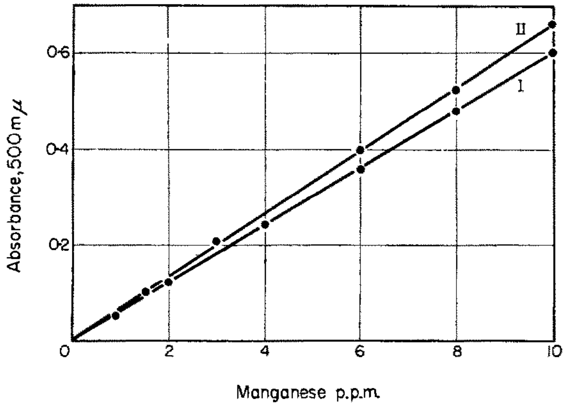


FIG. 1. (I) Mn-complex formed after ion-exchange separation; (II) Mn-complex formed directly from standard manganese solution

The sensitivity is 0·015 μg of manganese per cm^2 for log $I_0/I = 0{\cdot}001$. The molar absorbtivity is 3,630.

The spot-plate sensitivity is 0·2 μg of manganese per 0·05 ml. The reaction is not adaptable to spot-paper tests.

Effect of basicity

The colour reaction is best carried out in ammonium hydroxide solution, even though other bases may be used if circumstances make their use desirable. The maximum absorbance is independent of the ammonia concentration when the pH is above 10; hence no buffer is required. The rate of colour formation is dependent upon the basicity of the solution; at pH 10 several minutes are required for complete complex formation. If the complex is formed in solutions of ammonium hydroxide greater than about 0·5*M*, the maximum absorbance is reached almost instantaneously.

The complex will form in sodium or potassium hydroxide solutions, but the rate of formation is much slower than in an ammoniacal solution of the same molar concentration. Also, these bases may cause interference due to the formation of precipitates with certain metallic ions.

Effect of excess reagent

The absorbance of the manganese-complex increases with increasing reagent concentration up to a maximum at a molar ratio of reagent to manganese of 12:1. Above this ratio, additional reagent has no effect on the absorbance. A sufficient quantity of reagent was used in all analyses to furnish a ratio of 25:1 for the highest manganese concentration.

Stability

The manganese complex is quite stable under optimum conditions, namely, a large excess of reagent. If the ratio of reagent to manganese is of the order of 3:1 or 4:1 the complex decomposes rapidly, with the precipitation of manganese hydroxide. In 0·35*M* solutions of ammonium hydroxide, containing a molar ratio of reagent to manganese of 20:1, the absorbance remains unchanged for more than 24 hours. With a ratio of 25:1 the absorbance remains unchanged for several hours, regardless of the ammonium hydroxide concentration.

Effect of temperature

The absorbance of solutions of the manganese-complex is constant over the range 15°–35°.

Order of addition of reagents

The order of addition of reagents has no effect upon the maximum absorbance of the complex. It may, however, influence the rate of colour formation, *i.e.*, time to reach maximum intensity. If ammonium hydroxide is added directly to the manganese solution and sufficient time is allowed for the manganese hydroxide to precipitate and coagulate, the formation of the complex proceeds slowly upon the addition of the reagent. However, if the manganese, the benzohydroxamic acid and the ammonium hydroxide are added and mixed promptly, the order of addition has little or no effect upon the absorbance maximum. The normal sequence is to add the reagent to the manganese^{II} solution and then to add the ammonium hydroxide.

Dimethylformamide as solvent

The benzohydroxamic acid-manganese complex is readily formed in solutions of ethanol, methanol, and dimethylformamide. The characteristics of the manganese complex in dimethylformamide have been established. Its absorbance has a maximum at 500 mμ in water, but the addition of dimethylformamide causes a displacement of the absorbance curve below 500 mμ (see Fig. 2). The absorbance spectra of the reagent in water or in dimethylformamide (DMF) are almost the same, *i.e.*, neither absorb between 380 mμ and 700 mμ.

At 360 mμ and at 500 mμ, the manganese-complex in DMF obeys Beer's law. At 500 mμ, the absorbance of the manganese-complex in DMF is not affected by the amount of water present, a convenient feature. No measurements were made on an anhydrous system, but the absorbance at 500 mμ was shown to be independent of the concentration of water in the solvent system from 1 to 100% water. Although the complex follows Beer's law at 360 mμ, this wavelength is not recommended for three reasons:

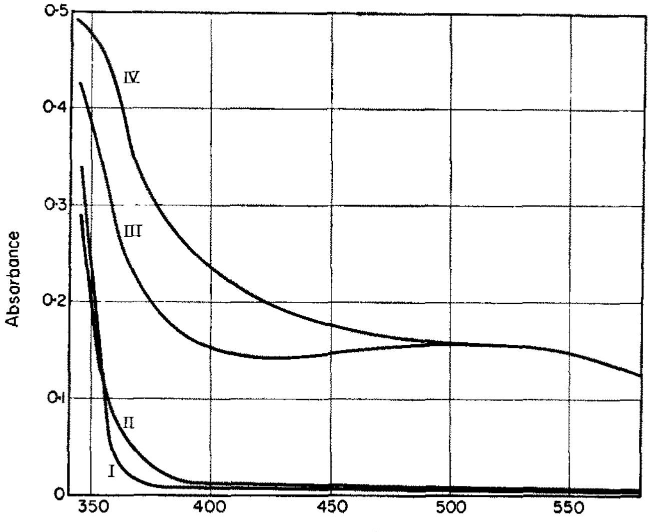


FIG. 2. (I) Benzohydroxamic acid in aqueous ammonia, (II) in ammoniacal dimethylformamide, (III) the Mn-complex in aqueous ammonia, (IV) in ammoniacal dimethylformamide.

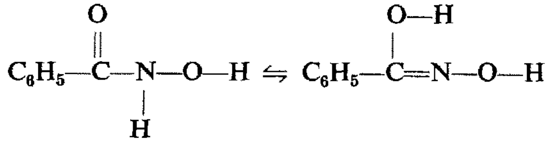
(1) the absorbance is dependent upon the amount of water in the solvent,

(2) the absorbance of the manganese complex is not at a maximum and its value is sharply changed by small variations in the wavelength of the light source, and

(3) many ions interfere seriously at 360 mμ but do not interfere at 500 mμ. The concentration of ammonium hydroxide required for maximum complex formation in DMF is identical to the requirements of an aqueous system and is not critical. The rate of complex formation, however, is much faster in DMF than in water, when equivalent quantities of ammonium hydroxide are used.

STRUCTURE

There are two possible structures of the reagent molecule:

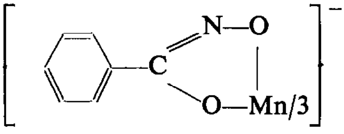


$$C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{N}{-}O{-}H \leftrightharpoons C_6H_5{-}\overset{\overset{\displaystyle O{-}H}{|}}{C}{=}N{-}O{-}H$$

(I) (II)

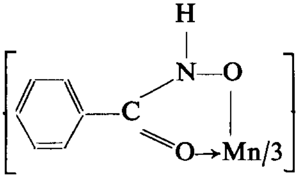
On the basis of an ultraviolet absorption study of several hydroxamic acids, Plapinger[7] concluded that benzohydroxamic acid exists predominately in the keto-form (I). In basic solution, however, it was shown that a considerable portion of the acid exists in the enol-form (II).

The fact that the complex will not form except in a basic medium, and the fact that it decomposes immediately upon the addition of enough acid to neutralise the base, indicate that the reactive species of the compound is the enol-form (II). The proposed structure (III) necessitates enolisation of the compound and oxidation of the manganese to the +3 state.



(III)

If the reaction proceeds through the keto-form, the following structure is possible:



(IV)

This last structure is however, ruled out, because of the behaviour of the complex on an anion-exchange resin. It is very strongly adsorbed by Dowex-1,8X anion-exchange resin, and continued elution of the adsorbed complex with dilute ammonium hydroxide does not cause it to migrate down the column. When solutions of the manganese-benzohydroxamic complex containing 0·1 mg of manganese are passed through the column, the complex is strongly retained and the effluent is colourless. Under these conditions, the coloured band of the complex does not extend more than about 2 mm down into the resin bed. The polarity of the complex is further indicated by its inextractability into various non-polar organic solvents. Formaldoxime ($CH_2{=}N{-}OH$) also reacts with manganese^{II} to form a manganese^{III} complex, whose colour is almost identical with manganese-benzohydroxamic acid complex.[3] Manganese^{II} does not react with N-phenylbenzohydroxamic acid to give a coloured complex because, in this compound, the enol-form is blocked by substitution of the phenyl group on the nitrogen.

It was not possible to obtain a satisfactory mole ratio by any of the usual methods, because of the precipitation of manganese hydroxide when the manganese was in excess and the relative instability of the complex, except when there is a large excess of reagent. Visual examination of solutions prepared for the continuous variations method of Job[4] showed, at the instant of mixing, a 3:1 ratio of reagent to manganese. A mole ratio of 3:1 has also been reported for the manganese-nicotinohydroxamic acid complex;[1] consequently, it seems likely that the empirical formula is R_3Mn.

Moreover, the tendency of manganese ions to form six co-ordinate bonds in complexes also indicates a 3:1 ratio of reagent to manganese.

There is sufficient evidence for the oxidation state of the manganese in the complex to assure us that it is in the tervalent state, and that the oxidation is accomplished by dissolved oxygen. For example, if a mixture of the reagent and manganese ions is boiled to eliminate the dissolved oxygen, the complex will not form on the addition of base and the solution remains colourless if air is excluded. On exposure to air or the addition of dilute hydrogen peroxide, however, the characteristic reddish-brown complex colour appears at once.

Oxidising agents, such as hydrogen peroxide, have no effect upon the maximum absorbance of the complex, but in weakly basic solutions these agents will cause the rate of complex formation to increase markedly.

Reducing agents, such as sodium thiosulphate or stannous chloride, will not destroy the manganese complex once it is formed, but boiling in contact with metallic zinc or tin will destroy it. The effect of a strong reducing agent was also observed in our studies of interference. Solutions containing a 10:1 ratio of cobalt to manganese did not give the characteristic colour of the manganese complex when kept in closed flasks; however, on exposure to air the manganese-complex colour slowly appeared. Under the reaction conditions, cobalt forms a green complex with the reagent, having a mole ratio of 3:1 of reagent to cobalt. Green was the only colour in evidence until the mixed sample was exposed to air. The reducing power of cobalt^{II} complexes, in which the six co-ordinate positions of the cobalt are satisfied, is well known.[6] The phenomenon mentioned above can be explained by assuming that the cobalt^{II} complex is more easily oxidised than the manganese^{II} complex and thus, in a closed container, would use up the available oxygen if present in sufficient excess, thereby preventing the formation of the manganese^{III} complex.

INTERFERENCES

Since the colour reaction requires a basic medium, ions that precipitate cause an interference due to the turbidity they produce in the solution. Fortunately, many of the metallic ions, such as Mg, Zn, Ni, and Cu are soluble in ammonium hydroxide, or excess ammonium salts, and hence, may be tolerated in large excess. The interference caused by various ions was determined by forming the manganese complex in the presence of a 10:1 excess by weight of the test ion. The only ions that caused a variation in absorbance of $\pm 5\%$ or more were Fe^{II}, Fe^{III}, Co^{II} and Cu^{II}. Li^{1+}, K^{1+}, Na^{1+}, Ca^{2+}, Ba^{2+}, Be^{2+}, Al^{3+}, Zn^{2+}, Mg^{2+}, Sn^{2+}, Sn^{4+}, Cr^{3+}, Pt^{6+}, F^{1-}, Cl^{1-} $NO_3{}^{1-}$, $SO_3{}^{2-}$, $SO_4{}^{2-}$, $S_2O_3{}^{2-}$, $SiO_3{}^{2-}$, $MoO_4{}^{2-}$ and $WO_4{}^{2-}$ show no interference.

When the ratio of interfering ions to manganese is increased, ions such as aluminium^{III} and chromium^{III} interfere by precipitating. However, if the weight ratio is decreased to 1:1, the ions listed in Table I can be tolerated. Iron^{III} interferes because of the low solubility of hydrous ferric oxide and also because its gelatinous precipitate carries down manganese and effectively prevents formation of the manganese-complex.

Various complexing agents will prevent the formation of the manganese-complex by competing with the benzohydroxamic acid for the available manganese. Large molar excesses of such ions as cyanide, tartrate, citrate and ethylenediamine-tetracetate prevent the formation of the manganese-complex.

SEPARATION OF INTERFERING IONS

Because of the interference of iron^{II}, iron^{III}, cobalt^{II} and copper^{II}, these ions were separated from manganese^{II} by an ion-exchange technique developed by Kraus and Moore.[5] The separation is accomplished by adsorption of these ions on Dowex-1, 8X from 12*M* hydrochloric acid and elution of the manganese with 6*M* hydrochloric acid. In 6*M* acid the iron, cobalt and copper are retained on the resin column.

TABLE 1.—INTERFERING IONS

Ion[a]	Effect on A_s, ±%
Ni^{II}	−1
Ti^{III}	+0·5
Cu^{II}	+8
Co^{II}	+31 after exposure to air
PO_4^{3-}	−0·6

[a] One mg of interfering ion and 0·1 mg of manganese^{II} in a total volume of 10 ml in each case.

ANALYSIS OF STANDARD SAMPLES

In order to evaluate the accuracy of the method, National Bureau of Standards (NBS) samples of steel, bronze and magnesium alloys were analysed for manganese. The steel and bronze samples required separation of the manganese, but the magnesium alloy was analysed *in situ.*

The samples are dissolved in dilute acid to prevent a vigorous reaction which might cause mechanical losses. Also, evaporations are made at low temperature with infrared lamps to avoid possible loss from spray or bumping. The sample weight and final volume after dissolution are chosen so that a 1-ml aliquot will contain a sufficient amount of manganese for one determination (30 μg to 100 μg).

If the major constituent of a sample is iron, cobalt or copper, or combinations of these, the concentration of manganese that can be determined is limited by the capacity of the resin column. With the column described in the section on apparatus, the capacity is sufficient for samples up to about 0·1 g, having a manganese content of 0·02–0·03%. If a large percentage of the sample constituents is not adsorbed on the resin column, a larger sample may be used.

Procedure for samples requiring separation

Dissolve the samples in a minimum of dilute hydrochloric acid, or in a mixture of hydrochloric and nitric acids, and evaporate almost to dryness. Dilute to volume with 12*M* hydrochloric acid and mix thoroughly. Withdraw a 1-ml aliquot and place it on an ion-exchange column which has been conditioned with concentrated hydrochloric acid. After the aliquot has passed into the resin bed, add two 1-ml portions of 12*M* acid, then elute with 2-ml portions of 6*M* acid until the manganese has been removed. Discard the first 2 ml of the effluent and collect the remainder. A total of 12 ml of 6*M* acid is required. Evaporate the effluent almost to dryness, transfer to a 10-ml graduated flask, add 1 ml of 2% reagent solution, make alkaline with ammonium hydroxide, and dilute to volume. Measure the absorbance at 500 mμ and read the manganese concentration from the calibration curve.

Ten samples of NBS sample No. 164 (manganese bronze) were analysed by the procedure given above. An average value of 4·69% of manganese was obtained; the standard deviation was 1·2% (see Table II). The Bureau's average value is 4·68% and the spread 4·65–4·72%.

NBS sample No. 158 (silicon bronze) contains almost 3% of silicon. The silicon was removed by hydrofluoric acid, after dissolution in a platinum dish. Values for this and other samples are listed in Table III.

TABLE II.—NBS SAMPLE NO. 164 (Mn-BRONZE)

% Mn	$d \times 10^{-2}$	$d^2 \times 10^{-4}$
4·72	3	9
4·65	4	16
4·60	9	81
4·63	6	36
4·67	2	4
4·74	5	25
4·76	7	49
4·72	3	9
4·74	5	25
4·63	6	36

Average 4·69 $\Sigma d^2 = 2·9 \times 10^{-2}$

NBS. average 4·68

$$\sigma = \sqrt{\frac{2·9 \times 10^{-2}}{9}} = 0·054 \text{ or } 1·2\%$$

TABLE III.—RESULTS OF ANALYSES OF NBS SAMPLES

NBS sample Type and No.	NBS values, % Mn		New method, % Mn	
	Range	Average	Range	Average
Mn-Bronze 164	4·65–4·72	4·68	4·60–4·76	4·69
Si-Bronze 158	1·30–1·33	1·31	1·30–1·33	1·31
Steel 14c	0·455–0·470	0·462	0·453–0·472	0·462
Mg-Alloy 171	0·44–0·46	0·45	0·443–0·446	0·444

Determination of manganese without separation

Manganese may be determined in the presence of a high concentration of magnesium without separation. However, the latter is insoluble in basic solution, except in the presence of an excess of ammonia. Hence, ammonium chloride was used to hold the magnesium in solution in the basic medium required for the formation of the manganese complex.

Magnesium, in the presence of ammonium chloride, causes the manganese complex to form at a much slower rate than usual. This effect can largely be overcome by using a higher reagent concentration. There is a negligible effect on the maximum absorbance of the complex. For example, 100 μg of manganese, 1 ml of 2% benzohydroxamic acid, 2 ml of saturated ammonium chloride solution, 0·02 g of magnesium and 1 ml of concentrated ammonium hydroxide in a total volume of 10 ml gave an absorbance (after 10 minutes) equal to 98% of the value found for manganese alone. Increasing or decreasing the ammonium chloride concentration by a factor of 4 or 5 does not cause a detectable change in the absorbance. The possible formation of a magnesium complex with the reagent could not be determined because of the dependence of the magnesium hydroxide solubility on the ammonia concentration.

The National Bureau of Standards has only one magnesium alloy (No. 171) available. It contains 0·45% of manganese.

Samples were dissolved in dilute hydrochloric acid and diluted to volume. A 1-ml aliquot, containing approximately 0·01 g of the alloy, was taken for analysis. To this was added 0·5 ml of saturated ammonium chloride and 5 ml of benzohydroxamic acid reagent solution. The solution was then made alkaline by the addition of 1 ml of concentrated ammonium hydroxide. After 10 min, the absorbance of the solution was measured.

Four samples were analysed and the following values were obtained: 0·443%, 0·443%, 0·445% and 0·446%, giving an average value of 0·444%. The NBS average value is 0·45% of manganese, the range being 0·44–0·46%.

Zusammenfassung—Mangan(II) reagiert mit Benzhydroxamsäure in ammoniakalischer Lösung unter Bildung eines stabilen rotbraunen Komplexes (Abs. Max. 500 mμ) Das Reagens selbst absorbiert nicht bei dieser Wellenlänge und die Ammoniakkonzentration ist nicht kritisch wenn oberhalb pH 10 gearbeitet wird. Die Empfindlichkeit ist 0·015 μg Mn/ccm for log $I_0/I = 0·001$; Die Empfindlichkeit auf der Tüpfelplatte ist 0·2 μg Mn per 0·05 ml. Beer's Gesetz ist hinauf bis zu 10 ppm in 1-cm Absorptionsgfässen erfüllt. Die Farbreaktion findet in nichtwässrigem Medium statt. Optimale Bedingungen für Dimethylformamid als Lösemittel würden ausgearbeitet. Störungen durch Eisen, Cobalt und Kupfer werden durch Abtrennung dieser Ionen mittels Ionenaustausch vermieden. Die Entwicklung der Methode schliesst Studien über den Einfluss der Temperatur ein, sowie über den Effekt von pH, Verhältnis der Konzentrationen von Reagens zu Mangan, Stabilitat des Komplexes und Zeitbedarf der Farbentwicklung. Die photometrische methode wurde auf die Bestimmung von Mangan in Stählen, Bronzen und Magnesiumlegierungen angewendet.

Résumé—Le manganèse (II) réagit sur l'acide benzohydroxamique en solution ammoniacale pour former un complexe stable brun rougeâtre (max. 500 mμ). Le réactif n'absorbe pas à cette longueur d'onde et la concentration de l'ammoniaque n'est pas gênante au-dessus de pH 10. La sensibilité est de 0,015 μg de Mn par cm^3 pour log $I_0/I = 0{,}001$; la sensibilité "spot plate" est de 0,2 μg de Mn par 0,05 ml.

La loi de Beer est suivie jusqu'à une concentration de manganèse de 10 p.p.m. dans les cellules d'absorption de 1 cm. La réaction colorée a lieu dans des solvants non aqueux; les conditions les meilleures pour la réaction dans le diméthylformamide ont été établies. La gêne du fer, du cobalt et du cuivre est évitée par la séparation par échange d'ions du manganèse et de ces ions. Le développement de cette méthode comprend une étude de l'influence de la température, du pH, du rapport réactif/manganèse, de la stabilité du complexe et de la vitesse de formation de la couleur.

La méthode spectrophotométrique a été appliquée avec succès au dosage du manganèse dans l'acier, le bronze et l'alliage de magnésium.

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INVESTIGATIONS WITH IRIDIUM-192 OF SEPARATIONS OF PLATINUM AND RHODIUM FROM IRIDIUM—I

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Summary—^{192}Ir has been used as a tracer to study the interference of iridium in the quantitative analysis of platinum and rhodium by the classical method of Gilchrist and Wichers and by the new method of Payne.

Radioactivation analysis is currently being employed in this laboratory to determine very low concentrations of impurities in platinum metals. The work is being supported by radio-tracer studies to evaluate the efficiency of different chemical procedures for the separation and quantitative analysis of metals of the platinum group. This paper reports on the use of ^{192}Ir as a tracer in a study of the interference of iridium in the analysis of milligram amounts of rhodium and platinum by (*a*) the classical method of Gilchrist and Wichers,[1] and (*b*) the new method of Payne.[2] In both of these methods for the separation and determination of all six platinum metals, osmium and ruthenium are separated at an early stage from the other metals by distillation as the volatile tetroxides.

In the procedure of Gilchrist and Wichers palladium, rhodium and iridium are precipitated as hydrated dioxides by controlled hydrolysis using sodium bromate, and, in this manner, are separated from platinum, which remains in solution. The hydrated dioxides are dissolved in hydrochloric acid and palladium is specifically precipitated with dimethylglyoxime. The rhodium and iridium in solution are then parted by reduction of the former to metal with titanium^{III} in a sulphuric acid medium. Each separated element is finally determined gravimetrically as the metal.

In the procedure of Payne,[2] the separation of platinum, palladium, iridium and rhodium is carried out by means of partition chromatography, using a column of cellulose and acid solutions of methyl isobutyl ketone. The chromatographic method has been developed from that of Rees-Evans *et al.*[3]

Ayres and Berg[4] have pointed out some of the difficulties inherent in the precipitation separations and gravimetric determinations. These workers[5] have used spectrographic methods to study the separation of palladium with dimethylglyoxime from platinum, iridium and rhodium. Ayres and Maddin[6] have reported a similar investigation of the separation of rhodium from iridium by the reduction of the rhodium in solution to metal, using titanium^{III} as reducing agent.

EXPERIMENTAL

Reagents

^{192}Ir tracer was supplied as $(NH_4)_2IrCl_6$ in hydrochloric acid solution from the Radiochemical Centre, Amersham. The material was of high specific activity—250 millicuries ^{192}Ir/g of iridium. Nuclear data for ^{192}Ir are given in Table I.

Compounds of platinum metals provided by the Mond Nickel Company were used to make up stock solutions. All of the compounds had been analysed spectrographically and contained < 0·01 % of total impurities.

Stock rhodium solution: A solution containing *ca.* 10 mg of Rh/ml was prepared by dilution of a standardised solution of H_3RhCl_6 in 6*M* hydrochloric acid.

Stock platinum solution: A standardised solution of H_2PtCl_6 in 6*M* hydrochloric acid was diluted with 6*M* hydrochloric acid to give a solution containing *ca.* 10 mg of Pt/ml.

Labelled iridium solution: This was prepared by thoroughly mixing a suitable quantity of the iridium tracer with a solution containing *ca.* 1 mg of Ir/ml as $(NH_4)_2IrCl_6$ in 0·2*M* hydrochloric acid. Exchange between the radioactive and inactive iridium takes place under these conditions.[7]

The concentrations of the respective platinum metals in the stock solutions were confirmed by gravimetric analysis.[2]

Table I.—Nuclear data for iridium-192
Half-life: 74·4 days

Type of radiation	β^-	EC	γ
Energy, *MeV*	0·097 (1 %) 0·26 (8 %) 0·54 (35 %) 0·67 (50 %)	(6 %)	0·296 0·308 0·316 0·468 0·484 0·604 0·613 others

Table II.—Separation of rhodium and platinum from iridium by the method of Gilchrist and Wichers

Run	Rhodium taken, *mg*	Platinum taken, *mg*	Iridium taken, *mg*	Iridium found radiometrically, *mg*		
				in final rhodium	in final platinum	in final iridium
G 1	29·80	29·42	10·50	0·079	0·032	10·3
2	29·80	29·42	10·50	0·029	0·030	10·5
3	29·80	29·42	31·50	0·060	0·006	31·9
4	29·80	29·42	31·50	0·228	0·002	31·9
5	29·80	29·42	42·00	0·114	0·095	42·0
6	29·80	29·42	42·00	—	0·047	42·0

Acids and most other reagents used were of AnalaR grade. Cellulose powder for the chromatographic column was Whatman Standard Grade material.

Procedures

(*a*) *Test of the separation of platinum and rhodium from iridium in the method of Gilchrist and Wichers.* Solutions made up by mixing known aliquots of the platinum, rhodium and labelled iridium stock solutions were used for the investigation. The three platinum metals in the solutions were separated and determined by the procedure of Gilchrist and Wichers.[1] In runs G3–6 (Table II) the reduction of rhodium by titanium^{III} chloride was followed potentiometrically using the technique of Ayres and Maddin.[5] This enabled the amount of excess titanium^{III} chloride to be kept to a minimum.

In each run an aliquot of the labelled iridium solution was taken as a standard. The hydrated dioxide of iridium was precipitated with sodium bromate, and then ignited and reduced under hydrogen to metal following the techniques used by Payne.[8]

The recovered samples of platinum, rhodium and iridium from the mixtures and the iridium from the standard were brushed on to tared aluminium counting trays (A.E.R.E. Cat. No. 4-3/1068) and weighed. The powdered metal samples were then affixed to the trays by the addition and evaporation of a few drops of a 1% solution of collodion in acetone. The samples were counted under identical conditions with a NaI(Tl) γ-scintillation counter, type 1186A. All measured counting rates were corrected for background. From the specific activity of the iridium standard and the activities of the other samples, the iridium content of the separated metal samples could be determined. No correction for the decay of the ^{192}Ir was necessary, as in a given run the samples from the mixture and the standard were counted consecutively.

(b) *Tests of the separation of platinum and rhodium from iridium in the chromatographic procedure of Payne.* Synthetic mixtures of platinum, rhodium and labelled iridium were prepared for investigation from the stock solutions. A given sample was placed in a 250-ml beaker and boiled with 20 ml of *aqua regia* to destroy ammonium salts. Ten ml of 2% lithium chloride solution and 10 ml of perchloric acid were added, and the solution was evaporated until all free perchloric acid had been expelled. After cooling, the sides of the beaker were rinsed with the minimum amount of water and evaporation was continued until fuming ceased completely.

TABLE III.—SEPARATION OF RHODIUM AND PLATINUM FROM IRIDIUM BY THE METHOD OF PAYNE

Run	Rhodium taken, *mg*	Platinum taken, *mg*	Iridium taken, *mg*	Iridium found radiometrically, *mg* in final rhodium	in final platinum	in final iridium
P 1	9·93	9·81	10·50	0·064	0·137	10·4
2	9·93	9·81	10·50	0·107	0·009	10·5
3	29·80	29·42	42·00	0·109	nil	42 0
4	29·80	29·42	42·00	0·166	—	42·0

The cooled residue was treated six times with 5-ml quantities of 6*M* hydrochloric acid and each time was evaporated to dryness. The final residue was dissolved in 20 ml of conc. hydrochloric acid and boiled under the cover of a watch-glass, until the volume was reduced to *ca.* 5 ml. The cover was then removed and the solution was evaporated gently until reduced to a volume of *ca.* 2 ml.

The chromatographic procedure was then followed, and the separated platinum, rhodium and iridium were finally converted to metals, using the technique of Payne.[2]

For each run a labelled iridium standard was employed, as in the tests of the procedure of Gilchrist and Wichers.

All the final metal samples were assayed radiometrically as described above and the iridium contents of the separated metals were determined.

RESULTS AND DISCUSSION

Results obtained for the iridium contents of final metal precipitates obtained using the procedure of Gilchrist and Wichers are shown in Table II. Corresponding results obtained by the method of Payne are listed in Table III.

The method of Gilchrist and Wichers provides a convenient separation of platinum from rhodium and iridium, and the amounts of iridium contaminating final samples of platinum are relatively unimportant. However, the separation of rhodium and iridium from each other is rather tedious and the complete removal of excess titanium by cupferron is difficult. In a number of cases, weights of final metal precipitates were up to 3% higher than the weights of element taken. More satisfactory gravimetric results were obtainable if the final precipitates were treated with hydrofluoric acid and nitric acid to remove traces of silica and salts, as in the scheme of Payne.

The amounts of iridium found in the separated rhodium are similar to those found by Ayres and Maddin.[6]

The procedure of Payne is more rapid than that of Gilchrist and Wichers for the separation of platinum, rhodium and iridium. The chromatographic method gives rise to little contamination of the final platinum with iridium, provided that prior conversion to chloro-acids is complete. (In test P1 a preliminary removal of ammonium ions was not made, and this may account for the rather high iridium content of the recovered platinum). Small, but fairly consistent amounts of iridium were found in the rhodium samples.

Acknowledgment—The authors wish to thank Mr. S. T. Payne for helpful discussion and for providing them with details of his method before publication.

Zusammenfassung—Iridium-192 als Tracer wurde verwendet um die durch Iridium verursachten Störungen bei der quantitativen Bestimmung von Platin und Rhodium zu studieren. Die Studie erstreckte sich auf die klassische Methode nach Gilchrist und Wichers und die neue Methode nach Payne.

Résumé—L'iridium 192 a été utilisé comme traceur pour étudier l'interférence de l'iridium dans l'analyse quantitative du platine et du rhodium par la méthode classique de Gilchrist et Wichers et par la nouvelle méthode de Payne.

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SHORT COMMUNICATIONS

Effect of chloride ions on the determination of nitrate by Leithe's method

(*Received* 30 *July* 1960)

DURING an ion-exchange study[1] requiring exact nitrate determinations, we attempted to use the method developed by Leithe,[2] based on the reduction of the nitrate by iron^{II} sulphate and titration of the excess of iron^{II} sulphate with potassium dichromate, using ferroïn as indicator.

The results obtained were, however, higher than expected, and it appeared to us that the chloride ion concentration might affect the quantity of dichromate used. In Leithe's study he mentions the accelerating effect of chloride ions on the reaction, but he does not mention that the concentration of the latter determines the quantity of dichromate used.

In the present study we have attempted to follow the reaction, studying the influence of the chloride concentration and of the time of heating, as well as trying to find the mechanism through which chloride influences the titration.

TABLE I.—EFFECT OF CHLORIDE CONCENTRATION ON BLANK SOLUTIONS

1*N* HCl, *ml* added	0	3	4	5	10	15	20	150
0·1*N* $K_2Cr_2O_7$, *ml* used	27·70	27·65	27·60	27·55	27·35	27·15	27·15	27·15

The procedure described by Leithe was used, the only difference being that the iron^{II} sulphate used was about 0·1*N* and not 0·2*N*. The influence of chloride ions was studied in two sets of solutions; in the one, nitrate ions were present, but not in the other (blank solutions). In a few experiments, hydrochloric acid was replaced by sodium chloride, but there was no significant difference between the two. It is assumed that the somewhat unusual choice (by Leithe) of ferroïn as an indicator for the titration of iron^{II} with dichromate can be explained by the fact that the present nitrate determinations are carried out in very high concentrations of sulphuric acid. Under these conditions, the redox potential of ferroïn decreases from 1·06V to 0·76V while that of dichromate rises[3] from 1·01V to 1·35V.

A series of experiments was done to check the influence of the time of heating. It appears from these experiments that by boiling the solution for 3 minutes, the reaction is completed (in the presence or in the absence of chloride ions) and all of the compound $FeNOSO_4$ is destroyed; by prolonging the heating to 5–8 minutes no appreciable changes were found. If the heating was prolonged to 15 minutes, some iron^{II} was oxidised and results were higher than expected. The completion of the reaction in 3 minutes in all of the experiments shows that chloride ions do not have any accelerating effect, in contrast to the results found by Leithe.[2]

Table I summarises the influence of chloride concentration on the quantity of dichromate used with blank solutions. It appears from this table that quantities of 1*N* hydrochloric acid between 3 and 15 ml have the greatest influence, yet no stoichiometric relation exists between hydrochloric acid and iron^{II} sulphate. It can also be concluded from these experiments that the chloride ions react with the iron^{II} ions and not with the nitrate. The addition of hydrochloric acid causes a strong yellow colouring of the solution, quite different in shade from an iron^{III} solution. It was also seen that chloride ions influence the quantity of dichromate used only in cases where the solutions were boiled and not when the titration was made directly without any heating. This may also explain why every text-book of analytical chemistry mentions the possibility of titrating iron^{II} with dichromate in 1-2*N* hydrochloric acid.

An attempt was made to find the theoretical reason for the chloride effect. A possibility taken

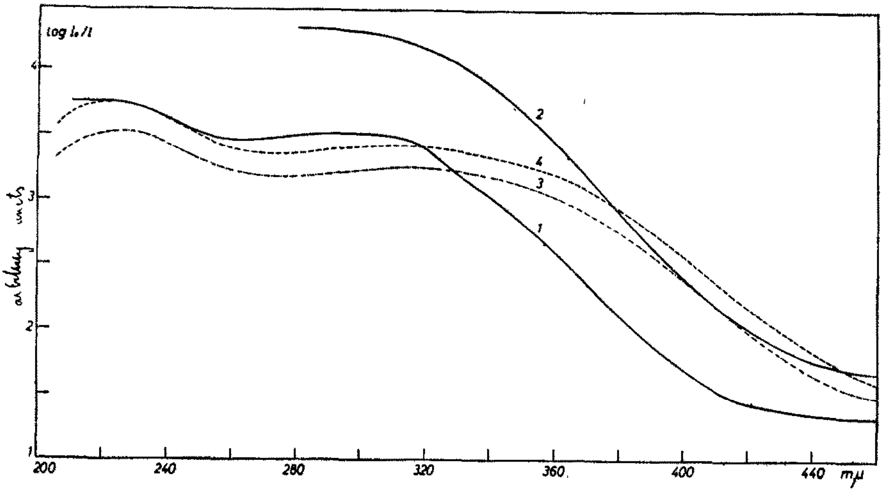

FIG. 1. Absorption spectra of iron solutions in 50% H_2SO_4:
1. 25 ml 0·1*M* $FeSO_4$ + 25 ml H_2O.
2. 25 ml 0·1*M* $FeSO_4$ + 25 ml 1*N* HCl.
3. 0·6 ml 0·1*M* $FeCl_3$ + 25 ml 1*N* HCl + 24·4 ml H_2O.
4. 0·8 ml 0·1*M* $FeCl_3$ + 25 ml 1*N* HCl + 24.2 ml H_2O.

TABLE II.—EFFECT OF CHLORIDE CONCENTRATION ON NITRATE DETERMINATIONS

NO_3^-, *mg* present	1*N* HCl, *ml* added	0·1*N* $K_2Cr_2O_7$		NO_3^-, *mg* found	Deviation	
		ml used in blank determinations	*ml* used in NO_3^- determinations		*mg*	%
6·2	—	27·90	24·9	6·2	0	0
6·2	25	27·25	24·2	6·3	+0·1	1·6
18·6	—	28·70	19·50	18·96	+0·36	2·2
18·6	10	27·70	18·55	18·88	+0·28	1·5
18·6	25	27·70	18·70	18·60	0	0
24·8	—	28·30	16·20	25·0	+0·2	0·83
24·8	10	27·70	15·55	25·1	+0·3	1·25
24·8	25	27·60	15·50	25·0	+0·2	0·83
31	—	28·15	13·30	30·70	−0·3	1·0
31	5	27·65	12·50	31·30	+0·3	1·0
31	10	27·60	12·52	31·27	+0·27	0·86
31	25	27·8	12·65	31·30	+0·3	1·0
37·2	—	27·65	9·22	38·0	+0·8	2·3
37·2	25	27·20	9·10	37·6	+0·4	1·1

into account was the formation of a complex between iron^{II} and chloride ions. Such complexes are known to exist and three species are cited, $[FeCl]^+$,[4,5] $[FeCl_3]^-$, and $[FeCl_4]^{2-}$.[6] The evidence for the last two was found by adsorption on an anion-exchanger from concentrated hydrochloric acid solutions.

Evidence for such a complex was also found in the absorption spectra given in Fig. 1. The absorption values obtained for an iron^{II} solution containing chloride ions, using a Beckman DU Spectrophotometer with quartz cells and quartz cell spacers, are nearly 10 times greater than for the same solutions in absence of chloride. For comparison, the absorption spectrum of iron^{III} solutions was also determined and found to have a completely different shape in the ultraviolet region. An ion-exchange equilibrium study was also made in order to define the complex formed, yet no evidence for the adsorption of a complex ion on a cation-exchanger has been found. This can be explained either by the inactivation of the resin by the very high concentration of sulphuric acid (about 50% in weight), or by the absence of cationic species in the solution, as indicated by Kraus.[6] This problem will be studied further and the results published in another communication.

The stability of the existing complex species is probably also enhanced by the high concentration of sulphuric acid, since a dilution of the solution causes a rapid fading of the colour. The formation of these complexes probably causes some small changes in the redox potential of the system, which causes the small differences in dichromate used.

A second assumption made was that, by heating a solution containing chloride ions, a partial catalytic oxidation to iron^{III} by air may occur, but the absorption spectra obtained from these solutions did not show the presence of iron^{III} ions (Fig. 1). Potentiometric titrations (using a Beckman H-2 pH meter with a platinum electrode) of iron^{II} solutions, in the absence or in the presence of chloride ions, do not show perfectly parallel curves, as would be the case if some iron^{III} ions are present; but, on the other hand, the differences are too small to make other interpretations possible.

Table II shows the results obtained in a series of nitrate determinations. It can be seen from this table that if the blank and the analysed solutions contain no chloride ions at all, or if both contain the same concentrations of chloride ions (or at least more than 20–25 ml of $1N$ hydrochloric acid), the reaction proceeds equally well and with nearly the same deviations. This table also shows that, taking these precautions, one can easily determine amounts of nitrate from 6–37 mg with an average error of ±1%.

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Summary—Chloride ions were found to influence the equivalence point in the determination of nitrate by Leithe's method. This is explained by the formation of a complex between chloride and iron^{II} ions, which causes some small changes of the redox potential of the solution.

From the analytical point of view there is no difference, whether the determination is carried out in the absence or in the presence of chloride ions; but in the later case, the blank and the analysed solutions should contain the same quantity of chloride ions.

Zusammenfassung—Es wurde gefunden dass Chlorionen den Equivalenzpunkt der Nitrat-Bestimmung mit Bichromat beeinflussen. Dieses scheint verursacht zu sein durch die Bildung eines Komplexes zwischen Chlorionen und zweiwertige Eisenionen, der das Redox-potential der Lösung verändert.

Vom analytischen Standpunkt ist kein Unterschied ob die Bestimmung in Abwesentheit oder Gegenwart von Chlorionen ausgeführt wird, aber im letzten Fall muss die Blindlösung und die Lösung zum analysieren die selben Mengen Chlor enthalten.

Résumé—Il a été trouvé que les ions chlore influencent le point d'équivalence du dosage du nitrate par la methode au bichromate. Ceci est expliqué par la formation d'un complexe entre les ions chlore et les ions ferreux ce qui provoquerait des petits changements du potentiel redox de la solution.

Du point de vue analytique il n'y a pas de différence si le dosage est effectué en absence ou en présence des ions chlore mais dans ce dernier cas le blanc et la solution á analyser doivent contenir la même quantité des ions chlore.

REFERENCES

[1] C. Heitner-Wirguin, J. E. Salmon and E. B. Mayer, *J. Chem. Soc.*, 1960, 460.

[2] W. Leithe, *Mikrochemie*, 1946, **33**, 48; 1947, **33**, 149; 1948, **33**, 310; 1951, **36/37**, 265; *Analyt. Chem.*, 1948, **20**, 1082.

[3] I. M. Kolthoff, R. Belcher, V. A. Stenger and G. Matsuyama, *Volumetric Analysis*. Interscience Publishers, New York, 1957, Vol. III, p. 124, 175.

[4] H. Olerup, *Diss., Lund*, 1944, 78.

[5] H. McConnel and N. Davidson, *J. Amer. Chem. Soc.*, 1950, **72**, 5557.

[6] K. A. Kraus and G. E. Moore, *ibid.*, 1953, **75**, 1460.

Deuterium analysis by infrared spectrophotometry*

(*Received* 1 *August* 1960)

THE infrared spectroscopic method for the analysis of deuterium in organic compounds, which we described recently,[1] was based on the use of the Perkin-Elmer Model-21 spectrophotometer. Later work has shown that measurements of adequate precision for many purposes can be made with the simpler, and more widely available Perkin-Elmer Model-137 Infracord spectrophotometer, if a modified type of cell holder is employed. The object of tnis communication is to describe this technique, together with improved procedures for handling volatile and hygroscopic liquid samples.

(*a*) *Analysis of deuterium-enriched water with the Perkin-Elmer Model*-137 *Infracord spectrophotometer*

A matched pair of 0·2-mm calcium fluoride cells are used, identical with those described in the previous publication.[1] The macro-cell, containing natural-abundance water in the control beam, is mounted in the normal fashion in the standard Infracord cell holder. The standard Infracord micro-cell is not suitable for the micro-sample of deuterium-enriched water because it has too large a parasitic volume, and the holder does not permit sufficiently precise re-positioning of the cell after its removal from the spectrometer for re-filling.

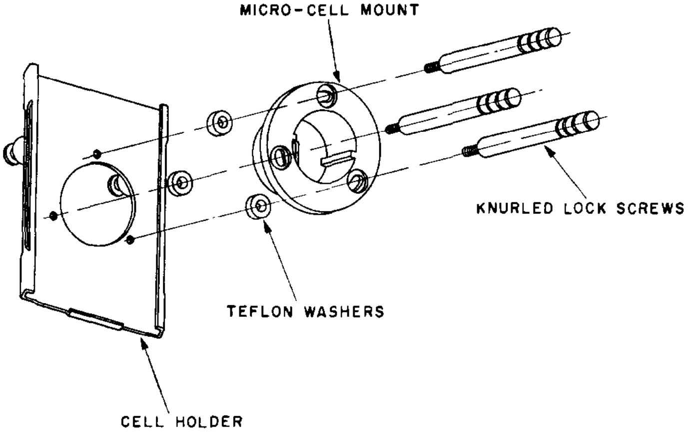

FIG. 1.

An adaptor has, therefore, been designed which permits the modified micro-cell used with the Model-21 instrument to be mounted in the Infracord spectrometer with the sample tray removed. Adjustments are provided for its accurate and reproducible alignment in the optical beam. This adaptor (Fig. 1) consists of a regular Model-21 micro-cell mount attached to the Infracord cell holder by means of three long-handled knurled lock screws. These 1/4″-diam. screws have threaded ends of 1/16″ diam., which pass through oversized, oval slotted holes in the collar of the micro-cell mount, and screw into the cell holder. Teflon washers of 1/8″ ext. diam. and approximately 1/16″ thickness separate the micro-cell mount from the cell holder and allow the micro-cell mount to fit flush with the face of the spectrometer case.

For the initial adjustment, both cells are filled repeatedly with natural-abundance water, and the spectrometer is set to 2500 cm^{-1} (4 μ), with the "100%-Adjust" Control near its counter-clockwise limit. The three screws are loosened slightly, and the micro-cell mount is positioned for maximum energy transmission. The extension handles permit these adjustments to be made easily, without obscuring the radiation beam; when optimum transmission is achieved, the screws are tightened against the Teflon washers. Following these adjustments the micro-cell can be repeatedly removed and replaced to give the same energy transmission.

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* Published as Contribution No. 6002 from the Laboratories of the National Research Council of Canada.

To perform an analysis, the routine instrumental adjustments for gain, "dead spot", balance, zero and 100% transmission are first carried out. With the spectrometer set to 4 μ, and with natural-abundance water in both cells, the "100%-Adjust" control is manipulated to give a pen reading of 95% transmission. The sample beam is next closed by *gradually* moving an opaque shutter across the optical path, and this procedure is repeated several times to insure reproducibility. The selection of the optimum slit width will depend on the sensitivity and alignment of the particular spectrometer and should be established by trial and error. In the case of our instrument, optimum sensitivity was achieved with a slit width of 100 scale units.

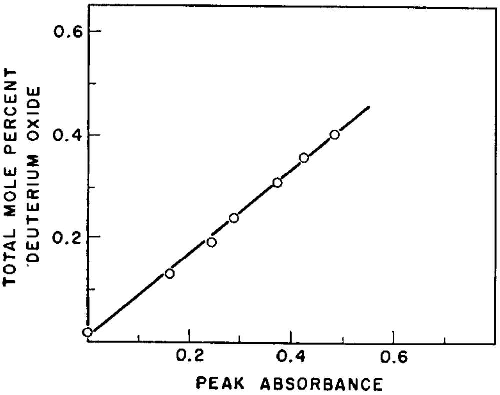

FIG. 2.

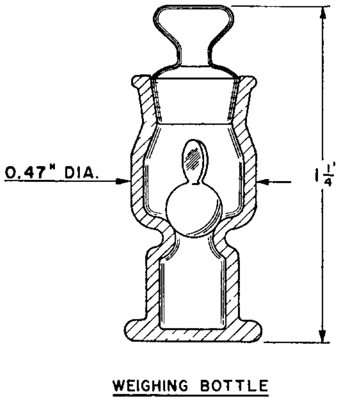

FIG. 3.

With plain white paper on the recording drum, both beams unobstructed, and natural-abundance water in both cells, the spectrum is next scanned from 3·5 μ to 4·5 μ to establish the baseline. The radiation is then slowly closed off from the sample cell and the spectral region re-scanned to obtain the 100% absorbance line. The subsequent procedure is as described previously for the Model-21 spectrophotometer, both cells being removed from the spectrophotometer while the micro-cell is filled with deuterium-enriched water, in order to maintain temperature equivalence.

The standard calibration curve obtained in this fashion (Fig. 2) agrees closely with that obtained for the Model-21 spectrophotometer, though there is slightly greater scatter in the points. Measurements of the same water sample at 24-hr intervals show little variation. It must be emphasized that such reproducibility is only obtainable if the closing and opening of the sample beam to radiation is performed very slowly, since the instrument is operating with little energy in the servo-loop.

(*b*) *Isotopic dilution of volatile compounds*

Difficulties may be encountered in the isotopic dilution of volatile or hygroscopic liquids because of manipulative losses or changes during weighing. These have been appreciably reduced by the use of the double chamber weighing bottle shown in Fig. 3. The deuterium-enriched compound is first weighed into the lower chamber, which can be closed by a solid glass spherical stopper which rests on the constriction in the bottle. Both the stopper and the constricted area on which it seats have finely ground surfaces. The complete bottle is first weighed empty with both the inner and outer stoppers in place. The isotopically enriched compound is then introduced into the lower chamber, the stoppers are replaced, and the bottle re-weighed. The approximate calculated amount of natural-abundance diluent material is next introduced into the upper chamber, the top stopper is replaced and the bottle is weighed again. The two materials may now be mixed by tilting and shaking the bottle without opening it. By this means, loss of the volatile isotopically enriched material or its exchange or dilution by atmospheric water vapor during the addition of the diluent is diminished.

(*c*) *Transfer of volatile samples to the combustion tube*

The combustion procedure requires that the copper oxide be first introduced into the Vycor tube, where it is pre-heated *in vacuo*. After addition of the sample, the ampule must be constricted, evacuated, and finally sealed at the constriction. During this process volatile compounds may be lost unless suitable cooling arrangements are provided. If appreciable quantities of gas remain in the cell, an explosion may occur in the furnace.

It has been found convenient to carry out the second evacuation using the arrangement shown in Fig. 4. The sample is introduced as far down the Vycor tube as possible, and the lower part of the tube is then cooled by immersion in a mixture of acetone and solid carbon dioxide. While the lower end is kept cool, the upper end of the tube is constricted to a capillary with an oxy-hydrogen flame. The tube is then attached to the vacuum line. Stop-cock 1 is closed, stop-cock 2 is opened, and the Vycor tube is maintained in the acetone-carbon dioxide bath while the trap is cooled with liquid air. After 5 min, stop-cock 1 is opened and the system is evacuated for a further 5 min. Stop-cocks 1 and 2 are next closed, and the liquid air coolant is withdrawn. Stop-cock 1 is re-opened and pumping is continued until the trap attains room temperature. Stop-cock 2 is then opened, pumping is continued and the capillary in the Vycor tube is sealed, as previously described.

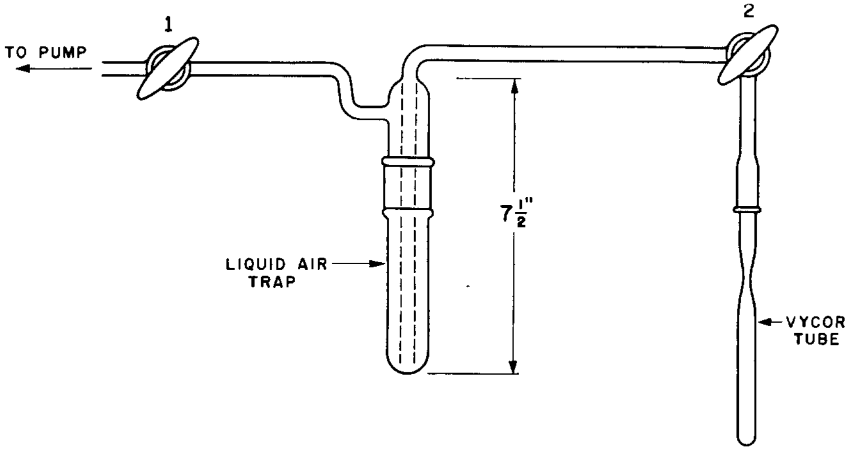

FIG. 4.

Using these weighing and transfer techniques it has been found possible to obtain satisfactory analyses of *cyclo*-pentanone-α, α-d_4 (b.p.$_{760\,\mathrm{mm}}$, 160°) and diacetyl-d_6 (b.p.$_{760\,\mathrm{mm}}$. 88°), which otherwise gave low and variable deuterium assays.

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Summary—An improved method for the infrared spectrophotometric determination of deuterium is described.

Zusamménfassung—Eine verbesserte Methode zur infrarot-spectrophotometrischen Bestimmung von Deuterium wird beschrieben.

Résumé—Les auteurs décrivent des techniques perfectionnées d'analyse, par spectrophotométrie infrarouge, du deutérium dans les composés organiques.

REFERENCE

R. N. Jones and M. A. MacKenzie, *Talanta*, 1960, **3**, 356.

Talanta, 1960, Vol. 7, pp. 127–128. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

New electrode system sensitive to very small gaseous samples

(*Received* 12 *September* 1960)

Sir:

We wish to report what appears to be a new electrical phenomenon responsive to the chemical composition of gases and vapours. The nature of this effect is best understood by reference to Fig. 1, which depicts a typical assembly capable of eliciting such a response. A carrier-gas stream consisting, for example, of an argon-oxygen mixture (90%–10%) is used to sweep small gaseous samples through a Vycor capillary tubing having a platinum anode inside and a cathode of the same metal wrapped on the outside. The anode contact is somewhat critical, the best response being produced by a light frictional contact on the inside surface of the tubing. The cathode lead is not of major importance. The glass tubing with its contents are heated to temperatures ranging from 500°–700°.

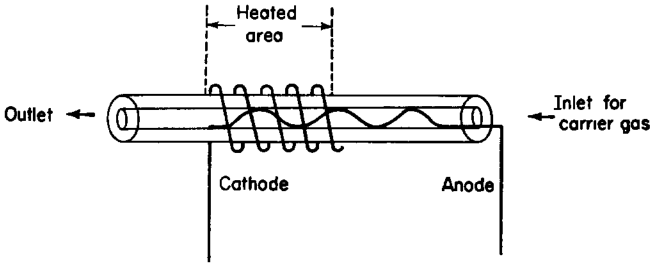

Fig. 1.

If in the above assembly small samples of the order of a few micrograms of hydrogen, methane, ethyl acetate, and other organic substances are injected into the gas stream, the electrode current elicited by a potential of, for example, 280 V is markedly enhanced. The extreme sensitivity of the phenomenon is evident in Fig. 2, showing a strong response to 0·16 μg of ethyl acetate vapour. Injection of even a small amount of carbon dioxide, on the other hand, produces a marked drop in the current.

Current-voltage plots obtained in the absence of injected samples are of some interest. A typical plot for argon or for the argon-oxygen mixture is shown in Fig. 3. Although the absolute magnitude of the current induced is a relatively sensitive function of temperature (apparent heat of activation is approximately 46 kcal/mole), the shape of the curve obtained is relatively independent of temperature, a rather sharp rise occurring for argon at 245 ± 10 V, irrespective of temperature, nature of the non-metallic contact (Pyrex, Vycor, glazed porcelain), and the area of contact. This critical voltage appears to be characteristic for each carrier gas employed, ranging from 245 for argon to 450 for nitrogen.

The response to hydrogen or organic samples in an argon-oxygen stream increases markedly above the critical voltage (245 V), the signal to base line current ratio improving sharply above this potential. There appears to be some specificity in response, since the signal to base line current ratio at different voltages for hydrogen differs significantly, relatively speaking, from that for ethyl acetate.

The cathode contact, it has been found, may be (1) placed outside as shown, (2) sealed to the glass, (3) placed in frictional contact inside the capillary, or (4) suspended in the heated zone inside the capillary in the gas stream. Apparently sufficient electron emission occurs at the temperatures employed to complete the circuit. The capillary material, whether Pyrex, Vycor, or ceramic, conducts sufficiently at the higher temperatures to constitute a relatively insignificant barrier to current flow.

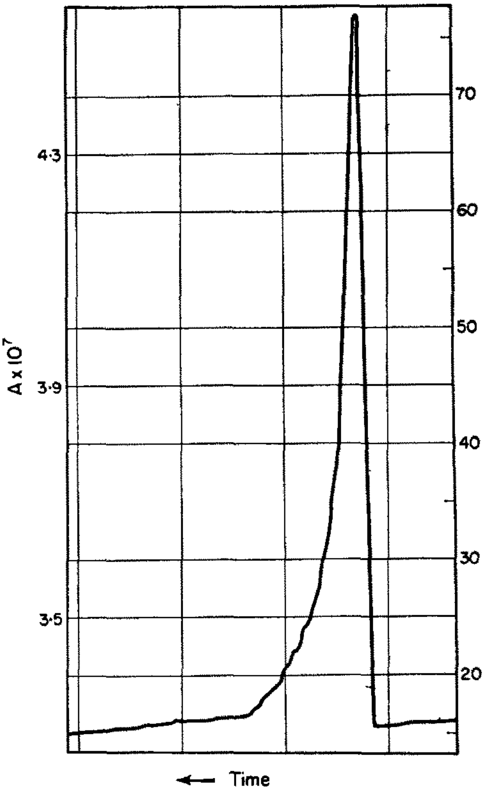

FIG. 2.

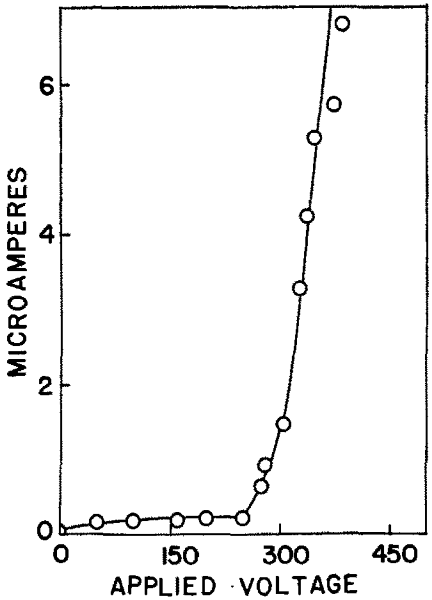

FIG. 3.

Under certain anode conditions the cathode can be made responsive to gaseous composition at very much lower voltages. We have also noted a marked increase in pure gas-phase conductivity (both electrodes suspended) for certain heated samples, but not for hydrogen and organic substances. These and the anodic phenomenon will be reported more fully later.

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Talanta, 1960, Vol. 7, pp. 129 to 130. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged

Thursday 1 *December* 1960: **Society for Analytical Chemistry,** Scottish Section: *Ramsay Dinner.* Glasgow.

Friday 2 *December* 1960: **Society for Analytical Chemistry,** Scottish Section, **Chemical Society, Society of Chemical Industry** and **Royal Institute of Chemistry:** Joint Meeting: address by Mr. R. C. CHIRNSIDE. Royal College of Science and Technology, Glasgow, C.I.

Saturday 3 *December* 1960: **Society for Analytical Chemistry,** North of England Section: *Some experiences in the estimation of metals in foodstuffs:* Mr. H. PRITCHARD, M.Sc., F.R.I.C. City Laboratories, Mount Pleasant, Liverpool. 2.15 p.m.

Wednesday 7 *December* 1960: **Society for Analytical Chemistry:** *The flask combustion technique.* London.

Wednesday 7 *December* 1960: **Society for Analytical Chemistry,** Western Section and **Royal Institute of Chemistry,** Cardiff and District Section: Joint Meeting: *Radioactivity in relation to water supplies:* Mr. F. P. HORNBY, B.Sc., F.R.I.C. Newport.

Thursday 8 *December* 1960: **Society for Analytical Chemistry,** Biological Methods Group: Discussion on *Problems in the control of neomycin quality:* opened by Mr. J. W. LIGHTBOWN, M.Sc., Dip. Bact. *The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Tuesday 13 *December* 1960: **Society for Analytical Chemistry,** Midlands Section: *The analysis of waters used in industry:* Mr. K. B. COATES. Regent House, Birmingham. 6.30 p.m.

Wednesday 14 *December* 1960: **Society for Analytical Chemistry,** Microchemistry Group: Discussion Meeting. *The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Thursday 15 *December* 1960: **Society for Analytical Chemistry,** Midlands Section: *The Development of the analytical balance:* Mr. K. M. OGDEN. Technical College, Nottingham. 7.00 p.m.

Thursday 5 *January* 1961: **Polarographic Society:** *The Applications of Polarography in the Food Industry.* Papers will be read in the morning and afternoon and the proceedings will be completed by a showing of a film on *Polarography.* Lunch and tea will be available. South East Essex Technical College, Longbridge Road, Dagenham. 11.00 a.m.

Tuesday 10 *January* 1961: **Society for Analytical Chemistry,** Midlands Section: *Polarography for Trace Analysis:* Mrs B. LAMB, B.Sc. Technical College, Wolverhampton. 7.00 p.m.

Thursday 12 *January* 1961: **Society for Analytical Chemistry,** Western Section: Annual General Meeting followed by Joint Meeting with **Royal Institute of Chemistry,** Bristol and District Section: *Polarography.* Bristol.

Wednesday 25 *January* 1961: **Society for Analytical Chemistry,** Microchemistry Group: Discussion Meeting. *The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Friday 27 *January* 1961: **Society for Analytical Chemistry,** Scottish Section: Annual General Meeting followed by *Chemical research in the electrical supply industry:* Mr. J. M. WARD, B.Sc., F.Inst. Pet., F.R.I.C. Glasgow.

Saturday 28 *January* 1961: **Society for Analytical Chemistry,** North of England Section: Annual General Meeting followed by Chairman's Address: Dr. J. R. EDISBURY, D.Sc. *Nag's Head Hotel,* Lloyd Street, Manchester. 2.15 p.m.

B.S.I. News announces the following new British Standard:

B.S. 3265: *Method for the determination of tar acids in black and white disinfectant fluids:* 1960. The method specified is suitable for application to disinfectant fluids containing coal-tar acids, or similar acids derived from petroleum, or mixtures of these; it is not applicable to fluids containing additional active ingredients. The acids determined by the method are described as tar acids, irrespective of their actual source. (Price 4s. 6d.)

The following Amendment Slips are also announced:

B.S. 1016: *Methods for the analysis and testing of coal and coke: Part 9:* 1960: *Phosphorus in coal and coke.* Amendment No. I. PD 3859. (Gratis)

B.S. 3069: 195 9. Quantitative chemical analysis of binary mixtures of nylon 6 or nylon 6.6 and certain other fibres. Amendment No. I. PD 3805. (Gratis).

Talanta, 1960, Vol. 7, pp. 131 to 132. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

A polarographic study of D-glucuronolactone. Roger J. Thibert and Albert Boyle. (26 *February* 1960).

Spectrophotometric methods for the determination of osmium-I: Extraction and ultraviolet spectrophotometric determination of osmium tetroxide. Gerald Goldstein, D. L. Manning, Oscar Menis and J. A. Dean. (27 *February* 1960).

Spectrophotometric methods for the determination of osmium-II: Extraction and determination of osmium *in situ* with 1:5-diphenylcarbohydrazide. Gerald Goldstein, D. L. Manning, Oscar Menis and J. A. Dean. (27 *February* 1960).

Spectrophotometric methods for the determination of osmium-III: Reaction of osmium tetroxide with 1:5-diphenylcarbohydrazide in aqueous solution followed by extraction of the complex. Gerald Goldstein, D. L. Manning, Oscar Menis and J. A. Dean. (27 *February* 1960).

Spectrophotometric determination of copper, nickel, cobalt, iron and manganese as their pyridine thiocyanates. Gilbert H. Ayres and Stephen S. Baird. (23 *May* 1960).

The spectrofluorimetric determination of anthracene, fluorene and phenanthrene in mixtures. Glenn A. Thommes and Elmer Leininger. (8 *July* 1960).

Infrared spectra of some organo-phosphorus extractants. C. A. Horton and J. C. White. (15 *July* 1960).

The quantitative determination of uranyl ion by means of the uranyl-sensitised photodecomposition of oxalic acid. A. E. Taylor, G. E. Heckler and Donald R. Percival. (16 *July* 1960).

Precipitation and determination of tantalum and niobium from homogeneous solution with 3:3′:4′:5:7-pentahydroxyflavanone. Frank L. Chan. (28 *July* 1960).

Spectrophotometric determination of rhenium with 4-methyl-1:2-*cyclo*-hexanedionedioxime (4-methylnioxime). James L. Kassner and Shih-Fan Ting. (29 *July* 1960).

Determination of calcium in biological material: The use of Calcein as an indicator in the EDTA titration. Taft Y. Toribara and Larysa Koval. (30 *July* 1960).

Some physical and chemical properties of vanadium di- and tri-chlorides. Headlee Lamprey and Paul F. Forsyth. (5 *August* 1960).

Ethanol-water-hydrochloric acid eluents in anion-exchange systems. D. H. Wilkins and G. E. Smith. (18 *August* 1960).

Non-aqueous solvents in anion-exchange separations. James S. Fritz and Donald Pietrzyk. (18 *August* 1960).

The analysis of beryllium and beryllium oxide-V: The determination of cadmium. Silve Kallmann, H. Oberthin, J. Oberthin and J. O. Hibbits. (21 *August* 1960).

The determination of iron with 1:10-phenanthroline. J. O. Hibbits, W. F. Davis and M. R. Menke. (22 *August* 1960).

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Bathophenanthrolinedisulphonic acid and bathocupreinedisulphonic acid, water-soluble reagents for iron and copper. DAVID BLAIR and HARVEY DIEHL. (29 *September* 1960).

Co-precipitation in some binary sulphate systems. ALLEN I. COHEN and LOUIS GORDON. (30 *September* 1960).

A new procedure in the preparation of anhydrous perchloric acid employing anhydrous magnesium perchlorate. G. FREDERICK SMITH. (30 *September* 1960).

Application of complementary tri-stimulus colorimetry-III: The determination of indicator constants and the use of screening conditions in the calculation. H. FLASCHKA. (4 *October* 1960).

Applications of infrared spectroscopy-IV: The causes of anomalous alkoxyl determinations given by sugars and polyhydric alcohols. D. M. W. ANDERSON and J. L. DUNCAN. (4 *October* 1960).

New selective micromethods in the analysis of metals-II: Titrimetric determination of small amounts of nickel at an equivalent ratio of 1:24. K. BURGER. (4 *October* 1960).

The micro-Kjeldahl determination of nitrogen: An investigation of the effects of added salts and catalysts. P. R. W. BAKER. (4 *October* 1960).

Eine neue polarimetrische Methode zur Bestimmung der optisch inaktiven Ionen-II: Bestimmung des Quecksilbers. CANDIN LITEANU und MARIA COSMA. (5 *October* 1960).

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The solubility of zinc complexes of 8-quinolinol and some derivatives of 8-quinolinol. LYNNE L. MERRITT, JR. and CHARLES W. WEBER. (6 *October* 1960).

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EDITOR'S FOREWORD

THE editorial board and publishers of TALANTA take great pleasure in honouring the eightieth year of

HOBART H. WILLARD

by presenting this special issue, to which contributions have willingly been made by his former co-workers,

GILBERT H. AYRES
ALBERT J. BOYLE
FRANK L. CHAN
JOHN A. DEAN
HARVEY DIEHL
LOUIS GORDON
RICHARD B. HAHN
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ELMER LEININGER
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G. FREDERICK SMITH
ALBERT E. TAYLOR
TAFT Y. TORIBARA

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HOBART H. WILLARD

HARVEY DIEHL
Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.

HOBART H. WILLARD, Emeritus Professor of Chemistry at the University of Michigan, will reach his eightieth birthday in June of 1961. There will thus reach the venerable age of four score, ripe in wisdom, in good health, and with unimpaired intellectual vigour, one of America's most creative chemists and outstanding teachers of chemistry.

Willard began his career in chemistry in a home laboratory and received his formal training at Michigan (A.B., 1903; A.M., 1905) and at Harvard (Ph.D., 1909). Following the Harvard period he resumed his instructorship at Michigan and rose rapidly through the various ranks to professor (1922). The Michigan tenure continued uninterrupted to 1951, the prescribed retirement age of seventy, but retirement meant simply a change in scene for he has continued research and teaching, in less vigorous but no less fruitful fashion, at the laboratories of the Atomic Energy Commission at Oak Ridge and Los Alamos and on single semester assignments at other universities, New Mexico (1951, 1952), Southern Illinois (1956, 1958), Washington State (1957), and Valparaiso (1959, 1960).

Willard's long academic career was marked by the usual activities of a university professor-chemist: a moderate teaching load at the undergraduate and graduate levels, the direction of graduate students, research, university committee work, the writing of text-books, participation in the affairs of the American Chemical Society, lecture trips, a share of industrial consulting work. All of these he carried on with extraordinary energy and with great enthusiasm. This astonishing performance was carried on, too, with a healthy interest in other fields of science and with an intense desire that his research be of service to others. It was also accompanied by a harmonious family life. And as was eminently fitting, recognition came both nationally and locally: in 1951 the Fisher Award of the American Chemical Society for outstanding contributions to analytical chemistry, in 1953 the Annual Award of the Association of Analytical Chemists of the Detroit Section of the American Chemical Society, in 1948 the Henry Russell Lectureship of the University of Michigan.

It is pleasing indeed to have one of our profession reach the age of eighty; it is doubly pleasant that he should reach this age in full mental and physical vigour. Mankind is certainly fortunate when such a long and busy life is devoted to creative work and to the education of youth.

EARLY PROFESSIONAL YEARS

Although born in Erie, Pennsylvania (June 3, 1881), Willard's boyhood was spent under exceptionally happy circumstances in the small, southern Michigan farming community of Union City.

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Willard was early attracted to chemistry, and was fortunate in that a sympathetic father, a newspaper editor, procured for him texts and chemicals on business trips to

Chicago. The faculty of the University of Michigan, too, proved co-operative in forwarding to him for analysis the materials given out as unknowns in the course in qualitative analysis. As a consequence of intensive study backed by good experimental work in his home laboratory, Willard was immediately admitted to advanced course work in chemistry on his entrance into the University.

Willard's undergraduate years at Michigan were marked by the usual mixture of academic, social and fraternal activities characteristic of mid-western university life in the pre-World War I period. Willard was robust physically, alert, and popular, and it was during this period that the first of numerous stories originated which came later to surround him in Paul Bunyonesque fashion. It was during this period also that he became a vegetarian—after hearing a lecture by the physician John Harvey Kellogg. It was during these years, too, that Willard's first publication appeared, that on the silver perchlorate coulometer with Professor Carhart and Mr. Henderson.

The nature of the research that men do is often determined by, and is certainly profoundly influenced by, their early training and associations. Willard's early experience with perchloric acid determined the nature of his research efforts for some years, first on the use of perchlorates in atomic weight work and then on the uses of perchloric acid in chemical analysis. Again, chemistry at the University of Michigan bore a practical, or applied chemistry stamp. Science with practice, with the emphasis on practice, was a general characteristic of all the mid-western state colleges and was the natural face of a civilisation just emerging from a rugged, frontier economy. At Michigan this approach to science was especially marked because of the presence on the campus of chemistry professors whose interests were in applied analysis—A. B. Prescott, O. C. Johnson, and E. D. Campbell. Prescott, a pharmacologist as well as a chemist, and Johnson were the authors of *Qualitative Chemical Analysis*, a text which went through seven editions and for two generations shared honours in the United States with the texts of Fresenius and Treadwell-Hall. Campbell, although primarily a chemist, contributed greatly to metallurgy, principally along the lines of methods of chemical analysis of ferrous materials and of the effects of alloying elements on steel. The strongly practical bent of these men lent to their teaching an earthy quality which was transmitted to and flowered in Willard, for the majority of his contributions are practical solutions to the problems of analysing things as they are actually found in nature or are produced by industry.

Willard chose Harvard for his doctoral work on the advice of Moses Gomberg, then a young instructor newly back from Europe and in the midst of his epoch-making work on tervalent carbon. This, it will be recalled, was the period when all Americans, and indeed most Europeans, secured their research training in the laboratories of the German Universities. Willard's break with tradition was dictated by the emergence of the Harvard laboratory under T. W. Richards as the leading institution for atomic weight measurements.

The great stability and high oxygen content of the alkali metal perchlorates suggested to Willard that they afforded an excellent scheme for determining the silver-oxygen ratio. Richards approved this suggestion, and Willard for his Ph.D thesis (1909) measured the conversion of lithium chloride to silver chloride and of lithium chloride to lithium perchlorate and thus obtained the atomic weights of both silver and lithium. The silver value of 107·871 was superseded in later years by the value 107·880, but, remarkably enough, is closer to the very recent value, 107·8731, obtained at the National Bureau of Standards by the mass spectrographic method.

Willard's first paper, after returning to Michigan, dealt with the preparation of perchloric acid dihydrate by the oxidation of ammonium perchlorate with nitric and hydrochloric acids. All of the perchloric acid manufactured between 1924 and 1940 was made by this process, and currently it is again being used. The paper is a prophetic one, for it closes with a long paragraph pointing out the remarkable properties of perchloric acid dihydrate and suggesting a number of uses of the acid in analysis and in electrochemistry, all of which were subsequently worked out in brilliant fashion by Willard or by his student G. Frederick Smith.

Willard was once heard to remark, later in his life when he was approaching retirement, and when he was encouraging a younger man who had started on a university career, that he wished he had begun a more vigorous research programme at an earlier date. The implication that he had wasted a few years was hardly justified, for World War I drew him off to Detroit to supervise an analytical laboratory connected with aircraft production. Then too, this was a period of intense reading, for we find him acquiring complete sets of the *Zeitschrift für analytische Chemie*, *Chemical Abstracts*, the *Journal of the American Chemical Society*, and an extensive collection of German doctoral theses. Exhaustive reading, coupled with an excellent memory, made it possible for him to recall vast amounts of chemistry, and to quote authors, journals and years at will. This facility has stayed with him to an astonishing extent into his later years.

Willard's first graduate student was Lucien Greathouse, whose Ph.D. thesis dealt with the periodate method for manganese, a method which was widely adopted and is the standard procedure to this day. The work on the perchloric acid dehydration of silica, the first of three investigations with Wallace Cake, dates from this time too. These two contributions were certainly a most auspicious beginning as a research director, but more followed quickly. The other two papers with Cake deal with the use of hypobromite as a standard oxidising agent and its use in the determination of amino nitrogen and of sulphide. Another investigation, with C. C. Meloche, was on the determination of bromide in brines.

THE 1920'S

Willard's next major effort was with his student Roy K. McAlpine on the revision of the atomic weight of antimony, one of the few atomic weight values to reach the post-war period grossly in error. Willard and McAlpine measured the antimony tribromide-silver and antimony tribromide-silver bromide ratios using antimony tribromide prepared from elaborately purified metallic antimony and bromine and distilled in the absence of moisture and oxygen. The titrimetric and gravimetric methods agreed well, and gave a value of 121·773.

The four papers which appeared in 1922 with Dorothy Hall are a critical review of the gravimetric and titrimetric methods for the determination of cobalt. In these papers phenylthiohydantoic acid is introduced as a precipitating reagent for cobalt and copper.

Concurrently there was progressing, with two graduate students, two other investigations, both destined to open up large fields for analytical chemistry.

Taking note of the singular behaviour of palladium in a dichromate titration, Willard concluded that palladium might even function as a reference electrode. Actually, it behaves as an indicator electrode only slower in response and with smaller potential change than platinum. Platinum-palladium together then yield a differential titration curve. The details of this were worked out by Willard and Florence Fenwick, and the idea was extended to electrode pairs of the same metal but with polarisation deliberately produced by the passage of a small current. Two papers describing these bimetallic electrode systems were published in 1922, opening up a new and useful chapter in potentiometric titrations. The following year Willard and Fenwick published three papers detailing applications of the bimetallic electrode couples: to the determination of vanadium in alloy steel, to neutralisation reactions by a clever conversion of an oxidation-reduction system to one responsive to hydrogen ion concentration, and to the determination of sulphide by titration with silver nitrate in alkaline solution.

The other work of Willard in the early 1920's was that with G. Frederick Smith on perchlorate chemistry. The first of three papers, all published in 1922, describes the properties of magnesium perchlorate, the second the separation of sodium from lithium by precipitation of the chloride from a butyl alcohol solution of their perchlorates, and the third the solubilities of the alkali and alkaline earth perchlorates in water and in organic solvents. Magnesium perchlorate has, of course, been since used as the drying agent *par excellence* in all analytical work. The solubility work laid the basis for the perchlorate method for the separation and determination of potassium; the latter method was worked out later by Smith as an instructor at the University of Illinois (Smith, 1923, 1925; Smith and Ross, 1925) and has become the standard method for potassium.

Looking back at this period we can feel the energy Willard was deploying to his work. It must certainly have been a stimulating experience for the graduate students who came at this period, judging from the number of papers they published; four with Dorothy Hall, eight with Florence Fenwick, three with G. F. Smith and twenty-two with Philena Young.

The papers with Philena Young published between 1928 and 1934, are concerned principally with ceric sulphate as a standard oxidising agent. This subject was developed concurrently by Willard and by N. H. Furman of Princeton University. Furman's interests were largely in the theoretical aspects of the subject, Willard's almost exclusively in the applications; the two programmes thus were neatly complementary. In quick succession, then, Willard and Young published on the preparation of ceric solutions, on the determination of iron, iodide, arsenic, antimony, cerium, vanadium, chromium, thallium, organic acids, tellurium, and mercury, and later, on further studies on the preparation and stability of ceric solutions and on indicators for use in ceric titrations. The latter papers with Philena Young were done on a post-doctoral fellowship and during summers when she returned to Ann Arbor from her teaching position at Wells College, and are concerned with the determination of chromium and vanadium in alloy steels by differential oxidation and reduction. The difficulties inherent in these determinations are evident in the sequence of papers on the subject, a complete understanding of the chemistry being gradually attained and the procedures gradually elaborated to their final form. The problem was wrapped up in the 1933 paper, even for those alloys containing tungsten. The final paper (1934) is a most ingenious scheme by which both chromium and vanadium are determined on the same sample, both being oxidised to their higher valence, the excess oxidising agent removed, both reduced with excess standard ferrous sulphate, the excess ferrous sulphate then titrated in high acidity, the acidity reduced and the vanadyl titrated using the same indicator.

Reflecting again Willard's great interest in applied analysis are the three papers dealing with the determination of tervalent chromium, of boric acid, and of sulphate in chromium plating baths, done respectively with Young, Ashworth and Schneidewind. The determination of sulphate in the presence of tervalent chromium is complicated because a portion of the sulphate is often bound to the chromium so tightly that it is not precipitated as barium sulphate. Willard's solution was to add acetate, which combines more firmly with the chromium and displaces the sulphate so that it is immediately precipitated.

The 1920's closed with work by three other students. With Kassner, Willard investigated lead perchlorate, preparing the anhydrous, hydrated and basic forms and determining their compositions and solubilities. In another study with Kassner the solubilites of lead sulphate, chromate and molybdate in perchloric acid solutions and in nitric acid solutions were measured, the solubilities being significantly less in the perchloric acid solutions.

Of the three papers with Boldyreff, the first describes a simple reference electrode prepared by sealing a platinum wire into the tip of a burette, the opening of the burette dipping into the solution being titrated. This rather cute device has never been much used, probably because it is easier to control the flow from the burette by watching the drops form than by watching the meniscus. The second of the papers with Boldyreff prescribes the conditions for the reduction of mercury salts to metallic mercury by hydrazine and the collection and drying of the mercury. The third paper defines the conditions, 475° to 500°, for igniting calcium oxalate to calcium carbonate for weighing.

The oxidation of chromium to chromate by boiling perchloric acid, and the application of this to the titrimetric and gravimetric determination of chromium in chromic oxide, chromite, steel and ferrochrome, was worked out in detail with R. C. Gibson and reported in 1931.

Late in the 1920's, Willard engaged in the first of a series of major lawsuits in which he took part as a chemistry expert. This first one was a patent infringement charged by the Parker Rust Proof Company against the Ford Motor Company and involved the chemistry of the iron phosphates.

THE 1930'S

One especially interesting investigation of the early 1930's was that with R. D. Fowler on the thermal decomposition of anhydrous mixtures of metal sulphates. The idea was to effect the differential decomposition of an anhydrous mixture of metal sulphates by a careful regulation of temperature, and by later cooling and extracting the undecomposed sulphate with water to effect a separation of the metals involved. This project was well thought out and beautifully executed experimentally. Various binary mixtures of anhydrous sulphates formed by evaporation were studied. It was found that non-isomorphous sulphates, of aluminium and zinc for example, could be preferentially decomposed yielding basic sulphates or oxides, and a ready separation of the unchanged sulphate by dissolution in water was possible. Anhydrous mixed crystals of isomorphous sulphates, of nickel and cobalt for example, or of two rare earths, however, decompose into mixed crystals of basic sulphates or oxides, and a separation becomes impossible. A sufficient number of systems was studied so that the results appear to be general, and thus a separation scheme which had been bruited about for a century was laid to rest.

During the 1930's Willard renewed work on the periodates. Between 1931 and 1934 he published a series of papers with J. J. Thompson dealing with the gravimetric and titrimetric determination of mercury and of lead, based on the precipitation of mercurous paraperiodate, $Hg_5(IO_6)_2$, and of triplumbic paraperiodate, $Pb_3H_4(IO_6)_2$; and with the titrimetric determination of manganese following periodate oxidation to permanganate and removal of excess permanganate by precipitation as mercuric periodate. Another paper dealt with the detection of iodate and periodate in the presence of each other. With another student, R. R. Ralston, he perfected a procedure for the preparation of free periodic acid, a technique currently in use for the manufacture of periodic acid, unchanged in all the details as initially devised. The procedure involves two successive electrolytic oxidations, of iodine in hydrochloric acid to iodic acid at a platinum anode in a partition cell, and of the iodic acid in water solution to periodic acid at a lead dioxide anode in a partition cell. The periodic acid is finally recrystallised from concentrated nitric acid.

The periodic acid prepared by the electrolyic process often contains a little platinum, and after a year is contaminated with iodic acid brought about by the decomposition. Such decomposition is obviated in another method of preparation published by Willard in the first volume of *Inorganic Syntheses.* In it iodine is oxidised by sodium chlorate in a slightly acid solution to sodium iodate, the latter then being oxidised to the periodate by chlorine in an alkaline solution and isolated as trisodium paraperiodate, $Na_3H_2IO_6$. Barium paraperiodate, $Ba_3H_4(IO_6)_2$, is then prepared and converted to periodic acid by treatment with concentrated nitric acid, in which barium nitrate is insoluble, so that it can be filtered off. The final recrystallisation of the paraperiodic acid is made from concentrated nitric acid.

With a convenient source of periodic acid available, it became possible to consider the determination of potassium by precipitation as the periodate. This procedure was worked out with A. J. Boyle.

Two other papers with J. J. Thompson appeared during the early 1930's. One described a method for perchlorate, based on reduction with starch and sulphuric acid, the liberation of free chlorine with permanganate, and the distillation of free chlorine into standard arsenite. This scheme of distilling the free halogen was applied also to the determination of halogen in organic compounds, following decomposition of the sample with fuming sulphuric acid and persulphate. Although widely applicable, the method has never really caught on with the analytical chemist, possibly because the apparatus required appears to be too complex.

The early 1930's saw also the publication of another paper that was to become a classic in the literature of analytical chemistry, the separation of fluoride by distillation of fluosilicic acid, followed by titration with thorium nitrate using zirconium-alizarin lake as indicator. This work was done with O. B. Winter at the Michigan Agricultural Experiment Station at East Lansing. Earlier attempts to separate fluoride by distillation as anhydrous hydrofluoric acid invariably gave inconsistent results. The deliberate introduction of water (steam at 135°) causing the formation and distillation of fluosilicic acid was truly a master stroke. The method has been universally adopted, and although the titration phase has been subjected to considerable tampering by others, the distillation procedure is universally used as originally set forth. The method made possible an accurate measure of small amounts of fluoride, and the consequences of this have been manifold.

The middle 1930's saw also the publication of a number of isolated studies, each significant but not immediately related to some larger project. One was a study with R. C. Thielke of the preparation of potassium molybdocyanide and molybdicyanide. Molybdicyanide is a strong oxidising agent in alkaline solution. With a convenient source of molybdicyanide at hand, conceivably it should have been possible to apply it as a standard oxidant. Solutions of molybdicyanide are not stable, particularly when exposed to light, and this militated against any extensive development as a standard oxidising agent such as that which occurred with ceric sulphate.

With Edwin Goodspeed, Willard made a study of the separation of strontium from calcium, by precipitation of strontium nitrate from concentrated nitric acid by the addition of sufficient 100% nitric acid to bring the concentration to 80%. The separation is clean; it also separates strontium from some twenty-five other elements and although awkward it had not been superseded twenty-five years later.

The three papers with Heman Fogg on the analytical chemistry of gallium represented one of the first attempts to apply chemical methods to the determination of gallium, the spectrographic method having been the sole and traditional tool from the time of the discovery of the element. The final proposals were a colorimetric method using quinalizarin, and precipitation of the basic sulphate, a thorough study having been made of the separation from aluminium, iron, and indium and of the interference of other elements.

Two other fruitful pieces of research, done with people off the Michigan campus, produced methods of great utility. The 1,10-phenanthroline method for iron was worked out with Frances Cope Hummel of the Research Laboratory of the Children's Fund in Detroit, specifically for the determination of iron in foods, blood and fæces. The paper was published simultaneously with papers by Saywell and Cunningham (the idea was G. Frederick Smith's who suggested to these authors the wet-ashing of wine with perchloric acid followed by a measurement of the iron as the phenanthroline compound) and by Fortune and Mellon who made a thorough study of the spectrophotometry and interferences of the process. The honour for introducing this popular method was thus shared by three groups. The other work was that with John Center of the Oliver Iron Mining Company of Hibbing, Minnesota, and had to do with the determination of phosphorus in iron ore by measuring the colour of the complex vanadophosphomolybdate.

The three papers with George M. Smith, published in 1939, and dealing with tetraphenylarsonium chloride, uncovered some rather astonishing bits of chemistry. The compound was first prepared by Professor F. F. Blicke of the College of Pharmacy at Michigan, and it is fortunate that he directed Willard's attention to it. Tetraphenylarsonium chloride forms insoluble salts with perchlorate, permanganate, periodate and perrhenate. Moreover, it can be accurately titrated potentiometrically with iodine in the presence of iodide. George M. Smith worked out the details of this titration, and showed also that the chloro-complexes of mercury, tin, vanadium and zinc form insoluble compounds with tetraphenylarsonium chloride, and that a titration of the excess reagent permitted the determination of these metals.

One of the students who worked with Willard in the closing years of the 1930's was

Lynne L. Merritt, Jr., whose thesis work dealt with the use of ozone to effect the oxidation of elements to their higher valence states for later titration with a standard reducing agent. The published paper carries a description of a neat apparatus for generating ozone, and describes the action of ozone on a variety of elements. It contains also detailed directions for the determination of manganese in steel and in ores, for the determination of vanadium in steel, and for the determination of iodide. In the last method, iodine is oxidised to periodate, the excess ozone is removed with a stream of carbon dioxide, and the periodate is determined colorimetrically.

During the 1930's Willard was engaged in a succession of patent infringement suits related to chromium plating. The suits centred around the presence of sulphate in the bath, and the chromic oxide to sulphate ratio. Willard's success in these patent affairs can be judged from the number of cases that he was called in on, and from the fact that the side calling him always won. One suit in particular made chemico-legal history of a sort by going all the way to the Supreme Court. The case was concerned with a patent covering a welding rod coating consisting of an alkaline earth silicate and calcium fluoride, which had been circumvented by the substitution of manganese silicate for magnesium silicate. Willard's thesis was that manganese was essentially an alkaline earth and he marshalled sufficient evidence to convince the Courts. Legally now in the United States, it appears, manganese is an alkaline earth (339 U.S. 605).

Willard had great interest in apparatus as far as it was useful as a tool. Thus, he followed closely and with great interest the development of the polarograph and of the glass electrode, experimenting constantly with them himself. He published two papers on the design of instruments, one with Hager (1936) on an electronic titrimeter, and another with Ayres (1940) on a photoelectric colorimeter. In view of the competence and tremendous success of the people who did enter the instrument design business, it is fortunate for chemistry that Willard remained on the side-lines of this field and devoted his superb talents to purely chemical problems. He entered his last decade at Michigan, then, with a brilliant record of achievements in analytical chemistry, an unlimited number of ideas for further exploitation, and his mind firmly focussed on problems he could handle best.

THE CLOSING DECADE AT MICHIGAN

The war broke as Willard entered his last ten years at Michigan. Numerous, non-creative duties intervened, the number of graduate students dropped and the activities of those who remained were directed into matters of military interest, so that often the work presented as thesis material was non-classified and often only a minor phase of some larger effort. The renewed interest in inorganic chemistry which accompanied the advent of atomic energy made Willard's vast knowledge of inorganic and analytical chemistry of particular value, and fortunately it was effectively employed.

Of the work published during the war years, the three papers with Taft Toribara deal with some "off-beat" and intriguing chemistry of tin. In the first paper, a study of the tin oxalate-potassium oxalate system was made and potassium oxalatostannate, $K_6Sn(C_2O_4)_7 \cdot 4H_2O$, was isolated. In the second, the chemistry involved in the action of hydrogen sulphide on tin in oxalic acid solution was straightened out, and in particular the conditions for stability of dipotassium dioxalatothiometastannate, $K_2SnS(C_2O_4)_2 \cdot 2H_2O$, established. In the third paper the information gathered in the first two were utilised in a titrimetric method for tin. The tin is converted to potassium oxalatostannate at pH 2·5, potassium sulphide is added, forming dipotassium dioxalatodistannate, the hydrogen sulphide is then swept from the solution by a current of carbon dioxide, and finally the sulphur in the compound is titrated with iodine. The tin does not change valence during the entire operation. The method was checked on standard samples, and all in all is a pretty bit of work.

The work with Zuehlke on germanium also was done in the early 1940's and as with tin was again a question of straightening out the nature of the sulphur compounds, thiogermanic acid and its salts. The titrimetric method finally recommended is based on the quantitative formation of potassium thiogermanate in an acetate-buffered solution by treatment with potassium sulphide, removal of the excess hydrogen sulphide by carbon dioxide, and titration of sulphur with iodine. Willard and Zuehlke also found that 5,6-benzoquinoline formed an insoluble derivative with trioxalatogermanic acid and could be used for the gravimetric determination of germanium.

In a paper with Arno Heyn the determination of bromide in brines by hypochlorite oxidation to bromate and subsequent indirect iodometric titration was examined critically, and the procedure was placed on a firm basis.

Willard's great interest in oxidation-reduction reactions led him to an examination of titrations with strong oxidising agents in alkaline solution. The 1947 paper with Manalo has an excellent general survey of this field, and in the experimental work describes fifteen diphenylamine derivatives which can be used as indicators in titrations with ferricyanide, hypobromite and sodium vanadate. Their use was checked in titrations of a large number of inorganic and organic substances. In the course of the work it was necessary to measure the formal potentials of certain couples in alkaline solutions. Values for the ferricyanide-ferrocyanide, hypobromite-bromide, arsenate-arsenite and vanadate-vanadyl couples in solutions $1M$ to $15M$ in sodium hydroxide were reported in a later paper.

Two studies of colorimetric methods were published in the late 1940's, on cobalt with dithio-oxamide, with Mosher and Boyle of Wayne University. Both are rather short papers but are thorough studies of the conditions and interferences.

Tetraphenylarsonium chloride, introduced by Willard and G. M. Smith in 1939, developed such an extensive use in the succeeding decade that it prompted an investigation of the corresponding phosphonium and stibonium compounds. New procedures were developed for synthesising these compounds (Willard, Perkins and Blicke, 1948) and the compounds were then subjected to an intensive study. The properties of both are similar to those of the arsonium compound in that they form insoluble, crystalline salts with permanganate, perrhenate, pertechnetate, perchlorate, periodate, fluoroborate and certain complex metal chlorides. They can also be titrated iodometrically in the presence of potassium iodide. And, quite astonishingly, the salts are all extractable into chloroform; the tetraphenylphosphonium permanganate, for example, is completely insoluble and completely extractable.

At intervals throughout his career Willard made studies of the applications of organic compounds as analytical reagents for the metals, but the field of organic chemistry and its subdivisions of ultimate analysis and functional group analysis apparently held little attraction for him. Perhaps he felt like Berzelius a hundred years earlier, when he wrote to Wöhler that organic chemistry was an impenetrable forest into which one could only enter with trepidation. Almost his sole excursion into the field was the work with Wooten on the colorimetric and iodometric determination of resorcinol and other phenols. Wooten brought the problem with him from the Reichhold Chemicals, Inc. and the methods he and Willard devised proved highly useful to an important segment of the chemical industry.

One of Willard's last graduate students was Charles Horton, with whom he developed methods for the determination of traces of fluoride. An examination of a large number of organic compounds as possible indicators in the titration of fluoride with thorium yielded several good ones, particularly purpurin sulphonate, Alizarin Red S, Eriochromcyanin R and Chrom Azurol S. Two fluorescent indicators were found too, morin and quercetin, and the best conditions were worked out for a fluorometric titration. Fluoride in microgram amounts can be titrated with thorium using the fluorometric end-point, and the final method was adapted to the determination of fluoride following alkaline decomposition of an organic fluorine compound, or following the Willard and Winter distillation. Among the older methods of determining fluoride a favourite approach has been to measure the bleaching effect of fluoride on coloured compounds of titanium and zirconium. In the latter part of the work with Horton aluminium was used in the same way, the excess aluminium, that not bound to fluoride, being determined by extraction of the oxinate into chloroform for fluorometric measurement, or being measured fluorometrically with morin in 50% alcohol. As with all of Willard's investigations these are thorough studies leaving not the smallest detail unattended.

John Dean was also among the last of Willard's Ph.D. men. He and Willard devised an ingenious polarographic method for aluminium based on the change in half-wave potential of a dihydroxyazo dye on complexing with aluminium. Pontachrome Violet SW proved a suitable dye and the method was found sensitive to 5 μg. of aluminium in 50 ml. The effects of pH, time of standing, temperature, and diverse ions were all thoroughly studied, and the method was checked by the analysis of NBS samples of a variety of materials.

Willard's last decade at Michigan closed suitably with his reception of the Fisher Award. In his Fisher Award address, published in *Analytical Chemistry* of December 1951, Willard might have reviewed some phases of his own work or have presented resumes of his individual contributions such as has been attempted here. Instead, he chose to acknowledge his indebtedness to his many fine students and co-workers for their contributions to their joint efforts, and then to survey the development of analytical chemistry during his lifetime. The acknowledgements are done in graceful fashion and he pays particular tribute to his former student G. Frederick Smith for the brilliant way that he carried on in research in analytical chemistry after leaving Michigan, and especially for the tremendous service he has rendered the profession by making newly discovered reagents commercially available. The address is entitled *From Buret and Balance to Spectrometer and Titrimeter*. It is a splendid review of analytical chemistry in the first half of the twentieth century. Willard's grasp and appreciation of every facet of the subject stands out starkly. In particular, his understanding of the role of physical methods and of instruments is revealed, and quite understandably he closes with the admonishment to use them when helpful but not to neglect the chemical side of the subject.

Willard's papers in the post-Michigan years reflect his activities after retirement. For the most part they represent problems he helped to solve in connection with his consulting activities at the laboratories of the Atomic Energy Commission or of the various universities where he took short-term teaching positions.

One especially interesting paper in this group is that on the determination of protein-bound iodine. This was done with Albert Boyle, one of his earlier Ph.D. men who had later earned the M.D. degree and entered medical research at Wayne University. Following precipitation of the protein in serum with trichloroacetic acid, the remaining protein is destroyed and iodide is oxidised to iodate by digestion with chloric acid in the presence of a little chromate. The chloric acid and organic matter are then removed by evaporation to small volume, and the iodine is measured by its catalytic action on the ceric-arsenite system. The method is a brilliant application of analytical chemistry to a tough biochemical problem, and judging from the sale of the iodine-free cerium salt needed it is very widely used. The use of 28% free chloric acid makes such experts in the business of destroying organic matter as G. Frederick Smith blanch, but apparently the procedure as finally described is safe. There are two sentences in the paper, though, which can hardly fail to produce a chuckle in the reader: "Toward the end of the digestion, there is a distinct crackling of the solution, which is probably due to the decomposition of chloric acid. This occurs irrespective of whether or not organic material was originally present."

One piece of work, done at the University of New Mexico with Martin and Feltham, is a colorimetric method for vanadium based on dissolving in acetone the precipitate of vanadate with cupferron. Vanadium can be separated from copper by cupferron precipitation if ethylenediaminetetra-acetate is added to tie up the copper. Utilised together these processes make possible the determination of vanadium in the presence of copper.

Willard's vast knowledge of the analytical chemistry of the rarer elements has been put to great use at the laboratories of the Atomic Energy Commission. We may never have a real measure of his value to the programme of the Commission but can get a glimpse of it from the paper with Mosen and Gardner on the determination of thorium in uranium alloys published in 1958. The procedure involves precipitating the thorium as the fluoride using lanthanum as a carrier, concluding by a titration of the thorium with ethylenediaminetetra-acetate.

In the post-Michigan period, also, Willard published two papers with Van Lente and Van Atta of Southern Illinois University. One deals with student experiments with a flame photometer, and the other describes apparatus for coulometric titrations using the silver coulometer for the measurement of the current passed.

PRECIPITATION FROM HOMOGENEOUS SOLUTION

In this review of Willard's scientific work we have so far ignored one important work done during the 1930's, that with Tang on the precipitation of aluminium as the basic sulphate. This was purposely done to permit discussion of the entire subject of precipitation from homogeneous solution as a unit, for it constitutes one of Willard's major contributions. Although the idea was conceived in the 1920's, and the early work was published in 1930's (Tang 1937, Fogg 1937), it really bore fruit in the 1940's. The precipitation of the hydroxide of a metal by the addition of a base usually does not produce a separation of one metal from another even though the pH of the solution may be such that a separation should appear possible. Thus, aluminium, which is precipitated completely at pH 4·5, cannot be separated from nickel, even though the latter by itself is not precipitated from a solution of pH 6. A local concentration of alkali exists where the drop of the precipitating solution agent, ammonia or sodium hydroxide, strikes the solution and locally the pH is sufficiently high to precipitate both the aluminium and the nickel. The nickel precipitate is enclosed by the aluminium hydroxide, and although the pH of the main body of the solution is sufficiently low to hold the nickel in solution, it is carried along with the aluminium hydroxide. Willard reasoned that if the hydroxyl ion could be generated by a chemical reaction taking place throughout the solution, local concentration effects would be avoided, and a purer precipitate should result. This proved to be the case, although a secondary, "anion" effect was found. The slow decomposition of urea in a boiling solution proved to be a convenient way to generate ammonia internally, and the separation of aluminium from a number of elements proved to be remarkably clean. The precipitate is a basic salt rather than a hydroxide, and the nature of the anion determines the character of the precipitate. Thus, the aluminium precipitated from a sulphate or succinate solution is crystalline, more dense, and more readily filtered than one precipitated from a chloride solution. The same technique, that is, raising the pH by the decomposition of urea, was applied to the precipitation of calcium oxalate (Chan, thesis 1933). In a single precipitation of this kind calcium can be separated as cleanly from magnesium as by a double precipitation in the normal fashion with ammonia.

Following the work on aluminium and calcium, similar work was done with gallium by Willard and Fogg. Just as with aluminium, the precipitate from a sulphate solution produced by the hydrolysis of urea led to a dense, readily filterable precipitate which provided a clean separation of gallium from zinc, manganese and calcium.

The next application of precipitation from homogeneous solution was with Harry Freund, on the precipitation of zirconyl acid ethylphosphate by hydrolysis of triethylphosphate. The product was obtained as a dense, granular, easily filterable precipitate, in contrast to the gelatinous zirconium phosphate obtained by direct precipitation. The process was then applied to the separation of hafnium from zirconium by fractional precipitation.

Later, with Hahn (1949), several other hydrolytic procedures for the precipitation of zirconium from acid solution were tried, and a detailed study was made of the separations from other metals made possible by hydrolysis of trimethyl phosphate from solutions 3·6*N* in hydrochloric acid. Although the composition of the precipitate was somewhat variable, ignition at 950° yielded zirconium pyrophosphate for weighing, and the process effected the separation of zirconium from a large number of metals.

One especially fine application of the precipitation from homogeneous solution was that by Gordon, 1948, to the determination of thorium in monazite sand. The method begins with a perchloric acid attack of the mineral, which dissolves the monazite but leaves the quartz, rutile and ilmenite. Thorium and the rare earths are then precipitated as the oxalates, the oxalate being generated by the decomposition of methyl oxalate in a hot, acid solution. In contrast to the usual gelatinous precipitate, the oxalates so precipitated are crystalline. A re-precipitation is made to remove the trace of phosphate carried down. Oxalate and filter paper are then decomposed with nitric and perchloric acids, and after reduction of the quadrivalent cerium with iodide, the thorium is precipitated at pH 5·5 to 5·9 as the formate by the decomposition of urea. A re-precipitation is then made. Some interesting side-lights appeared in this work. The basic thorium formate clings tenaciously to the walls of the beaker, and the last of the thorium can be removed only by refluxing hydrochloric acid in the beaker for a few minutes; the thorium so recovered is then precipitated by ammonia. Basic thorium formate carries down any trace of silica present, and the precipitate must be given a hydrofluoric acid-sulphuric acid treatment before the final ignition to the oxide. The paper with Gordon is an exceptionally thorough one, with all of the minor aspects worked out in detail, and even with a study made of the errors in the older iodate method. A modification of the procedure was published somewhat later by Gordon, Vanselow and Willard, in which the thorium formate-urea precipitation was replaced by precipitation with tetrachlorophthalic acid. This again is a precipitation from homogeneous solution, and effects the separation of thorium from the rare earths.

In another study with Gordon, tin was precipitated as a basic stannic sulphate at pH 1·3 by boiling with urea. The precipitate formed was extremely dense, but unfortunately adhered to the walls of the beaker tenaciously, so tenaciously indeed that it could be stripped off as a film. Manganese, nickel and iron were adsorbed so strongly that the procedure was not recommended for the determination of tin.

Still another study was that with John Sheldon on the precipitation from homogeneous solution of iron as the basic formate with urea. A dense, readily filtered precipitate was obtained, which provided an excellent separation from bivalent metals and provided an excellent separation of iron preparatory to the determination of other metals in the filtrate.

Even nickel dimethylglyoxime, a notoriously bad precipitate to filter, yielded to precipitation from homogeneous solution. In the work with Bickerdike (1952) sufficient dimethylglyoxime in 1-propanol was added to the nickel solution which was at an acidity which would prevent precipitation. The precipitation was then brought about by the decomposition of urea on boiling. The large crystals which formed filtered readily, and large amounts of nickel could be handled readily.

The precipitation of cerium from homogeneous solution presented a more difficult problem. Ceric iodate was the obvious choice for the chemical form for precipitation, but of the two routes, internal generation of iodic acid or internal oxidation of cerous to ceric in the presence of iodate, only the latter worked. Either persulphate or bromate could be used as the oxidising agent, but attention had to be paid to the concentration of nitric acid present. The determination was concluded by ignition to ceric oxide. The procedure separates cerium from lanthanum and the rare earths, and from a large number of other metals. This work was done with Willard's last Ph.D. student, Sylvia T'sai Yu.

The subject of precipitation from homogeneous solution was reviewed by Willard (1950). The technique was extended by others, notably by Louis Gordon, and by 1959 had expanded sufficiently to be the subject of a monograph by Louis Gordon, Murrell L. Salutsky and Hobart H. Willard, *Precipitation from Homogeneous Solutions*.

WILLARD AS A TEACHER

The long line of chemistry students, graduate and undergraduate, who received their training in quantitative analysis under Willard at Michigan were subjected to an exceptionally rigorous course, as up-to-date as the very latest chemical journal, backed by an enormous collection of well-prepared and carefully analysed samples, brilliantly and enthusiastically taught, but graded with no sympathy whatever for human frailty or the fumbling that often accompanies learning. Presumably the presence of anyone in a quantitative analysis course denoted a professional interest in chemistry; quantitative analysis was the bread-and-butter course, the very foundation of any professional career in chemistry, and it had better be learned thoroughly; and not just in the class room but at the workbench; and not by just going through the routine but by actually securing the correct result; or by repetition until the correct result was obtained.

The undergraduate and graduate courses were conducted as recitation only, with extensive reading assignments and oral quizzes which were deadly frightening to the novice and embarrassing to the unprepared, but stimulating to the diligent and even a great deal of fun to those with wit or with an appropriate bit from the recent chemical literature.

For a long period Willard refused to write a text, contending that the subject was changing so rapidly that no text-book could be kept reasonably up-to-date. Rather he relied on mimeographed material bound anew each semester, and with new material inserted in the most unlikely places. That excellent teaching could be accomplished with such disorganised text material was understandable only to those who experienced it. At one time there was even sold on the Ann Arbor campus an index to the Manual on Advanced Quantitative Analysis prepared by one frustrated student. Following unsuccessful approaches to Willard by various publishers, one house finally prevailed upon him by the process of locating a co-author. By a brilliant stroke, E. J. Crane of Van Nostrand brought Willard and Professor N. Howell Furman together. The Willard and Furman text came into existence in 1933 and was an instant success. Appearing in May, it had to be reprinted in September, and twice reprinted the following year. For ten years it dominated the field, and only slowly gave way to the proliferation of competing and often disgracefully similar texts which appeared. The fourth edition, 1956, with Clark Bricker, is currently (1960) doing well. This is a remarkable longevity for a chemistry text.

It was almost inevitable that the notes for the advanced course should be organised and published too. This was done by Harvey Diehl and appeared in 1943 as *Advanced Quantitative Analysis*, a companion volume to Willard and Furman. In its own less spectacular way this text too won adoption and a place in the literature of analytical chemistry.

About 1934, Willard organised a course in instrumental analysis, recognising from the very start the role physical chemistry and instruments were to play in the development of analytical chemistry. Again, the successive mimeographed notes and laboratory procedures were an accurate reflection of the development of the art: first the dipping refractometer, the interferometer and potentiometric titration apparatus, then emission spectrographic equipment, the polarograph, the glass electrode, the vacuum tube titrimeter, the photoelectric colorimeter, apparatus for graded cathode potential electrodeposition, and so on. And, here again the material was finally assembled into book form, this time with the efficient cooperation of Lynne L. Merritt, Jr. and John A. Dean. *Instrumental Methods of Analysis* was a highly successful venture, and as with the elementary book set the tone for the competition which rapidly followed.

The three texts constitute a trilogy which is unique in American scientific publications.

Willard's forceful personality dominated his teaching, but it was a very dull student indeed who could not see that behind it all was a highly competent professional, full of knowledge, and effervescent with the interest that always accompanies great creative endeavour. The teaching was always tied closely to practice, it was always up-to-date, it was aimed at developing real proficiency in the student and of having him achieve the highest possible accuracy. Even the apparent lack of sympathy was deliberate. The philosophy behind it was developed by experience and is expressed clearly in the two papers that Willard contributed to the teaching of analytical chemistry, one to the *Journal of Chemical Education* (1928) and another to the *Journal of the Association of American Medical Colleges* (1941). Literally, by example, by text books, and by the graduates he sent out into teaching positions, Willard set the pattern for the teaching of quantitative analysis for a generation.

Of Willard's Ph.D. men, about half went into college teaching: McAlpine (Michigan), G. Frederick Smith (Illinois), Kassner (Alabama), Young (Wells College), Tang (Peking), Fowler (Johns Hopkins), Hart (Carlton, Syracuse), Fogg (New Hampshire), Diehl (Iowa State), Filson (Central Michigan), G. M. Smith (Vanderbilt, Baylor), Boyle (Wayne), Merritt (Indiana), Heyn (Boston), Leininger (Michigan State), Manalo (Phillipines), Taylor (Idaho State), Freund (Oregon State), Gordon (Case), Hahn (Wayne), Dean (Tennessee). Of these many have developed research programmes of their own; two indeed have received the Fisher Award, G. Frederick Smith in 1954 and Diehl in 1956. One side-light of this secondary contribution to analytical chemistry is that some of the student's students have entered teaching, and then in turn their students have too. This process has gone on to even the fifth generation: G. Frederick Smith (Illinois), Brandt (Purdue), Pflaum (State University of Iowa), and Howick (Arkansas); and Diehl (Iowa State), Banks (Iowa State), Margerum (Purdue), and Clarke (Hercules Powder).

One of the characteristics of the American university system, particularly as practised in the mid-west, is the so-called extension system, under which the teaching activity is deliberately taken off the university campus and systematically made available to the entire population. The extension system has been especially successful in the fields of agriculture and home economics. Willard was always generous with his time in all matters pertaining to chemistry, and the numerous lectures he delivered away from the Michigan campus constituted a one-man extension programme. These lectures for the most part were delivered to the local sections of the American Chemical Society, some one hundred and fifty in number. During the 1930's, the Washington office began to organise the local section lectures into tours by the speakers. These tours were sometimes quite extensive, running to as many as twenty speaking engagements and covering a large area of the country. Willard took part in this programme enthusiastically, and at one time or another lectured before practically all of the local sections. He was an interesting and forceful speaker, and always in demand. The value of these lectures, like that of a great deal of teaching, cannot be assessed directly, but those who have appeared before the local sections can attest to the warm response and the intense appreciation shown by the local membership. Willard's influence in this direction was certainly profound.

CONCLUDING REMARKS

Reviewing Willard's research record, one is struck by the number of analytical methods he devised which have become the standard or preferred procedures. The perchloric acid dehydration of silica, the periodate method for manganese, the fluosilicic acid distillation of silica, the various oxidation-reduction procedures for chromium and vanadium, the 1,10-phenanthroline method for iron.

It is interesting to speculate why Willard did not develop an extensive programme of atomic weight determinations at Michigan. Technically he was competent, as was amply demonstrated by the work on antimony with McAlpine. Perhaps he found the work unattractive; but more likely he sensed that the chemical methods were shortly to be superseded by the mass spectrographic method and wisely refrained from beating a dying horse. In any case it is fortunate that he devoted his vast energies to other fields, for we have as a consequence the initiation of great advances in the broad fields of perchloric acid chemistry, bimetallic electrodes, ceric oxidimetry, oxidation-reduction methods, periodic acid chemistry, organic precipitating reagents, and precipitation from homogeneous solution. Atomic weight determinations and instrument design were well left to others. Here was a master chemist doing exactly what he was uniquely equipped to do.

Fifty-five years of research and teaching by Hobart H. Willard have left this world a better place to live in.

The French chemist Chevreul reached the age of one hundred and three, spanning the nineteenth century with a long lifetime of creative achievement. We hope Willard will match Chrevreul's record and that his next twenty-five years will be both pleasant and productive.

THE PH.D. STUDENTS OF HOBART H. WILLARD

1.	Lucien H. Greathouse	1917
2.	Dorothy Hall	1920
3.	R. K. McAlpine	1921
4.	Florence Fenwick	1922
5.	G. Frederick Smith	1922
6.	J. L. Kassner	1926
7.	Philena Young	1928
8.	A. W. Boldyreff	1930
9.	R. C. Gibson	1930
10.	Ning Kang Tang	1930
11.	R. D. Fowler	1931
12.	J. J. Thompson	1931
13.	R. R. Ralston	1932
14.	Frank L. Chan	1933
15.	C. S. Hart	1933
16.	H. C. Fogg	1933
17.	Edwin W. Goodspeed	1934
18.	George E. Lindemulder	1934
19.	R. C. Thielke	1935
20.	O. B. Hager	1935
21.	Headlee Lamprey	1935
22.	Ross W. Moshier	1935
23.	Dwight Williams	1936
24.	Harvey Diehl	1937
25.	M. H. Filson	1937

26.	George M. Smith	1938
27.	Albert J. Boyle	1938
28.	Lynne L. Merritt, Jr.	1940
29.	John H. Sheldon	1940
30.	Taft Y. Toribara	1942
31.	C. W. Zuehlke	1943
32.	Arno H. A. Heyn	1944
33.	Elmer Leininger	1945
34.	Gloria D. Manalo	1945
35.	Albert E. Taylor	1945
36.	Harry Freund	1946
37.	Louis Gordon	1947
38.	R. B. Hahn	1948
39.	A. L. Wooten	1948
40.	Lowell R. Perkins	1948
41.	John A. Dean	1949
42.	Charles A. Horton	1950
43.	Sylvia T'sai Yu	1951

For a complete list of the publications of Hobart H. Willard, see p. 316.

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SIXTY YEARS OF ANALYTICAL CHEMISTRY

HOBART H. WILLARD

ANALYTICAL chemistry is the oldest branch of this science. In 1856, at the University of Michigan, there was built a laboratory for instruction in analytical chemistry. This was the first laboratory in the United States devoted entirely to chemistry. Later, the main interest in chemistry was in organic chemistry. But after many years analytical chemistry again assumed an important position which it still retains.

At the beginning of this century the course in qualitative analysis at the University of Michigan, which was taught by Professor Otis Coe Johnson, was a strenuous one. The class met for lectures and quiz five days a week and five afternoons were spent in the laboratory. The student analysed forty dry "unknowns", after he had laboured with a considerable number of solutions. He balanced two hundred equations. Time was perhaps not so valuable in those days; at any rate the pace was not so rapid. The reactions of the various elements were thoroughly studied, and although from a modern point of view much time was wasted, the student acquired what might be called "chemical instinct," so that he knew what sort of a reaction to expect when various compounds were brought together. This chemical instinct is, even now, best acquired in a course in qualitative analysis. It is something that is never acquired by a student who is not enthusiastic about chemistry, and this ability readily distinguishes him from the mediocre student. It has sometimes been called "chemical horse sense." It is probably the ability to co-ordinate a large number of chemical facts.

Analytical chemistry at that time was largely a study of chemical reactions. Quantitative analysis emphasised an accurate technique and the ability to carry on filtration, ignition and other operations without loss of material, with a precision not demanded in other courses. Stoichiometric relationships were essential. The skill acquired in analytical chemistry resulted in increased accuracy in other fields of chemistry.

Laboratory work involved no very expensive equipment aside from a balance, and consisted largely of relatively simple operations carried out with great care to avoid the slightest loss. Most of the experimental work involved gravimetric methods and separations, some of them rather tedious and time consuming, such as the analysis of a complex silicate in which separations were performed one after another on the same sample following the directions of Fresenius or Hillebrand, with the hope that summation of results would be reasonably close to 100%. Little attention was paid to the theory involved, but accuracy was important. The length of time required for an analysis was not a matter of prime importance although the desirability of a short process was recognised.

The elements involved were the common ones. Except for simple acid-base, redox and complex-forming reactions, titrimetric methods were somewhat less common than gravimetric. Colorimetric methods were relatively few because even visual colorimeters were rather crude and no photoelectric ones were available. The analysis of organic compounds was not included in elementary courses.

The electrolytic deposition of metals was extensively used and this technique was accelerated by Edgar F. Smith, whose first book was published in 1890. Spectroscopy was not a quantitative method but was used qualitatively. A few organic reagents were available, but it was not until 1905, with the introduction of dimethylglyoxime as a reagent for nickel, that real interest in these reagents was initiated.

The reagent chemicals commercially available were not as pure as those furnished after the introduction of quality standards, and this often necessitated further purification by the analyst. Only the reagents furnished by Kahlbaum in Germany were analysed and approached in purity our present "analytical reagent" grade, and they were available only in the larger laboratories.

Pyrex and similar glassware, resistant to thermal shock, was not available, and the best glass for chemical use was that made in Jena, Germany. It was quite resistant to chemical attack but not to sudden changes in temperature. A small amount of fused quartz was available in Germany.

Space for publication of research was not so limited fifty years ago. The author's doctoral thesis was published in the *Journal of the American Chemical Society* and a translation of it appeared in *Zeitschrift für anorganische Chemie*. The older papers make more interesting reading because they include many details which could not be included today. Those who have read some of the papers that appeared in the old journals have found them fascinating, almost like conversing with the authors, and have regretted the necessity of curtailing contemporary publications until they are often only long abstracts. The number of pages in *Analytical Chemistry* has increased from 1588 in 1949 to 2148 in 1959, an increase of 35% in the last ten years, and the increase in the number of papers in all journals is much greater.

As one looks back sixty years it is amazing to note the gigantic changes that have occurred not only in the teaching of analytical chemistry, but also in the practice of it. From a relatively mediocre position it has risen to one of the most important. This is due to many factors. Analytical chemistry has always been indispensable to other fields of chemistry; and therefore as they have increased in scope, it necessarily had to expand also. The first World War gave the chemical industry in this country a great impetus.

The number of elements included in commercial products has increased tremendously and now includes nearly everything in the periodic table. For example, the term "rare earths" is no longer appropriate because they are used so extensively. The introduction of new elements was enormously accelerated by the development of the atomic bomb, which required the use of a great variety of materials. This necessitated the development of analytical methods for these new elements, which now enter into so many commercial products.

The older analysts worked largely with macro quantities. In recent times special attention has been directed to the determination of micro and even ultramicro amounts, requiring completely different techniques, often necessitating the use of radio-isotopes. As one man has said, "We are interested in a milligram in a carload." It would be difficult to find any line of work in which the demand for new analytical methods has not increased.

Because labour costs are high, and because manufactured products are being turned out so rapidly, the classical methods of analysis have become inadequate and have been replaced to a considerable extent by methods using instruments which measure physical properties. These methods have several advantages. They are more rapid, they require less labour, they are often non-destructive, and in many cases they make possible analyses which cannot be made in any other way. Although the instruments are often very expensive, this is usually justified by the savings effected in time and personnel.

The teaching of analytical chemistry has undergone radical changes in the past sixty years. Physical chemistry has entered into the analytical course to a large extent, and a modern course lays great stress on the theory involved, such as the equilibria in redox, acidimetric and complex-forming reactions. The first effort in this direction was made by Ostwald in his *Scientific Foundations of Analytical Chemistry* in 1894, but it was not until many years later that text-books really emphasised the theory and principles involved in quantitative analysis.

The analysis of organic compounds was not usually included in a course in quantitative analysis, but now it is customary to include a certain amount of it.

In the curriculum, qualitative analysis usually followed beginning chemistry, and this was followed by quantitative analysis. Gradually qualitative analysis has been included to a considerable extent in general chemistry; and in many schools it has been discontinued as a separate course. Organic chemistry and sometimes physical chemistry now frequently precede analytical. This makes it possible to broaden extensively the scope of quantitative analysis. It is now included to a certain extent in general chemistry and this has allowed the inclusion of some simple instrumental methods in the analytical course.

At this level it is reasonable to expect the student to grasp a much broader and deeper view of the theory and principles of analytical methods than would otherwise be possible. His appreciation of the wide scope and great applicability of analytical methods is inevitably greater because by this time he understands what chemistry is. He realises that analytical chemistry is not just a collection of tests and determinations, but comprises a great body of principles and methodology for the solution of those problems in all branches of chemistry which involve physical and numerical measurements. But equally important with theoretical knowledge is the development of good techniques and certain basic skills.

Gravimetric methods are now less emphasised because they play a minor rôle in contemporary analytical practice. The determination of organic functional groups is now almost always included, whereas the old quantitative course was usually limited to inorganic substances.

Although instrumental analysis belongs in a separate course, certain of the simpler instruments, such as pH meters and colorimeters are so universally found in modern laboratories that an introduction to their use is included in most elementary analytical courses.

Chromatography, ion-exchange, solvent extraction, *etc.* are commonly included in modern courses in quantitative analysis.

Chemical "instinct", the ability to predict the nature of a chemical reaction and to represent it by means of an equation, is best acquired by the type of drill that is possible in a course in qualitative analysis. This type of training has almost disappeared from chemical education in this country and constitutes a real loss.

Statistical treatment of experimental results has assumed considerable importance, and an increase in accuracy with less labour is the result of planning a series of experiments with this in mind.

Formerly the university had to rely almost entirely on its own funds to promote research, but now this is supported to a considerable extent by grants from other sources. This has greatly encouraged and accelerated research. In 1958, one-third of the papers appearing in *Analytical Chemistry* from universities acknowledged financial support from outside sources. Without such aid much of this research would have been impossible.

The number of journals publishing papers primarily in analytical chemistry has increased due to the greater amount of research in this field. The *Analytical Edition* of *Industrial and Engineering Chemistry* appeared in 1929; in 1947, this became the separate journal, *Analytical Chemistry*. *Analytica Chimica Acta* appeared in 1947, and *Talanta* in 1958.

The greatest advance in analytical chemistry has been in the field of instrumental methods, measuring by physical means chemical properties, rates of reaction, *etc.* The course in instrumental methods of analysis at the University of Michigan was begun in 1934, and has continued to increase in popularity and importance. In recent years a course of this type has been included to a greater or less extent in practically all chemical curricula. It is interesting to note that developments in electronics have been largely responsible for the great advance in this field. It often happens that progress in one direction comes to a halt until new discoveries in a different field make possible its continuance. Close collaboration between physicists and chemists is essential, as well as between chemists in general and analytical chemists. The rise in importance of analytical groups is undoubtedly related to this co-operation because it is through co-operation that progress is made.

Success in research is a combination of different forces working toward a common objective. The trend in analytical chemistry is toward consideration of the analytical chemist as a member of a research team. Modern instrumentation has multiplied the analyst's abilities.

Analytical chemistry in the past used to involve elemental analysis—the science of measurement applied to the reactions that could be made to follow a stoichiometric equation. Today analytical chemistry involves the use of complicated instruments in complicated systems. Each quantity to be determined is usually measured on a separate sample and often without destroying the sample. Steel mills use the quantometer spectrograph to record the impurities in a sample and transmit the answer to the furnace room at the same time. Direct reading and controlling devices are the rule rather than the exception. It is possible with an infrared spectrophotometer and a computer to have the analysis typed out when a card containing the spectrum is fed into the computer.

Any problem requiring advanced knowledge in two disciplines is solved most efficiently by the creative co-operation of two experts.

Instrument manufacturers advertise new and improved instrumentation for determinations which were previously long and tedious, if not almost impossible. An extensive discussion of new instruments and their many uses is beyond the scope of this paper. It is possible only to point out their possibilities by citing a few examples.

Automatic X-ray fluorescence instruments have been developed for the determination in steel and other alloys of elements of high atomic number without destruction of the sample.

Gas chromatographic techniques, a laboratory curiosity six or seven years ago are today a major tool in the laboratory, not only for analysis, but also for process controls.

Electronic computers are being widely used in the analytical laboratory for performing many repetitive calculations.

The use of radio-isotopes has made possible a careful study of the errors involved in separations, precipitations and other processes.

In reviewing the papers in the April, 1958, number of *Analytical Chemistry* one is impressed by the fact that although most of the thirty-one subjects covered were known twenty-five or thirty years ago, they were primarily only of academic interest. Although in the late 1930's, some of the subjects were being successfully applied, it was not until the early 1940's that advances in instrumentation made possible the many advances in analytical chemistry that we know today. These advances were facilitated by better electronics, such as amplifiers and other devices.

But not only will there be progress in instrumentation; there will, it is hoped, be progress in another important field not so frequently publicised—the search for new analytical reagents. We may never attain the goal of a specific reagent for each element, but we shall make progress in this direction. The discovery of a valuable reagent may be just as important as the design of a new instrument. It may, like the latter, save valuable time and make possible analyses previously difficult, tedious or impossible, and it will probably be much less expensive. Organic chemistry opens a limitless field for research in this direction. Much progress has already been made by Fritz Feigl, by G. F. Smith and others.

During the next ten years we can expect an increasing flow of new alloys, new materials and new machinery resulting from industrial and academic research. The analytical chemist will play an ever more important part in the development of new analytical reagents, techniques, instruments and concepts to make these products a reality. His importance has been recognised by the granting each year of the Fisher Award and the Anachem Award for outstanding contributions to analytical chemistry. The new generation of analytical chemists will face a vast array of new methods, reagents and techniques. The research of today will often be the routine of tomorrow. Analytical chemistry will play a greater rôle than ever before in our academic and industrial development. Although it may not be spectacular, it is a fascinating field and its importance will be recognised more and more as time goes on.

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THE SOLUBILITIES OF ZINC COMPLEXES OF 8-QUINOLINOL AND SOME DERIVATIVES OF 8-QUINOLINOL*

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Summary—The solubilities of *bis*-8-quinolinolo-zinc^{II}, *bis*-2-methyl-8-quinolinolo-zinc^{II} and *bis*-5:7-dibromo-8-quinolinolo-zinc^{II} have been measured over the pH range of 4·5 to 9 at ionic strengths of 0·114 and 0·230 and at 25° and 40°. A mathematical treatment of the results gave nearly constant solubility products only when a dissolved but undissociated molecule, in addition to all of the dissociated and partly dissociated species, was considered. The relative abundance of each species of molecule in solution has been calculated.

INTRODUCTION

SEVERAL measurements of the solubility products of the slightly soluble complexes of metals with 8-quinolinol have appeared in the literature.[1–4] Except for the excellent series by Näsänen and co-workers,[4] the calculations have always been made on the assumption of complete dissociation of the complex upon solution. Näsänen adjusted the pH of a solution containing metallic ions and complexing agent until precipitation began, measured the pH and the concentration of MO_x^+ either spectrophotometrically or potentiometrically, then computed solubility products taking into account the dissociation constants of the complexes and the ionisation constants of the complexing agent. Under his conditions of low pH and low concentration of ligand, the complex MO_x^+ was the predominant species in solution.

We have measured the solubility of the zinc complexes of 8-quinolinol, 2-methyl-8-quinolinol and 5:7-dibromo-8-quinolinol using radioactive zinc-65 as tracer. The measurements were carried out at ionic strengths of 0·114 and 0·230 and at temperatures of 25° and 40° and over a pH range from about 4·5 to about 9·0. In the calculations of solubility products we have considered all species of ions and molecules which may be present in the solutions.

EXPERIMENTAL

Reagents

Bis-8-quinolinolo-zinc^{II}: Eastman Kodak reagent grade 8-quinolinol was purified by two recrystallisations from alcohol. Zinc oxide from the Oak Ridge National Laboratory, Oak Ridge, Tenn., was purified by solution in hydrochloric acid, followed by two precipitations of any acid-insoluble sulphides from 0·25*M* hydrochloric acid solution with hydrogen sulphide gas, adjustment of the pH to 3 and precipitation of zinc sulphide by hydrogen sulphide. The zinc sulphide was ignited to zinc oxide and stored in a desiccator.

The zinc complex was formed in the usual manner by addition of a 2% solution of 8-quinolinol in alcohol to the solution of zinc ion in sodium acetate-acetic acid at 60°. A very slight stoichiometric deficiency of 8-quinolinol was employed. The precipitate was allowed to stand for 24 hr, filtered, washed with water and air-dried. The complex was redissolved in hydrochloric acid and re-precipitated by the addition of sodium acetate solution, then washed and dried as before.

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Bis-2-methyl-8-quinolinolo-zinc^{II}: The organic reagent was prepared according to the method of Merritt and Walker[5] and purified by vacuum distillation. The zinc complex was prepared in the same manner as the *bis*-8-quinolinolo-zinc^{II}.

Bis-5:7-dibromo-8-quinolinolo-zinc^{II}: The reagent was prepared by the method of Phillips[6] which is essentially that employed by Berg.[7] It was purified by reprecipitation from hydrochloric acid solution by partial neutralisation of the acid and recrystallisation from an acetone-benzene mixture. The zinc complex was formed in the same manner as the *bis*-8-quinolinolo-zinc^{II} complex except that the organic reagent was employed as a 0·06% solution in $3N$ hydrochloric acid containing 20–30% of acetone.

Buffer solutions: Buffer solutions of sodium acetate-sodium barbital-hydrochloric acid mixtures were prepared as suggested by Michaelis.[8] Sodium chloride was used to adjust the ionic strength to either 0·114 or 0·230.

Solubility measurements

Radioactive tracer techniques were used for determination of the solubilities. The zinc isotope ^{65}Zn ($t_{1/2}$ = 250 days) was employed.

In general, 600 ml of buffer solution was prepared at one time, divided into 150-ml portions and placed in contact with excess precipitate in 250-ml glass-stoppered Pyrex bottles. The samples were then rotated slowly in a constant-temperature water bath. From time to time samples were withdrawn through 10-mm diameter Corning No. 39535 medium-porosity fritted glass discs. Subsequent filtrations and sample countings were made to show that one filtration was sufficient to separate the solid completely and that no radioactive species of the solution was preferentially adsorbed on the discs. The pH of the filtered solutions was measured with a Beckman Model G pH meter, carefully standardised with buffer solutions of known pH,at the temperature of the water bath. Since pH is a critical factor, the pH of three or four identical runs was always measured and a precision of about 0·02 pH units was considered acceptable.

The filtered solutions were allowed to come to room temperature and 25-ml portions were pipetted into Marinelli type double-walled beakers and counted with a bismuth-wall Geiger-Müller tube. All measurements were corrected for background, then compared with the activity, measured at approximately the same time, of a solution of a weighed amount of the original zinc oxide used in preparing the complexes, dissolved in hydrochloric acid. Sufficient counts were registered so that the standard deviation of the counts was always below 5% of the sample activity corrected for background.

Samples were withdrawn at intervals and measured until the corrected activity remained constant over a period of 2 weeks in order to ensure that equilibrium had been attained. Usually 6-8 weeks were necessary.

RESULTS

The results of the solubility measurements are given in Tables I–III.

CALCULATIONS

Attempts were made to calculate solubility product constants from these results assuming complete ionisation of the dissolved material. If this is done the calculated solubility products vary by a factor of about 6000 over the pH range 4·5 to 9. Inclusion of stepwise dissociation of the complexes improves the result somewhat, but satisfactory values are only obtained after the presence of a dissolved but undissociated molecule is included. The following treatment, involving all known stability constants[9] of the *bis*-8-quinolinolo-zinc^{II} and the ionisation constants of the 8-quinolinol,[10] leads to the best values of the solubility product constants. This treatment has been applied only to the *bis*-8-quinolinolo-zinc^{II} complex since all necessary data for the other complexes are not known.

The reactions to be considered and their respective equilibrium constants are given below. The symbol HO_x stands for the 8-quinolinol molecule. Activity coefficients are neglected.

Table I. Solubility of *Bis*-8-quinolinolo-zinc$^{\mathrm{II}}$ in veronal-acetate buffers

pH	μ	T, °*C*	Total Zn in solution, *M*
4·84	0·230	25	$1{\cdot}277 \times 10^{-5}$
5·90	0·230	25	$5{\cdot}05 \times 10^{-6}$
7·15	0·230	25	$1{\cdot}79 \times 10^{-6}$
8·17	0·230	25	$7{\cdot}30 \times 10^{-7}$
8·70	0·230	25	$4{\cdot}75 \times 10^{-7}$
4·63	0·114	25	$4{\cdot}43 \times 10^{-6}$
4·72	0·114	25	$4{\cdot}33 \times 10^{-6}$
5·83	0·114	25	$2{\cdot}40 \times 10^{-6}$
5·95	0·114	25	$2{\cdot}32 \times 10^{-6}$
6·73	0·114	25	$9{\cdot}72 \times 10^{-7}$
8·83	0·114	25	$2{\cdot}16 \times 10^{-7}$
4·60	0·114	40	$9{\cdot}46 \times 10^{-6}$
4·62	0·114	40	$10{\cdot}5 \times 10^{-6}$
6·22	0·114	40	$5{\cdot}04 \times 10^{-6}$
6·40	0·114	40	$3{\cdot}30 \times 10^{-6}$
8·06	0·114	40	$1{\cdot}10 \times 10^{-6}$
8·11	0·114	40	$8{\cdot}04 \times 10^{-7}$
8·25	0·114	40	$4{\cdot}35 \times 10^{-7}$

Table II. Solubility of *Bis*-2-methyl-8-quinolinolo-zinc$^{\mathrm{II}}$ in veronal-acetate buffers; $\mu = 0{\cdot}114$

25°		40°	
pH	Total zinc concentration, *M*	pH	Total zinc concentration, *M*
4·86	$1{\cdot}20 \times 10^{-5}$	5·21	$2{\cdot}32 \times 10^{-5}$
5·11	$1{\cdot}09 \times 10^{-5}$	5·22	$2{\cdot}13 \times 10^{-5}$
6·79	$7{\cdot}60 \times 10^{-7}$	6·66	$3{\cdot}13 \times 10^{-6}$
8·84	$2{\cdot}09 \times 10^{-7}$	6·73	$2{\cdot}64 \times 10^{-6}$
		8·24	$8{\cdot}74 \times 10^{-7}$
		8·44	$9{\cdot}57 \times 10^{-7}$

Table III. Solubility of *Bis*-5:7-dibromo-8-quinolinolo-zinc$^{\mathrm{II}}$ in veronal-acetate buffers; $\mu = 0{\cdot}114$

25°		40°	
pH	Total zinc concentration, *M*	pH	Total zinc concentration, *M*
4·50	$3{\cdot}12 \times 10^{-5}$	4·60	$3{\cdot}40 \times 10^{-5}$
4·66	$2{\cdot}44 \times 10^{-5}$	4·61	$3{\cdot}05 \times 10^{-5}$
6·69	$1{\cdot}52 \times 10^{-6}$	4·62	$2{\cdot}96 \times 10^{-5}$
6·73	$1{\cdot}44 \times 10^{-6}$	6·56	$3{\cdot}06 \times 10^{-6}$
8·28	$5{\cdot}32 \times 10^{-7}$	6·71	$2{\cdot}45 \times 10^{-6}$
8·39	$4{\cdot}10 \times 10^{-7}$	8·06	$9{\cdot}86 \times 10^{-7}$
8·55	$3{\cdot}87 \times 10^{-7}$		

$$\mathrm{Zn(O_x)_2 \rightleftharpoons ZnO_x^+ + O_x^-};\quad k_2 = \frac{[\mathrm{Zn(O_x)_2}]}{[\mathrm{Zn(O_x)^+}][\mathrm{O_x^-}]} = 7{\cdot}95 \times 10^9 \tag{1}$$

$$\mathrm{ZnO_x^+ \rightleftharpoons Zn^{++} + O_x^-};\quad k_1 = \frac{[\mathrm{ZnO_x^+}]}{[\mathrm{Zn^{++}}][\mathrm{O_x^-}]} = 8{\cdot}13 \times 10^{10} \tag{2}$$

$$\mathrm{HO_x \rightleftharpoons H^+ + O_x^-};\quad k_a' = \frac{[\mathrm{H^+}][\mathrm{O_x^-}]}{[\mathrm{HO_x}]} = 1{\cdot}95 \times 10^{-10} \tag{3}$$

$$\mathrm{HO_x + H^+ \rightleftharpoons H_2O_x^+};\quad k_b' = \frac{[\mathrm{HO_x}][\mathrm{H^+}]}{[\mathrm{H_2O_x^+}]} = 1{\cdot}20 \times 10^{-5} \tag{4}$$

$$\mathrm{Zn(O_x)_2\,(s) \rightleftharpoons Zn(O_x)_2(1)} \tag{5}$$

Let the subscript T indicate the total concentration of any dissolved material. Then

$$\mathrm{Zn_T} = [\mathrm{Zn^{++}}] + [\mathrm{ZnO_x^+}] + [\mathrm{Zn(O_x)_2}] \tag{6}$$

and

$$\mathrm{O_{xT}} = 2[\mathrm{Zn_T}] = [\mathrm{ZnO_x^+}] + [\mathrm{O_x^-}] + [\mathrm{HO_x}] + [\mathrm{H_2O_x^+}] + 2[\mathrm{Zn(O_x)_2}]. \tag{7}$$

Let

$$p = \frac{[\mathrm{Zn(O_x)_2}]}{[\mathrm{Zn_T}]} = 2t \tag{8}$$

$$t = \frac{[\mathrm{Zn(O_x)_2}]}{[\mathrm{O_{xT}}]} \tag{9}$$

$$u = \frac{[\mathrm{Zn^{++}}]}{[\mathrm{Zn_T}]} \tag{10}$$

$$v = \frac{[\mathrm{ZnO_x^+}]}{[\mathrm{Zn_T}]} = 2w \tag{11}$$

$$w = \frac{[\mathrm{Zn(O_x)^+}]}{[\mathrm{O_{xT}}]} \tag{12}$$

$$x = \frac{[\mathrm{H_2O_x^+}]}{[\mathrm{O_{xT}}]} \tag{13}$$

$$y = \frac{[\mathrm{HO_x}]}{[\mathrm{O_{xT}}]} \tag{14}$$

and

$$z = \frac{[\mathrm{O_x^-}]}{[\mathrm{O_{xT}}]}. \tag{15}$$

Then

$$2t + w + x + y + z = 1 \tag{16}$$

and

$$p + u + v = 1. \tag{17}$$

Now

$$K_{\mathrm{S.P.}} = [\mathrm{Zn^{++}}]\,[\mathrm{O_x^-}]^2 = 4uz^2[\mathrm{Zn_T}]^3 \tag{18}$$

and it can be further shown that

$$z^3 + z^2\frac{1}{2k_2[\mathrm{Zn_T}]} + z\left[\frac{E - k\,[\mathrm{Zn_T}]}{4k_1k_2[\mathrm{Zn_T}]^2E}\right] - \frac{1}{4k_1k_2[\mathrm{Zn_T}]^2E} = 0 \tag{19}$$

where

$$E = \frac{[\mathrm{H^+}]^2}{k_a'k_b'} + \frac{[\mathrm{H^+}]}{k_a'} + 1. \tag{20}$$

The cubic equation (19) could be solved rigorously. Descartes rule of signs indicates not more than one positive root, however, and this was obtained by successive approximations. Since z represents a mole fraction, only a positive root has physical significance. The solutions of equation (19) for the corresponding values of the concentrations of ions and molecules in solution and the values of $K_{S.P.}$ calculated according to equation (18) for bis-8-quinolinolo-zinc^{II} are given in Table IV.

TABLE IV. CONCENTRATIONS OF IONS IN SOLUTION AND KS.P. VALUES FOR *Bis*-8-QUINOLINOLO-ZINC^{II} AT 25°

	pH	O_x^-	Zn^{2+}	ZnO_x^+	$Zn(O_x)^2$	Ks.P.
$\mu = 0{\cdot}230$	5	$7{\cdot}92 \times 10^{-11}$	$9{\cdot}79 \times 10^{-7}$	$6{\cdot}30 \times 10^{-6}$	$3{\cdot}97 \times 10^{-6}$	$6{\cdot}14 \times 10^{-27}$
	6	$1{\cdot}56 \times 10^{-10}$	$1{\cdot}56 \times 10^{-8}$	$1{\cdot}98 \times 10^{-6}$	$2{\cdot}46 \times 10^{-8}$	$3{\cdot}80 \times 10^{-27}$
	7	$2{\cdot}10 \times 10^{-10}$	$4{\cdot}29 \times 10^{-8}$	$7{\cdot}32 \times 10^{-7}$	$1{\cdot}23 \times 10^{-6}$	$1{\cdot}89 \times 10^{-27}$
	8	$2{\cdot}34 \times 10^{-10}$	$1{\cdot}45 \times 10^{-8}$	$2{\cdot}75 \times 10^{-7}$	$5{\cdot}10 \times 10^{-7}$	$7{\cdot}92 \times 10^{-28}$
	9	$2{\cdot}44 \times 10^{-10}$	$8{\cdot}43 \times 10^{-9}$	$1{\cdot}67 \times 10^{-7}$	$3{\cdot}25 \times 10^{-7}$	$5{\cdot}02 \times 10^{-28}$
$\mu = 0{\cdot}114$	5	$4{\cdot}41 \times 10^{-11}$	$6{\cdot}42 \times 10^{-7}$	$2{\cdot}30 \times 10^{-6}$	$8{\cdot}1 \times 10^{-7}$	$1{\cdot}25 \times 10^{-27}$
	6	$1{\cdot}20 \times 10^{-10}$	$9{\cdot}47 \times 10^{-8}$	$9{\cdot}25 \times 10^{-7}$	$8{\cdot}8 \times 10^{-7}$	$1{\cdot}36 \times 10^{-27}$
	7	$1{\cdot}76 \times 10^{-10}$	$1{\cdot}85 \times 10^{-8}$	$2{\cdot}64 \times 10^{-7}$	$3{\cdot}7 \times 10^{-7}$	$5{\cdot}68 \times 10^{-28}$
	8	$2{\cdot}24 \times 10^{-10}$	$7{\cdot}77 \times 10^{-9}$	$1{\cdot}41 \times 10^{-7}$	$2{\cdot}5 \times 10^{-7}$	$3{\cdot}88 \times 10^{-28}$
	9	$2{\cdot}41 \times 10^{-10}$	$4{\cdot}31 \times 10^{-9}$	$8{\cdot}43 \times 10^{-7}$	$1{\cdot}61 \times 10^{-7}$	$2{\cdot}50 \times 10^{-28}$

DISCUSSION

Certain assumptions and approximations have been made in obtaining these results. Activity coefficients have been neglected except, of course, for the hydrogen ion. Any formation of $Zn(OH)_3^-$ or $Zn(OH)_4^{2+}$ has also been neglected. A calculation using the values for the dissociation constants of these basic zinc ions as given by Dirkse, Postmus and Vandenbosch[11] indicates that only at pH 9 would there be any appreciable amount of $Zn(OH)_3^-$ ion present.

The results clearly indicate that the undissociated molecule and the partially dissociated molecule are the species present in largest concentrations over the pH range 5 to 9. Below a pH of about 5·8 the $Zn(O_x)^+$ ion is the predominant form, but above this pH the $Zn(O_x)_2$ species is predominant.

It is interesting to note that the concentration of the $Zn(O_x)_2$ molecule increases with decreasing pH. One might expect that the concentration of the undissociated molecule, which is in direct equilibrium with the solid, would remain constant. There are at least two possible explanations for the solubility behaviour of this species. Firstly, the molecule may be partially dissociated by the acid, forming ions of the type $Zn(O_x)(HO_x)^+$ or $Zn(HO_x)_2^{2-}$. The formation of an ion of this type would not be included in measurements of k_2, but would be counted as $Zn(O_x)_2$ molecules in this experiment. As second possibility is that the water molecules which bind the *bis*-8-quinolinolo-zinc^{II} molecules together in the crystal[12] are weakened by competing for hydrogen ions to form oxonium ions. A third possibility is that k_1 or k_2 or both are in error; however, a ten-fold decrease in the value of k_2 results in the solubility of $Zn(O_x)_2$ molecules being still 5 to 6 times greater at pH 5 than at pH 8. Thus it would appear that the k_1 and k_2 values would have to be in error by several orders of magnitude, which seems unlikely.

The values for the solubility product obtained here are in fair agreement with the value $pS_0 = 24{\cdot}500$, obtained by Näsänen,[4] considering the fact that Näsänen has extrapolated his values to zero ionic strength, his temperature was 20° and that he used somewhat different values for the dissociation and ionisation constants involved.

It will be interesting to calculate the absorption spectra of each species of ion using the concentrations found in this paper. Another application would be to determine the values of the dissociation constants and the solubility product by selecting the best values of the constants by the method of least squares. Further work along these lines is being carried out.

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Zusammenfassung—Die Loslichkeit von Bis-oxin-zink, Bis-2-methyl-oxin-zinc und Bis-5,7-dibrom-oxin-zink wurde gemessen im pH-Bereich 4,5-9 bei ionaler Konzentration 0·114 und 0·230 sowie bei 25° und 40°C. Mathematische Behandlung der Ergebnisse ergab ein nahezu konstantes Löslichkeitsproduct nur unter der Annahme, dass eine gelöste aber undissoziierten Molekul neben allen anderen dissoziierten oder teilweise dissoziierten Partikeln anwesend ist. Die relative Menge aller in der Lösung vorhandener Spezien wurde errechnet.

Résumé—Les solubilités du bis-8-quinolinolo-zinc (11), du bis-2-méthyl-8-quinolinolo-zinc (11) et du bis-5-7-dibromo-8-quinolinolo-zinc (11) ont été mesurées dans le domaine de pH 4,5-9 à des forces ioniques de 0,114 et 0,230 à 25° et 40°. Une étude mathématique des résultats donnait des produits de solubilité à peu près constants seulement quand on considèrait une molécule dissoute, mais non dissociée ajoutée à toutes les espèces dissociées et partiellement dissociées. L'abondance relative de chaque sorte de molécule en solution a été calculée.

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BATHOPHENANTHROLINEDISULPHONIC ACID AND BATHOCUPROINEDISULPHONIC ACID, WATER SOLUBLE REAGENTS FOR IRON AND COPPER

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Summary—Bathophenanthrolinedisulphonic acid and bathocuproïnedisulphonic acid have been isolated in solid form as sodium salts and characterised. Both materials retain the high sensitivity of the parent materials as spectrophotometric reagents, for iron and copper respectively. They are water soluble and unlike the parent reagents may be used in aqueous perchlorate solutions. Interferences are about the same as with the parent reagents, but the pH range for maximum colour formation extends two pH units further into the alkaline region. Iron^{II} tribathophenanthrolinedisulphonic acid is an excellent oxidation-reduction indicator, changing sharply from red to green in the cerate titration of iron^{II}; it may be used in solutions containing perchloric acid.

THE initial paper of Smith, McCurdy and Diehl[1] on bathophenanthroline (4:7-diphenyl-1:10-phenanthroline), a highly sensitive reagent for the spectrophotometric determination of iron, has been followed by several other papers detailing applications of the reagent to various materials bearing traces of iron.[2] In a like manner, bathocuproïne (2:9-dimethyl-4:7-diphenyl-1:10-phenanthroline), originally proposed by Smith and Wilkins,[3] is finding numerous applications[4] because its unqualified specificity and high sensitivity make it the superior reagent for the spectrophotometric determination of traces of copper.

The difficulty encountered in the use of these reagents in water solution is their low solubility in water. Both are soluble in alcohols, and also in water as the hydrochlorides, but in the neutral solutions needed for maximum colour development with the metals, the excess reagent tends to precipitate, rendering the solutions turbid. Even this is satisfactory if the procedures of the original authors are followed, for Smith and his co-workers extract the metal derivatives into amyl or hexyl alcohol and in these solvents make the final photometric measurement. The advantages of such extraction are considerable, for a significant concentration can be effected and the blank can be reduced essentially to zero by extracting from the various reagent solutions any iron and copper present. Workers with heavy loads of routine work, however, find the extraction a handicap, but in omitting it, *i.e.*, in making the photometric measurement on the water solution, are plagued with the turbidity difficulty.

Trinder[5] solved this problem by sulphonating bathophenanthroline, and later Zak[6] followed with a sulphonation of bathocuproïne. Both succeeded in providing a sensitive, water soluble reagent, free from turbidity in use. The art was thus advanced and the daily capabilities of the clinical analyst increased. As with pioneers at all times and stations, Trinder and Zak left problems for others: Can the sulphonated products be isolated in solid form suitable for commercial distribution and shipping? What is the composition of the sulphonated reagents? What is the nature of their metal derivatives? What are their sensitivities and the degree to which they are affected by foreign elements? Then too, is the perchlorate of the iron^{II} derivative of sulphonated bathophenanthroline water soluble so that it may be used as an oxidation-reduction indicator in a perchloric acid solution, in contrast to its parent material?

We have attempted to answer these questions.

EXPERIMENTAL

Apparatus and reagents

Spectrophotometric data were secured using a Cary Model 12 Recording Spectrophotometer and a Beckman DU Spectrophotometer using 1-cm matched cells. pH measurements were made with a Beckman Model G pH meter with Beckman No. 30740 amber bulb glass electrode. Potential measurements were made with a Leeds and Northrup No. 7552 potentiometer. The thermobalance used was one built in this laboratory.

The starting materials, bathophenanthroline and bathocuproïne, were obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio. The commercial chlorosulphonic acid used was first subjected to distillation to insure the absence of iron and copper. The Amberlite IR-120 used was a reagent-grade material. The water used was first distilled, then passed through a monobed ion-exchange resin.

Bathophenanthrolinedisulphonic acid (4:7-*diphenyl*-1:10-*phenanthrolinedisulphonic acid*)

Synthesis. One g of bathophenanthroline and 10 ml of freshly distilled chlorosulphonic acid were stirred vigorously (glass-coated magnetic stirring bar) for 20 hr at 25°. The mixture was cooled in ice and 100 ml of de-ionised water was added carefully. The mixture was then heated in a boiling water bath until a clear solution was obtained. Water and hydrochloric acid were removed by heating with aspiration leaving the excess sulphuric acid and the sulphonated material.

Concentrated ammonia was added until in excess. The resulting solution was evaporated to dryness on a steam plate. The residue was pulverised and treated with 200 ml of 95% ethanol. The mixture was heated to boiling, stirred for 30 min and the ammonium sulphate filtered out using suction. The filtrate was evaporated to dryness on a steam plate. The residue was dissolved in 100 ml of de-ionised water and the solution passed through a column of Amberlite IR-120 (a strong cation-exchange resin) in the hydrogen form. The resulting acidic solution was partially neutralised with iron-free sodium bicarbonate and the carbon dioxide formed expelled by boiling while the solution was still slightly acidic. The pH of the solution was then adjusted to 8·5 with dilute sodium hydroxide. The solution was evaporated on a hot plate and the residue pulverised. Yield 98%. Found: C 53·87, H 2·85, N 5·05, S 11·87, Na 8·77 (Huffman Microanalytical Laboratory, Wheatridge, Colorado) giving an empirical formula of $C_{24\cdot2}H_{15\cdot3}N_{2\cdot0}S_{2\cdot0}Na_{2\cdot1}$; disodium bathophenanthrolinedisulphonate: $C_{24}H_{14}N_2S_2Na_2O_6$. Equivalent weight (determined by passing a weighed sample of the sodium salt dried at 110° through a column of IR-120 in the hydrogen form and titration with standard sodium hydroxide, see Fig. 1): 263·0, 264·5 (first preparation), 264·5 (second preparation); calculated for $C_{24}H_{15}Na_2(SO_3Na)$ 434·4; for $C_{24}H_{14}N_2(SO_3Na)_2$ 536·5/2 or 268·2; for $C_{24}H_{13}N_2(SO_3Na)_3$ 638·5/3 or 212·8.

Properties. The disodium salt, a light tan solid, is extremely soluble in water. It is hygroscopic but after drying at 110° for 2 hr shows no change in weight up to 275° (thermobalance). It shows a light blue fluorescence under ultraviolet light.

The free acid is a syrupy liquid, highly hygroscopic, and is difficult to obtain in the solid form. It proved impossible to prepare an ammonium salt of stoichiometric composition.

Iron^{II} derivative. A solution of iron^{II} sulphate was treated with hydroxylamine hydrochloride, a ten-fold excess of disodium bathophenanthrolinedisulphonate, and sodium acetate. The absorption spectrum of the deep red solution was obtained on the Cary spectrophotometer (Fig. 2); at the wavelength of maximum absorption, 535 mμ, the molar extinction coefficient was 22,140.

The combining ratio of the iron^{II} and bathophenanthrolinedisulphonate ions was determined by a spectrophotometric titration, the iron concentration being held constant in a series of solutions and the concentration of reagent varied. Straight lines were obtained for the sloped and horizontal portions of the curve and the sharp break fell at the ratio Fe:bathophenanthrolinedisulphonate = 1:3·17.

The pH range over which iron^{II} tribathophenanthrolinedisulphonic acid is stable was determined by preparing a series of solutions, each solution having the same amount of iron, sodium sulphite and an excess of bathophenanthrolinedisulphonate; the pH was adjusted with hydrochloric acid or sodium hydroxide and after 1 hr the absorbancy of each solution was measured. Results are presented graphically in Fig. 3.

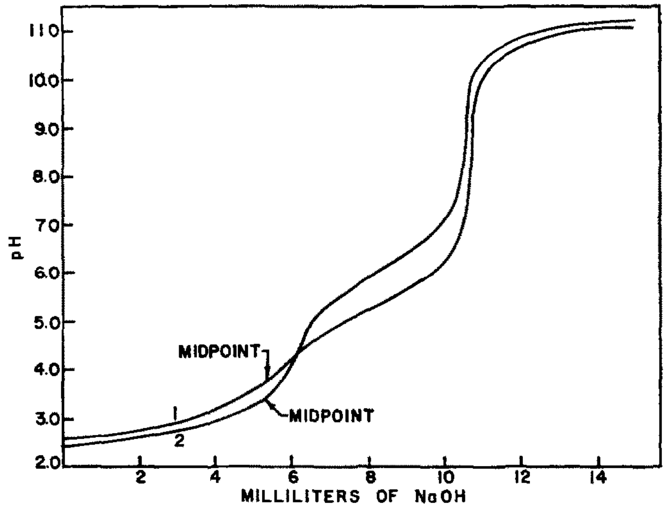

FIG. 1.—Titration of bathophenanthrolinedisulphonic acid (curve 1) and of bathocuproïnedisulphonic acid (curve 2).

Bathocuproïnedisulphonic acid (2:9-*dimethyl*-4:7-*diphenyl*-1:10-*phenanthrolinedisulphonic acid*)

Synthesis. Identical with that given above for bathophenanthrolinedisulphonic acid. Yield 97% Found: C 52·41, H 3·69, N 4·57, S 10·40, Na 8·11 (Huffman Microanalytical Laboratory) giving an empirical formula of $C_{26\cdot9}H_{26\cdot0}N_{2\cdot0}S_{2\cdot0}Na_{2\cdot2}$; disodium bathocuproïnedisulphonate is

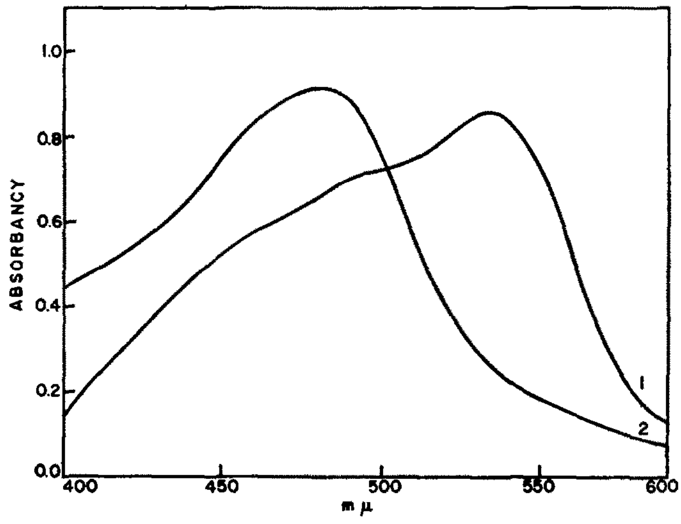

FIG. 2.—Absorption spectra of iron^{II} tribathophenanthrolinedisulphonic acid (curve 1) and of copper^{I} dibathocuproïnedisulphonic acid (curve 2).

$C_{26}H_{18}N_2S_2Na_2O_6$. Equivalent weight found (method given above, Fig. 1): 278·0 (first preparation), 273·4, 273·0 (second preparation); calculated for $C_{26}H_{19}N_2SO_3Na$ 462·5, for $C_{26}H_{18}N_2(SO_3Na)_2$ 564·6/2 or 282·3, for $C_{26}H_{17}N_2(SO_3Na)_3$ 666·6/3 or 222·2.

Properties. The disodium salt, a light tan solid, is extremely soluble in water; it is hygroscopic but once dried (110°, 2 hr) it shows no change in weight on heating to 275°. It shows a light blue fluoresence under ultraviolet light.

The free acid is a syrupy liquid, highly hygroscopic and difficult to obtain in the crystalline form. It was impossible to prepare an ammonium salt of stoichiometric composition.

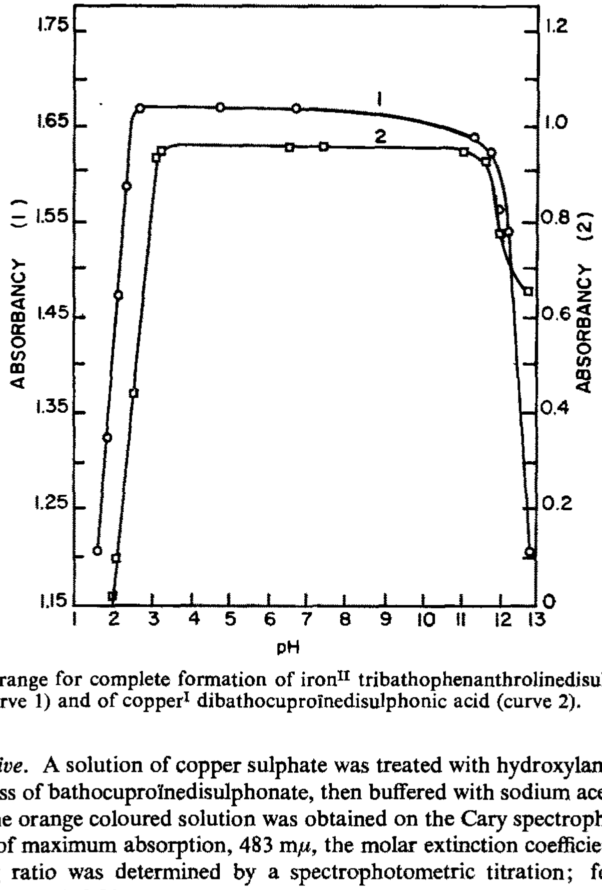

FIG. 3.—pH range for complete formation of iron^{II} tribathophenanthrolinedisulphonic acid (curve 1) and of copper^{I} dibathocuproïnedisulphonic acid (curve 2).

Copper^{I} derivative. A solution of copper sulphate was treated with hydroxylamine hydrochloride and a ten-fold excess of bathocuproïnedisulphonate, then buffered with sodium acetate. The absorption spectrum of the orange coloured solution was obtained on the Cary spectrophotometer (Fig. 2); at the wavelength of maximum absorption, 483 mμ, the molar extinction coefficient was 12,250.

The combining ratio was determined by a spectrophotometric titration; found Cu: bathocuproïnedisulphonate = 1:2·28.

The pH range over which copper is converted completely to copper^{I} dibathocuproïnedisulphonic acid was measured in the same fashion as described above for iron^{II} tribathophenanthrolinedisulphonic acid; the results are shown in Fig. 3.

Determination of iron with bathophenanthrolinedisulphonic acid

The spectrophotometric determination of iron with bathophenanthrolinedisulphonic acid was worked out by Trinder in the original paper.[5] We sought here to extend the studies of the interferences and to show that the method can be used in solutions containing perchloric acid, such as those resulting from the wet ashing of plant and animal material.

Interferences. The disturbing effects of various ions on the spectrophotometric determination of iron was determined on solutions made up to contain 6·5 × 10^{-7} moles of iron and 9·5 × 10^{-6} moles of bathophenanthrolinedisulphonate in a total volume of 50·0 ml. In all cases the order of addition of the reagents was the same, first the interfering ion, second the iron, next the hydroxylamine hydrochloride, then the sulphonated reagent, and finally the sodium acetate buffer. See Table 1. The method of calculating the relative error is that of Fortune and Mellon.[7]

TABLE 1—EFFECT OF VARIOUS IONS ON THE DETERMINATION OF IRON WITH BATHOPHENANTHROLINEDISULPHONIC ACID

Ion	Interfering ion concentration, *ppm*	Added as	Relative error* % of 0·726 *ppm* of Fe taken
Cu^{2+}	0·9	$CuSO_4$	+2·2
†Cu^{2+}	9·4	$CuSO_4$	+3·2
Co^{2+}	1·2	$CoSO_4$	+1·1
†Co^{2+}	5·8	$CoSO_4$	0·0
Ni^{2+}	1·4	$NiSO_4$	+1·1
†Ni^{2+}	5·5	$NiSO_4$	0·0
Zn^{2+}	13·8	$ZnSO_4$	+0·3
Mn^{2+}	25·3	$MnSO_4$	−1·1
Cr^{3+}	5·8	$K_2Cr_2O_7$	+1·6
Cr^{3+}	29·2	$K_2Cr_2O_7$	+4·7
Be^{2+}	14·6	$Be(ClO_4)_2$	+2·2
Al^{3+}	121·3	$Al_2(SO_4)_3$	Prec.
Mg^{2+}	58·7	$MgSO_4$	+0·3
Ca^{2+}	189	$Ca(C_2H_3O_2)_2$	−1·1
Sr^{2+}	571	$Sr(NO_3)_2$	0·0
Cd^{2+}	35·5	$Cd(NO_3)_2$	0·0
Sn^{4+}	307	$SnCl_4$	Prec.
Th^{4+}	546	$Th(NO_3)_4$	+0·3
UO_2^{2+}	653	$UO_2(NO_3)_2$	+1·6
Li^+	627	$LiCl$	0·0
ClO_4^-	17780	$NaClO_4$	+2·7
CN^-	536	KCN	No colour
PO_4^{3-}	1122	KH_2PO_4	0·0
F^-	543	NaF	+1·1
$C_2H_3O_2^-$	15320	$NH_4C_2H_3O_2$	0·0
Br^-	895	KBr	−2·3
I^-	1040	NaI	−0·8
Cl^-	5180	KCl	−0·8
NO_2^-	873	$NaNO_2$	−2·0
SO_4^{2-}	3470	$(NH_4)_2SO_4$	0·0
ClO_3^-	818	$KClO_3$	−0·8
SCN^-	1200	$NaSCN$	−1.7
$S_2O_3^{2-}$	1074	$Na_2S_2O_3$	Prec.
BO_3^{3-}	1800	$Na_2B_4O_7$	+0·3
BrO_3^-	1380	$KBrO_3$	+0·3
MoO_4^{2-}	93·2	Na_2MoO_4	0·0
$C_6H_5O_7^{3-}$	1627	$H_3C_6H_5O_7$	−1·7
$S_2O_8^{2-}$	1626	$(NH_4)_2S_2O_8$	−9·7

* Calculated using

$$\% \text{ Relative Error} = \frac{C_1 \frac{A_2}{A_1} - C_1}{C_1} 100$$

where C and A refer to concentration and absorbancy, respectively, and subscripts 1 and 2 to solutions without and with the interfering ion, respectively.[7]

† Solutions containing a large excess ($2·5 \times 10^{-5}$ moles) of bathophenanthrolinedisulphonate.

Determination of iron in yeast. As a check on the use of bathophenanthrolinedisulphonic acid for the determination of iron, a commercial yeast (Fleischmann's "Active Dry") was selected as a suitable and homogeneous material requiring wet ashing. A sample weighing 2 g was transferred to a 250-ml conical flask. Five ml of concentrated sulphuric acid were added and a reflux head[8] was placed in the neck of the flask. A blank determination was carried along simultaneously starting with the sulphuric acid. The yeast was charred by heating the mixture on a gas hot-plate for 15 min. The mixture was cooled, then 20 ml of equal parts by volume of 72% perchloric acid and 70% nitric acid were added. The reflux head was replaced and the mixture was boiled in such a fashion that the water and nitric acid were expelled in about 15 min and perchloric acid began to condense on the walls of the flask. This smooth refluxing of perchloric acid without undue escape of perchloric acid was continued 10 min. The mixture was then cooled and the reflux head and flask washed with approximately 30 ml of de-ionised water.

To this solution was added 5 ml of a 10% solution of hydroxylamine hydrochloride and 10 ml of a 0·1% solution of disodium bathophenanthrolinedisulphonate. Ammonium hydroxide was added until the pH of the solution reached 7 to 8 as shown by pH paper. The pH was then brought to between 4 and 5 by the dropwise addition of perchloric acid. The solution was then transferred to a 100-ml volumetric flask, diluted to the mark with de-ionised water and mixed. The absorbancy was then measured in a 1-cm cell at 535 mμ.

A calibration curve was prepared following the procedure of the paragraph immediately above, starting with various volumes of a standard iron solution (0·036 mg of iron/ml), prepared by dissolving electrolytic iron ignited in moist hydrogen (G. Frederick Smith Chemical Company, Columbus, Ohio) in sulphuric acid and diluting and aliquoting and again diluting as appropriate. The calibration curve was linear, indicating conformity to Beer's law, over the range 0 to 3·6 ppm of iron.

Known amounts of iron were added to certain samples of the yeast before digestion. The results on the yeast and on the spiked samples are summarised in Table II.

TABLE II—DETERMINATION OF IRON IN DRY YEAST WITH BATHOPHENANTHROLINEDISULPHONIC ACID

Sample number	Iron added, *mg*	Iron found, *mg*	Iron in yeast, *ppm*	
1	none	0·100	50·0	
2	none	0·102	51·0	
3	none	0·101	50·5	
4	none	0·101	50·5	
5	none	0·101	50·5	
6	none	0·099	49·5	
		Av. 0·101	Av. 50·3	
			Iron recovered, *mg*	Error, *mg*
7	0·036	0·139	0·038	+0·002
8	0·036	0·143	0·042	+0·006
9	0·036	0·138	0·037	+0·001
10	0·072	0·172	0·071	−0·001
11	0·072	0·169	0·068	−0·004
12	0·072	0·173	0·072	0·0

Determination of copper using bathocuproïnedisulphonic acid

The use of bathocuproïnedisulphonic acid for the spectrophotometric determination of copper was described by Zak.[6] We have extended the study by an investigation of the ions which could interfere with the method and have applied the reagent to the determination of copper in yeast in the presence of the perchlorate ion as a check on the method.

Interferences. A solution was prepared by adding first the ion under study, second $1{\cdot}9 \times 10^{-6}$ mole of copper, next the hydroxylamine hydrochloride, then $1{\cdot}4 \times 10^{-5}$ mole of disodium bathocuproïnedisulphonate, and finally the sodium acetate buffer. The solution was diluted to a volume of 50·0 ml and the absorbancy was measured at 483 mμ. The disturbance was reported as relative error in the amount of copper taken, Table III.

TABLE III.—EFFECTS OF VARIOUS IONS ON THE DETERMINATION OF COPPER WITH BATHOCUPROÏNEDISULPHONIC ACID

Ion	Interfering ion concentration, *ppm*	Added as	Relative error % of 2·41 ppm of Cu taken
Fe^{2+}	5·8	$FeSO_4$	+0·2
Fe^{2+}	57·8	$FeSO_4$	+1·2
Co^{2+}	1·2	$CoSO_4$	0·0
Co^{2+}	5·9	$CoSO_4$	+1·4
Ni^{2+}	1·4	$NiSO_4$	0·0
Ni^{2+}	6·9	$NiSO_4$	+1·4
Zn^{2+}	126	$ZnSO_4$	−0·3
Mn^{2+}	316	$MnSO_4$	0·0
Cr^{3+}	5·8	$K_2Cr_2O_7$	−0·2
Cr^{3+}	29·2	$K_2Cr_2O_7$	+3·1
Be^{2+}	14·6	$Be(ClO_4)_2$	+1·1
Al^{3+}	90	$Al_2(SO_4)_3$	Prec.
Mg^{2+}	67	$MgSO_4$	0·0
Ca^{2+}	170	$Ca(C_2H_3O_2)_2$	−0·2
Sr^{2+}	571	$Sr(NO_3)_2$	−2·1
Cd^{2+}	360	$Cd(NO_3)_2$	−0·2
Sn^{4+}	351	$SnCl_4$	Prec.
Th^{4+}	525	$Th(NO_3)_4$	−0·2
$UO_2{}^{2+}$	555	$UO_2(NO_3)_2$	+6·1
Li^+	642	$LiCl$	−0·2
$ClO_4{}^-$	16550	$NaClO_4$	0·0
CN^-	550	KCN	No colour
$PO_4{}^{3-}$	1284	KH_2PO_4	−0·3
F^-	696·	NaF	−1·2
$C_2H_3O_2{}^-$	15660	$NH_4C_2H_3O_2$	−1·2
Br^-	1000	KBr	0·0
I^-	840	NaI	−0·6
Cl^-	5130	KCl	−2·1
$NO_2{}^-$	882	$NaNO_2$	−0·2
$SO_4{}^{2-}$	3060	$(NH_4)_2SO_4$	−2·1
$ClO_3{}^-$	905	$KClO_3$	−1·1
SCN^-	975	$NaSCN$	−16·5
$S_2O_3{}^{2-}$	1330	$Na_2S_2O_3$	+3·2
$BO_3{}^{3-}$	1940	$Na_2B_4O_7$	−0·3
$BrO_3{}^-$	1028	$KBrO_3$	−0·3
$MoO_4{}^{2-}$	81	Na_2MoO_4	−0·2
$C_6H_5O_7{}^{3-}$	1627	$H_3C_6H_5O_7$	−0·8
$S_2O_8{}^{2-}$	1567	$(NH_4)_2S_2O_8$	−15·4

Determination of copper in yeast. Two g of the same yeast analysed for iron were analysed for copper. The procedure for destroying the organic matter was the same as detailed in the first paragraph above on the determination of iron in yeast.

To this solution were added 5 ml of a solution 10% in hydroxylamine hydrochloride and 2% in citric acid. Then 5 ml of a 0·1 % solution of disodium bathocuproïnedisulphonate were added. Ammonium hydroxide was added until the pH reached 7 to 8 as indicated by pH paper. The solution was then brought to pH 4 to 5 by the dropwise addition of dilute perchloric acid. The solution was diluted to exactly 100 ml and the absorbancy measured at 483 mμ.

A calibration curve was prepared by applying this same procedure to various volumes of a standard copper solution (0·079 mg of copper/ml), by dissolving electrolytically purified copper in nitric acid, converting to copper sulphate by evaporation with sulphuric acid and diluting as appropriate. The calibration curve was linear, indicating conformity to Beer's law, over the range 0 to 6·35 ppm of copper.

Known amounts of copper were added to some of the samples as a check on the accuracy of the method. The results are reported in Table IV.

Table IV—Determination of copper in dry yeast with bathocuproïnedisulphonic acid

Sample number	Copper added, *mg*	Copper found, *mg*	Copper in yeast, *ppm*	
1	none	0·053	26·6	
2	none	0·053	26·6	
3	none	0·052	26·0	
4	none	0·053	26·7	
5	none	0·052	26·0	
6	none	0·051	25·6	
		Av. 0·052	Av. 26·2	
			Copper recovered, *mg*	Error, *mg*
7	0·079	0·125	0·073	−0·006
8	0·079	0·129	0·077	−0·002
9	0·079	0·126	0·074	−0·005
10	0·158	0·203	0·151	−0·007
11	0·158	0·201	0·149	−0·009
12	0·158	0·202	0·150	−0·008

Iron^{II} tribathophenanthrolinedisulphonic acid as a redox indicator

Because iron^{II} tribathophenanthrolinedisulphonic acid does not form an insoluble perchlorate, it became of interest to learn if it could be used as an oxidation-reduction indicator in solutions containing perchloric acid.

Preparation of indicator solution. To 5·0 ml of 0·0375*M* iron^{II} perchlorate was added 0·302 g of disodium bathophenanthrolinedisulphonate. The resulting solution was diluted to 50 ml, giving a solution 0·00375*M* in iron^{II} tribathophenanthrolinedisulphonic acid.

Standard reduction potential. The formal reduction potential of iron^{II} tribathophenanthrolinedisulphonic acid was determined in both 1*M* sulphuric acid and 1*M* perchloric acid. A solution approximately equimolar in iron^{II} sulphate and iron^{II} tribathophenanthrolinedisulphonic acid and 1*M* in sulphuric acid was titrated with sulphatoceric acid prepared by dissolving cerium^{IV} hydroxide in sulphuric acid and adjusting the sulphuric acid concentration to 1*M*. A platinum foil and a saturated calomel electrode with agar salt bridge were used as electrodes. Two sharp breaks were obtained in the titration curve and the horizontal portion of the curve corresponding to the titration of the iron^{II} bathophenanthrolinedisulphonic acid was sufficiently broad (because of the large amount taken) to permit locating the mid-point with certainty. The mid-point of the first horizontal portion of the curve corresponded to values of the formal reduction potential of the iron^{III}–iron^{II} couple in

1*M* sulphuric acid already reported. The titration was repeated replacing the sulphuric acid with 1*M* perchloric acid in both the titrant and the solution titrated. The results are reported in Table V.

Table V.—Formal reduction potentials of iron^{II} tribathophenanthroline-disulphonic acid in 1*M* sulphuric acid and in 1*M* perchloric acid

	1*M* Sulphuric acid	1*M* Perchloric acid
E° on hydrogen scale, potentiometric*	1·09 V	1·01 V
E° on hydrogen scale, visual†	1·15 V	1·14 V

* From mid-point of titration curve.
† At colour change: green, no red remaining.

Use in the determination of iron in iron ore. A sample of iron ore weighing 0·2 to 0·3 g was transferred to a 500-ml conical flask. To this were added 15 ml of a mixture of equal volumes of 70% perchloric acid and 85% phosphoric acid.[9] A reflux head[8] was inserted into the neck of the flask and the mixture was heated on a hot plate until the ore had dissolved. The mixture was cooled and 70 ml of water added. The reflux head was replaced by a stirring rod and the mixture boiled for 4 min The solution was cooled and 30 ml of dilute sulphuric acid (1 : 1) added. The solution was then passed

Table VI.—Determination of iron in various ores. Cerate titration using iron^{II} bathophenanthrolinedisulphonate

Sample	Iron found, %	Average and standard deviation	Iron reported, %
NBS No. 29a	69·30	69·30	69·54
	69·36	$\sigma = 0·07$	
	69·26		
	69·21		
	69·37		
NBS No. 26	58·23	58·24	58·62*
	58·32	$\sigma = 0·08$	
	58·33		
	58·13		
	58·22		
Lerch Brothers, Incorporated, 1953 Standard†	58·03	58·04	58·19
	58·03	$\sigma = 0·04$	
	57·98		
	58·08		
	58·08		

Electrolytic iron (standardisation)	Normal concentration of cerate solution
	0·07350
	0·07338
	0·07323
	0·07335
	0·07327
	Av. 0·07335
	$\sigma = 0·00010$

* Based on a small number of determinations and not certified.
† Lerch Brothers, Incorporated, Hibbing, Minnesota.

through an amalgamated zinc reductor. The reductor was washed with dilute sulphuric acid (1:20), care being taken not to allow any air to be drawn into the zinc column during the washing operation. Four drops of 0·00375*M* iron^{II} bathophenanthrolinedisulphonate indicator were added and, with vigorous stirring, the iron^{II} was titrated with 0·1*N* perchloratoceric acid. The end-point was marked by a very sharp change from red to green.

The perchloratocerate solution was standardised against electrolytic iron ignited in moist hydrogen (obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio) in exactly the same manner.

The results obtained on three iron ores are reported in Table VI.

CONCLUSIONS AND DISCUSSION

It is evident that room temperature sulphonation with chlorosulphonic acid has produced a disulphonated material from both bathophenanthroline and bathocuproïne. The parent 1:10-phenanthroline cannot be sulphonated under these conditions. It appears reasonable then to assume that the sulphonic groups have entered into the phenyl groups of bathophenanthroline and bathocuproïne, and because a sulphonic group on a phenyl ring tends to hinder further addition to the ring, that one sulphonic group has entered each of the phenyl groups in each case.

Various work has shown that 1:10-phenanthroline and its derivatives act as mono-acidic bases, presumably because the spatial arrangement permits only one proton to enter easily. In these disulphonic acids it might be expected that one proton would be transferred to the ring nitrogen giving the molecule a zwitterion structure. The neutralisation titration curves, (Fig. 1) can be explained on this basis: the first titration corresponds to the neutralisation of the free sulphonic acid, the second to the neutralisation of the proton on the nitrogen. The dissociation constants are:

	pK_1	pK_2
Bathophenanthrolinedisulphonic acid	2·83	5·20
Bathocuproïnedisulphonic acid	2·65	5·80

The second acid dissociation constant of bathocuproïnedisulphonic acid is smaller than that of bathophenanthrolinedisulphonic acid, presumably because the basic character of the latter is enhanced by the presence of the 2— and 9-methyl groups.

The zwitterion structure probably accounts for the failure in either case to obtain a di-ammonium salt on neutralisation of the acids with ammonia and subsequent evaporation and drying.

In preparing either of the disulphonated products particular care must be taken to avoid the introduction of iron and copper inasmuch as the isolation scheme does not adequately separate the free acid from the highly coloured metal derivative. Distillation of the intermediates where possible and the use of reagent-grade chemicals and of de-ionised water help in producing an almost colourless product.

The combining ratios found, 3 for bathophenanthrolinedisulphonic acid and the iron^{II} ion, 2 for bathocuproïnedisulphonic acid and the copper^{I} ion, are the values expected. The combining ratio found for the copper^{I} compound, 2·28, is not as close to 2 as is desirable and we are at a loss to explain the discrepancy; possibly the starting material contained an impurity which was carried through, although the melting point of the bathocuproïne was satisfactory.

The absorption spectra recorded for the iron^{II} and copper^{I} derivatives of the sulphonated reagents (Fig. 1) are essentially the same as those reported by Zak.[6] The sensitivities of these reagents are essentially the same as those of the parent reagents.

	Wavelength of maximum absorption, *mμ*	Molar extinction coefficient
Iron^{II} bathophenanthroline		
Smith and others[1,2]	543	22,143 (water-alcohol)
	533	22,350 (*iso*amyl)
Iron^{II} bathophenanthrolinedisulphonic acid		
Trinder[5]	535	—
This work	535	22,140
Copper^{I} bathocuproïne		
Smith and others[3,4]	479	13,900 (water)
	479	14,160 (n-hexyl)
Copper^{I} bathocuproïnedisulphonic acid		
Zak[6]	485	—
This work	483	12,250

Sulphonation has thus conferred water solubility and freedom from precipitation in a perchlorate solution without impairing the sensitivity.

The wet oxidation of yeast before the determination of its content of iron and copper proved more difficult than anticipated. In preliminary work, digestion with nitric and perchloric acids failed to effect complete destruction of the organic material and the results were erratic. The results were somewhat better with the ternary mixture of nitric, perchloric and sulphuric acids. The preliminary charring with sulphuric acid and subsequent digestion with nitric and perchloric acids produced complete destruction of all organic matter and the results for iron and copper were then satisfactory.

The citric acid added in the procedure for copper is to prevent the precipitation of any iron as the hydrous oxide.

The pH range over which the metal derivatives of the sulphonated reagents are stable extends to nearly pH 11, some two pH units further than the parent reagents; this may be useful under certain circumstances.

The use of iron^{II} bathophenanthrolinedisulphonic acid as redox indicator is very advantageous in cerate oxidimetry since it is soluble in solutions containing perchlorate, whereas the other ferroïn compounds are difficultly soluble. The colour change is vivid and the end-point sharp. The demonstration of the utility of this indicator in the determination of iron in three iron ores is admittedly a bit unconvincing in that the results on all three of the ores studied are all significantly lower than the values reported by others. It did not appear that the perchloric acid-phosphoric acid solvent[9] failed to dissolve all of the ore nor that the method lacked precision. We suggest that our values are correct.

Acknowledgement—The authors wish to express their appreciation of grants of chemicals received from the G. Frederick Smith Chemical Company of Columbus, Ohio.

Zusammenfassung—Bathophenanthrolindisulfonsäure und Bathocuproindisulfonsäure wurden als Natriumsalze isoliert. Beide Substanzen weisen die hohe Empfindlichkeit für Eisen bzw. Kupfer auf, wie die Muttersubstanzen; sind jedoch wasserlöslich und können für Bestimmungen in wässrigen Lösungen (Perchlorat) verwendet werden. Die Störungen durch andere Ionen sind etwa dieselben doch wird der pH-Bereich, in dem die Bestimmungen durchgeführt werden konnen, um etwa 2 Einheiten ins alkalische Gebiet ausgedehnt. Ferro-tribathophenanthrolindisulfonat ist ein ausgezeichneter Redox-indicator (scharfer Farbumschlag von rot nach grun) in der cerimetrischen Titration von Eisen, in perchlorsäurer Lösung.

Résumé—Les acides bathophénanthrolinedisulfonique et bathocuproinésulfonique ont été isolés sous forme solide à l'état de sels de sodium, et caractérisés. Ces deux composés conservent la haute sensibilité des produits apparentés comme réactifs spectrophotométriques respectivement pour le fer et le cuivre. Ils sont solubles dans l'eau, et contrairement aux réactifs apparentés ils peuvent être utilisés dans des solutions aqueuses de perchlorate. Les interférences sont à peu près les mêmes qu'avec les réactifs apparentés, mais le domaine de pH où la formation de la couleur est la plus importante s'étend de 2 unités dans la région alcaline. L'acide tribathophénanthrolinedisulfonique ferreux est un excellent indicateur d'oxydo-réduction, qui vire nettement du rouge au vert dans le dosage du fer ferreux par le cerate; il peut être utilisé dans des solutions contenant de l'acide perchlorique.

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A POLAROGRAPHIC STUDY OF D-GLUCURONOLACTONE

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(*Received* 26 *February* 1960)

Summary—A polarographic study of D-glucuronolactone using a dropping mercury electrode is made. The effects on the wave of various supporting electrolytes, buffers, and maximum suppressors are investigated. The diffusion current shows a linear relationship to concentration for lithium chloride and potassium chloride as supporting electrolytes in the range of 10–100 μg/ml. Pyruvate interferes whereas D-glucose does not.

INTRODUCTION

THE fact that D-glucuronolactone (D-glucurone) is a lactone and is potentially reducible at the dropping mercury electrode suggested the possibility of a polarographic determination. Aldoses and ketoses give kinetic currents and their waves depend on the transformation of the non-reducible cyclic hemi-acetal form to the aldehydo- or keto-form at the electrode.[1,2] Carbohydrates may also be determined polarographically by forming their hydrazones, then reducing them at the dropping mercury electrode.[3,4]

A polarographic study of D-glucuronic acid was reported by Ishidate and Shimozawa.[5] These investigators were not able to obtain reproducible waves and the results were not quantitative for either D-glucuronic acid or D-glucurone. In this communication, an investigation of the effect of the supporting electrolyte, maximum suppressor, pH, types of buffers, and the interference of glucose is discussed.

EXPERIMENTAL

Apparatus

A Beckman pH-meter, Model G, was used to measure pH. An E. H. Sargent polarograph, Model XXI, with a Heyrovský-type cell was used to obtain the polarograms. A polarimeter with monochromator assembly, Rudolph 503, O. C. Rudolph and Sons, served to measure the specific rotation of D-glucurone solutions.

Reagents

The prepared D-glucurone solutions presented a specific rotation $[\alpha_D^{27}]$ of +20·3°. Polarograms obtained after digestion of D-glucurone solutions with nitric-perchloric acid mixture[6,7] gave the same wave as the supporting electrolyte (0·02*N* potassium chloride).

Procedure

The solutions to be analysed were prepared by mixing the appropriate concentrations of D-glucurone, supporting electrolyte, and maximum suppressor in a 100-ml volumetric flask and diluting to volume with distilled water. After proper mixing, the solution to be analysed was transferred to a 25-ml Heyrovský-type polarographic cell. Nitrogen was passed through the solution for 10 min and a polarogram was obtained for each solution, using a drop rate of 4 sec. The polarograms were run through the range of 0·0 to −3·0 V versus the mercury pool.

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RESULTS AND DISCUSSION

Supporting electrolytes

The relationship between diffusion current and concentration of D-glucurone using 0·2N potassium chloride solution as the supporting electrolyte and 0·005% gelatin as the maximum suppressor is given in Table I.

TABLE 1. EFFECT OF D-GLUCURONE CONCENTRATION ON DIFFUSION CURRENT

D-Glucurone concentration, *µg/ml*	Diffusion current, *mA*
100	1·41
80	1·00
80	1·02
60	0·882
40	0·495
20	0·176
20	0·148
20	0·159
10	0·096
10	0·132

The half-wave potential was observed to be −1·56 V versus the mercury pool. The polarographic wave has a sharp maximum at about −1·6 to −1·7 V versus the mercury pool using 0·005% gelatin as the maximum suppressor. Further work revealed that 0·01% gelatin completely suppresses the maximum but the total wave height is somewhat reduced.

Lithium chloride as a supporting electrolyte proved to be superior to potassium chloride if 0·005% gelatin was used as the maximum suppressor. The wave exhibits no maximum and, as is shown in Table II, the relationship of concentration to diffusion current is much more nearly linear than is the case with potassium chloride.

TABLE II. EFFECT OF D-GLUCURONE CONCENTRATION ON DIFFUSION CURRENT

D-Glucurone concentration, *µg/ml*	Diffusion current, *mA*
100	1·23
80	0·888
60	0·612
60	0·623
60	0·576
40	0·366
20	0·120
20	0·111
10	0·062

A typical polarogram using lithium chloride as the supporting electrolyte and 0·005% gelatin as the maximum suppressor is shown in Fig. 1. The half-wave potential is −1·60 V versus the mercury pool. Attempts to use ammonium chloride as a supporting electrolyte were not successful since the electrolyte gave a wave starting at −1·65 V versus the mercury pool.

Degree of hydrolysis

The influence of time on the wave height of D-glucurone was investigated. It was observed that a three-weeks old solution had a similar diffusion current (1·41 mA) to a one-day old solution (1·40 mA). The polarogram was run using 100 μg/ml of D-glucurone in 0·2*N* potassium chloride solution as the supporting electrolyte and 0·005% gelatin as the maximum suppressor. If the fresh solution is heated before analysis, the diffusion current is much less (1·02 mA), pointing to some hydrolysis. Standard solutions of D-glucurone were always stored at 0°–5°, thereby slowing down hydrolysis.

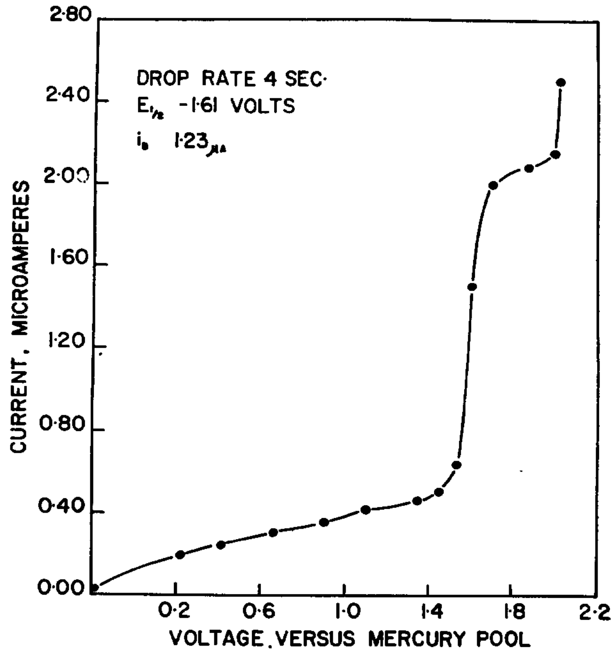

FIG. 1.—Polarogram of 100 μg/ml of D-glucurone using 0.02*N* LiCl as the supporting electrolyte.

Reduction of D*-glucurone in the presence of hydrochloric acid*

Polarograms of 100 μg/ml of D-glucurone in 0·1*N* potassium chloride solution using 4 drops of methyl orange solution (0·1 % in water) as the maximum suppressor, were run at various hydrogen ion concentrations. The effect of hydrogen ion concentration on the diffusion current is shown in Table III.

At acid concentrations above $1 \times 10^{-4}M$, the D-glucurone wave cannot be obtained, but rather a very large wave, beginning at about −1·5 V versus the mercury pool and going off scale rapidly, is observed. Under basic conditions no wave is obtained; upon neutralisation with hydrochloric acid, the wave re-appears. The wave exhibits a more pronounced maximum using methyl orange as the maximum suppressor, but the wave height is somewhat elevated.

TABLE III. EFFECT OF HYDROGEN ION CONCENTRATION ON DIFFUSION CURRENT

Concentration of HCl, *moles/litre*	Diffusion current, *mA*
1×10^{-4}	1·23
1×10^{-5}	1·68
1×10^{-6}	1·80
no acid present	1·70

Interference

The use of any of the standard buffer mixtures, completely suppressed the wave. The buffers usually caused the appearance of a gradual wave at about $-1{\cdot}32$ to $-1{\cdot}7$ V versus the mercury pool. This gradual wave completely eliminated the D-glucurone wave. The buffer systems used were: phthalate buffer,[8] pH 4; Coleman buffers, pH 2, 6, 9; K_2HPO_4–KH_2PO_4 buffer,[8] pH 6; $NaC_2H_3O_2$–$HC_2H_3O_2$ buffer,[9] pH 4; $(C_2H_5)_4NOH + H_3PO_4$ buffer, pH 2·1, 4·1, 6·0, 8·0, 9·4; barbiturate buffer, pH 6, Li_2HPO_4–LiH_2PO_4 buffer, pH 6. Even upon dilution, these buffers inhibited the D-glucurone wave. So extreme is the effect with any form of phosphate buffer, that if, for example, one drop of 0·1*M* potassium dihydrogen phosphate solution is added to the 25-ml polarographic cell containing 100 μg/ml of D-glucurone with potassium chloride as the supporting electrolyte containing 0·005% gelatin as the maximum suppressor, the D-glucurone wave is entirely suppressed. This suggested the possibility of an indirect polarographic determination of phosphate. Present studies indicate that this indirect method for phosphate is feasible. Barbiturate buffer enhanced the wave height because it exhibited a wave of its own in the region of the D-glucurone wave.

Pyruvic acid, when added to D-glucurone solutions, interferes with the D-glucurone wave height. The relationship is not linear, nor is it additive. (Pyruvic acid is converted to lactic acid at the dropping mercury electrode.[10])

Determination of D-*glucurone in the presence of* D-*glucose*

A D-glucose solution (1000 μg/ml) was analysed in 0·1*N* potassium chloride solution using 0·005% gelatin as the maximum suppressor. At sensitivities of 0·003, 0·004, 0·006, and 0·01 mA/mm, the polarograms showed a break at $-1{\cdot}80$ V versus the mercury pool in each case (*i.e.* no characteristic wave was observed). A solution of 50 μg/ml of D-glucurone and 1000 μg/ml of D-glucose in 0·1*N* potassium chloride solution using 0·005% gelatin as the maximum suppressor was analysed in the usual manner. The usual D-glucurone wave was obtained with a diffusion current of 0·60 mA and half-wave potential of $-1{\cdot}56$ V versus the mercury pool (Fig. 2).

CONCLUSION

D-Glucurone exhibits a polarographic wave in potassium chloride or lithium chloride as the supporting electrolyte using gelatin as the maximum suppressor. It is suggested that this wave is due to the lactone since it disappears at high pH levels (hydrolysis occurs) and decreases in magnitude upon heating solutions of D-glucurone before analysis.

The wave obtained with D-glucurone is not due to metal ions, since digestion to dryness of D-glucurone solutions with nitric-perchloric acid mixture causes the wave to disappear.

The complete inability of the system to function in the presence of any type of buffer sets it apart from many types of organic reductions which require well defined media with respect to pH.[11] The type of reduction occurring does not appear to be of the reversible type with controlled pH, but rather of the catalytic type in which the overvoltage of hydrogen is decreased by the lactone, and the diffusion current obtained is proportional to the concentration of the reducible species in solution.

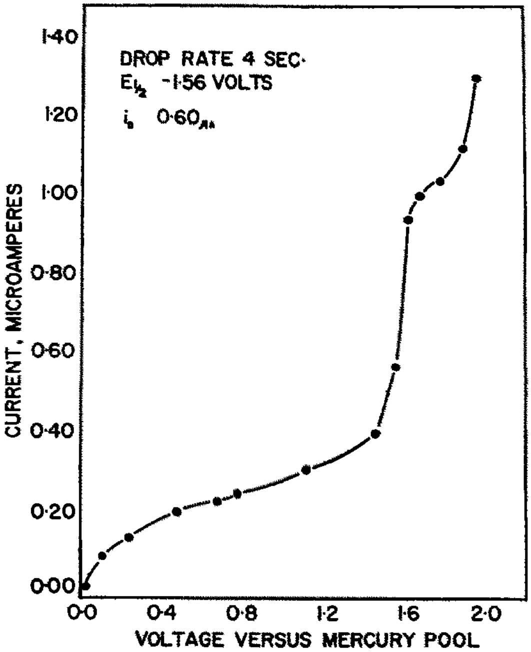

FIG. 2.—Polarogram of a mixture of 50 μg/ml of D-glucurone and 1000 μg/ml of D-glucose in 0.1*N* KCl as the supporting electrolyte.

Zusammenfassung—Eine polarographische Studie mit D-Glucurono-lacton an der tropfendên Quecksilberelektrode wird mitgeteilt. Der Einfluss verschiedener Grundlösungen, Elektrolyte, Puffer und Maximasuppressoren auf die Welle wurde studiert. In Lithium- oder Kaliumchlorid als Grundlösungen ist die Beziehung zwischen Diffusionsstrom und Konzentration linear im Bereich 10–100 μg per ml. Pyruvate stören während D-Glucose ohne Einfluss ist.

Résumé—Les auteurs ont fait une étude polarographique de la D-glucuronolactone en utilisant une électrode á gouttes de mercure. Les actions de différents électrolytes supports, des tampons et des suppresseurs de maximum sur la vague ont été étudiées. Le courant de diffusion varie linéairement avec la concentration dans le domaine 10 μg–100 μg par ml pour les électrolytes supports: chlorure de lithium et chlorure de potassium. Le pyruvate gêne, mais non le D-glucose.

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THE SPECTROFLUOROMETRIC DETERMINATION OF ANTHRACENE, FLUORENE AND PHENANTHRENE IN MIXTURES

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(*Received* 8 *July* 1960)

Summary—A procedure is presented for the spectrofluorometric determination of mixtures of anthracene, fluorene and phenanthrene. The determination depends on differences in fluorescence emission spectra and on selective excitation of anthracene fluorescence. Some of the fluorescence and absorption spectra involved overlap, but these difficulties can be overcome by empirical corrections. The average relative error in this method is less than 5% over the concentration range 0 to 5 ppm.

THE use of the spectrofluorometer has greatly facilitated the fluorometric resolution of mixtures of compounds, particularly those depending on selective excitation and significant differences in fluorescent emission spectra.

The fluorescence spectra, uncorrected for instrumental differences of sensitivity with wavelength, of anthracene, fluorene and phenanthrene in absolute methyl alcohol solution are shown in Fig. 1. Casual observation suggests a possible resolution of a mixture of these hydrocarbons in the following manner:

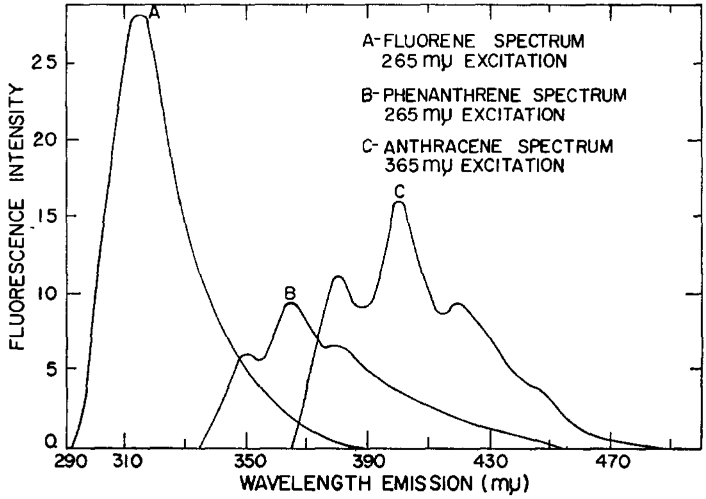

FIG. 1.—Fluorescence spectra of hydrocarbons

(*a*) Only anthracene is fluorescent under 365 mμ-excitation. Therefore, irradiation at this wavelength and measurement of the fluorescence intensity at 400 mμ should yield, directly, the anthracene concentration.

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(*b*) Although excitation with 265 mμ-radiation causes all three compounds to fluoresce, the fluorescence intensity measured at 316 mμ should be a measure of the fluorene concentration.

(*c*) At 350 mμ, under 265 mμ-irradiation, a fluorescence intensity measurement should be the sum of the phenanthrene and fluorene emissions at this wavelength. Since the fluorene concentration would be known from (*b*), the phenanthrene concentration could be determined providing the fluorescence intensities are additive.

In practice, however, the resolution is complicated by the fact that the absorption spectra of anthracene and phenanthrene[3] interfere. Anthracene absorbs at 350 mμ and both anthracene and phenanthrene absorb at 316 mμ. Consequently, only the anthracene emission at 400 mμ, under 365 mμ-excitation, is free from interference and the fluorescence readings at both 316 and 350 mμ are dependent on the concentrations of all three compounds.

Since the concentration of anthracene can be measured independently, a correction can be made for the interaction of anthracene with the fluorescent emission of the other hydrocarbons at 350 and 316 mμ. For example, if the assumption is made that the interaction is only due to absorption, the observed fluorescence intensity, I_f^a, is equal to the fluorescence intensity in the absence of anthracene, I_f°, minus the intensity absorbed by the anthracene present. Thus:

$$I_f^a = I_f^\circ - I_f^\circ(1 - 10^{-K_A C_A}) = I_f^0 \times 10^{-K_A C_A}$$

where K_A is the product of the molar absorptivity of anthracene at the wavelength of fluorescence measurement and the path length of the fluorescent emission, and C_A is the molar concentration of anthracene.

If the above assumptions were correct, a plot of $\log I_f^\circ - \log I_f^a$ versus C_A should be linear. Two such plots, showing the effect of anthracene on the fluorescence of fluorene at 350 and 316 mμ are shown in Figs. 2 and 3. Although the plots are not linear, they may be used for correction purposes.

The curves were obtained by observing the decrease in the fluorescence intensity of fluorene at 316 and 350 mμ as a function of anthracene concentration. The decrease was only a function of the anthracene concentration and was independent of the fluorene concentration. Furthermore, the 350 mμ-correction is also satisfactory for use with phenanthrene fluorescence.

With the above information and the appropriate calibration curves, mixtures of anthracene and phenanthrene or anthracene and fluorene can be resolved easily.

Mixtures containing phenanthrene and fluorene appear to be more difficult because of the mutual dependence of their fluorescence intensities at both 316 and 350 mμ. However, a simple graphical method[4] can be used to resolve this difficulty. Any combination of 316 mμ- and 350 mμ-fluorescence intensities must be unique for the concentrations of phenanthrene and fluorene involved. The fluorescence intensities of a series of fluorene and phenanthrene mixtures were measured at 316 and 350 mμ. These were plotted against each other and the points corresponding to identical fluorene concentrations were joined. Likewise, the points corresponding to identical phenanthrene concentrations were joined. The resulting calibration grid,

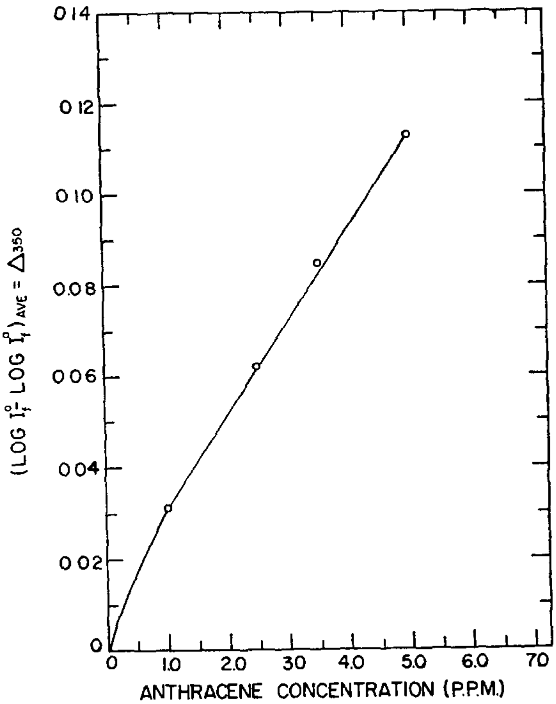

FIG. 2.—Anthracene absorption of 350 mμ emission

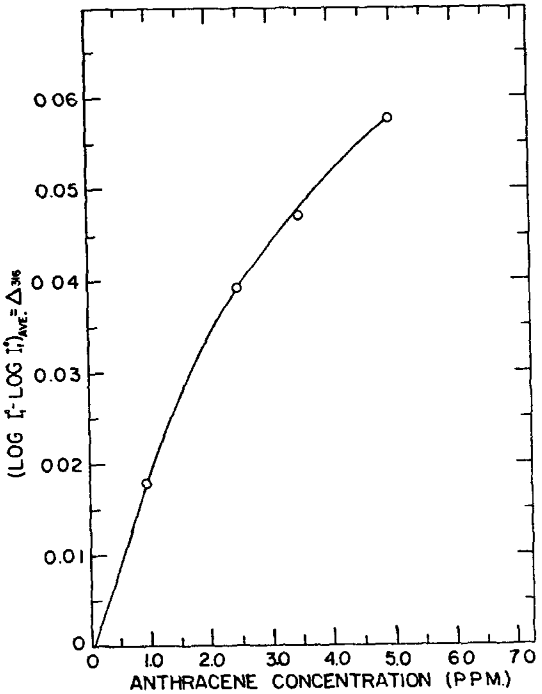

FIG. 3.—Anthracene absorption of 316 mμ emission

shown in Fig. 4, serves as a standard calibration curve for both fluorene and phenanthrene. If anthracene is present the 316- and 350 mμ-measurements must be corrected for anthracene absorption before using the calibration grid.

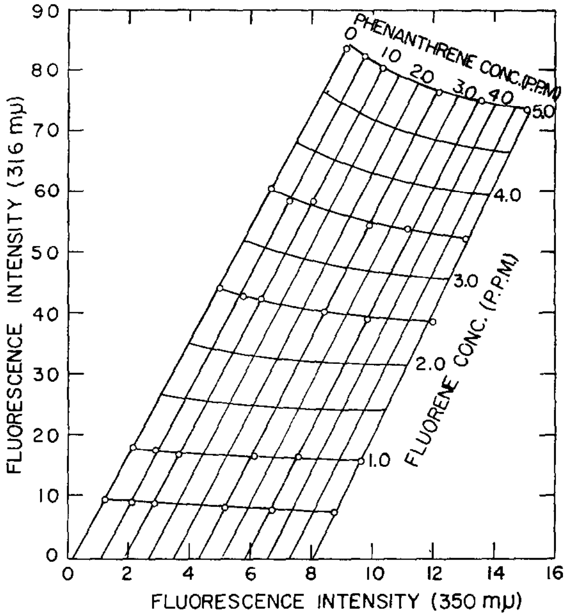

FIG. 4.—Calibration grid

EXPERIMENTAL

Reagents

The anthracene and phenanthrene were purified by azeotropic distillation, under reduced pressure, with ethylene glycol and diethylene glycol according to the procedure of Feldman *et al.*[2] The fluorene was purified by repeated vacuum sublimation. The starting materials in all of the purification procedures were Eastman White Label Chemicals. Baker's analysed absolute methanol was used as the hydrocarbon solvent.

Stock solutions of the three purified hydrocarbons were prepared which contained 0·5 mg of hydrocarbon per ml of solution. All subsequent solutions used were prepared by direct methanolic dilution of these stock solutions.

Apparatus

The spectrofluorometer employed was that described by the writers in a previous study.[5] The instrument was calibrated each time before use with a standard solution containing 3·50 ppm of anthracene. The instrument was set to read 17·0 at 400 mμ under 365 mμ-excitation. The methanolic solution of anthracene was chosen as a calibration standard because of the well known oxygen quenching of the fluorescence of polynuclear hydrocarbons.[1,6] Employing a standard which is also subject to oxygen quenching should eliminate any effect of day-to-day fluctuations in oxygen concentration.

Calibration graphs

A series of solutions of the three hydrocarbons was prepared to cover the range from 0·5 to 5·0 ppm. Each solution was made by transferring an aliquot portion of the appropriate standard stock solution to a 100 ml-volumetric flask, diluting to the mark with absolute methyl alcohol and mixing thoroughly.

The anthracene readings were obtained by measuring the fluorescence intensities of the anthracene solutions at 400 $m\mu$ under 365 $m\mu$-excitation. The anthracene calibration curve was prepared from these data.

The calibration grid for phenanthrene and fluorene was prepared by measuring fluorescence intensities at 350 $m\mu$ and 316 $m\mu$ under 265 $m\mu$-excitation of mixtures of phenanthrene and fluorene. The mixtures were prepared to cover the ranges of 0–5 ppm of phenanthrene and 0–5 ppm of fluorene.

The correction curve for anthracene absorption was prepared as stated before.

Calibration curves of the three hydrocarbons show linearity over the concentration range of 0–5 ppm; consequently, this was used as the upper concentration limit in this study. However, the plots are smooth curves above 5 ppm and the concentration range could probably be extended.

Procedure

A series of unknown solutions were prepared comprising the four types of possible mixtures. These were prepared by dilution of aliquot portions drawn from standard stock solutions. The solutions were then excited with 365 $m\mu$-radiation and the fluorescence intensity, if any, was measured at 400 $m\mu$. This measurement is used directly with the anthracene calibration curve, to obtain the concentration of anthracene present. The wavelength of excitation is changed to 265 $m\mu$ and fluorescence intensity measurements are made at 316 and 350 $m\mu$. These measurements are corrected for anthracene absorption, if it is present, and are used with the calibration grid to obtain the concentrations of phenanthrene and fluorene present. If initial measurements indicate that the concentration of any of the hydrocarbons is greater than 5 ppm, a suitable dilution with methyl alcohol can be made to bring the concentrations into the proper range.

TABLE I. RESULTS OF HYDROCARBON MIXTURE ANALYSIS

Anthracene			Phenanthrene			Fluorene		
Taken, *ppm*	Found (400 $m\mu$), *ppm*	Percent error	Taken, *ppm*	Found, *ppm*	Percent error	Taken, *ppm*	Found, *ppm*	Percent error
0·75	0·73	−2·6	4·00	4·06	+1·5	—	—	—
1·00	1·00	0	1·00	1·05	+5·0	—	—	—
1·50	1·44	−4·2	—	—	—	3·00	3·07	+2·3
2·00	1·95	−2·5	—	—	—	3·00	2·14	+7·0
3·00	2·95	−1·7	—	—	—	1·00	1·05	+5·0
—	—	—	1·00	0·85	−15·0	3·00	3·04	+1·3
—	—	—	2·00	1·90	−5·0	2·00	2·05	+2·5
—	—	—	3·00	2·92	−2·7	1·00	0·98	−2·0
—	—	—	3·50	3·75	+7·1	1·00	1·00	0
—	—	—	3·50	3·50	0	2·50	2·52	+0·8
—	—	—	5·00	5·05	−1·0	3·80	3·45	−1·4
1·00	0·97	−3·0	2·00	1·78	−11·0	3·00	3·15	+5·0
2·00	1·97	−1·5	3·00	2·93	−2·3	2·00	2·20	+10·0
2·00	1·97	−1·5	2·00	2·10	+5·0	2·00	2·20	+10·0
3·00	2·93	−2·3	1·00	0·99	−1·0	1·00	1·02	+2·0
3·50	3·50	0	3·00	3·00	0	3·00	3·20	+6·7
1·50	1·52	+1·4	4·00	4·34	+8·5	1·00	1·05	+5·0

RESULTS

The results obtained on the mixtures prepared are summarised in Table I. The average errors found in the determinations of the three hydrocarbons were as follows:

Anthracene, $E_{ave.} = 1·9\%$
Phenanthrene, $E_{ave.} = 4·6\%$
Fluorene, $E_{ave.} = 4·1\%$

The maximum error observed was 15%; however, errors of this order of magnitude are exceptional and in the majority of determinations the error is less than ±5%.

Acknowledgement—The authors are indebted to the Eastman Kodak Company for financial support during this investigation.

Zusammenfassung—Ein Methode zur spektrofluorimetrischen Bestimmung von Anthracen, Phananthren und Fluoren wird mitgeteilt. Die Bestimmung beruht auf den Unterschieden in den Fluoreszenspektren und der selektiven Anregung der Anthracenfluorescenz. Einige der Fluoreszenz- und Absortionsspektren überschneiden sich, jedoch kann diese Schwierigkeit durch Anbringen einer empirischen Korrektur überwunden werden. Der mittlere relative Fehler der Methode ist weniger als 5% im Konzentrationsbereich 0–5 ppm.

Résumé—Les auteurs présentent un procédé de dosage spectrofluorométrique de mélanges d'anthracène, de phénanthrène et de fluorène. Le dosage dépend des différences des spectres d'émission fluorescents et de l'excitation sélective de la fluorescence de l'anthracène. Certains des spectres de fluorescence et d'absoprtion considérés se recouvrent, mais ces difficultés peuvent être surmontées par des corrections empiriques. L'erreur relative moyenne dans cette méthode est inférieure à 5 pour cent dans le domaine de concentration 0–5 p.p.m.

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DETERMINATION OF CALCIUM IN LITHIUM SALTS

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Summary—Two procedures are described for the determination of traces of calcium in lithium salts. In both procedures the calcium is titrated with very dilute EDTA and the end-point is determined fluorometrically with Calcein as indicator. This titration is carried out in the presence of the lithium salt in one procedure; in the other, a preliminary separation of the calcium is made on the chelating exchange resin, Dowex A-1.

THE determination of small amounts of calcium in lithium compounds is of some significance owing to the detrimental effects of calcium in certain commercial uses of lithium salts. The ethylenediaminetetra-acetate (EDTA) titration offers an obvious way of circumventing the tedious gravimetric oxalate method but unfortunately the usual indicator, Eriochrome Black T, does not function properly in the presence of large amounts of lithium. We have now found that the fluorescein-methylene-iminodiacetic acid indicator (Calcein) of Diehl and Ellingboe[1] provides a fairly satisfactory fluorometric method of locating the end-point in this titration, but that if sufficient time is available greater precision can be obtained by making a preliminary separation of the calcium from the lithium with the chelating resin Dowex A–1.

Dowex A-1 is a co-polymer of divinylbenzene and styrene into which iminodiacetic acid groups have been introduced. The resin has a strong affinity for those cations which form non-ionised compounds with iminodiacetic acid and according to data published by the Dow Chemical Company,[2] calcium can be efficiently separated from sodium with this resin. This suggests that calcium might be similarly separated from lithium and this has proved true. Samples containing lithium chloride in amounts many times more than equivalent to the capacity of the resin in the column may be passed through the column; the calcium is absorbed quantitatively although only up to the point where calcium equivalent to about 1% of the capacity of the column has been taken up. The calcium is eluted with $2N$ hydrochloric acid, the acid neutralised with potassium hydroxide, and the calcium titrated with EDTA, the visual end-point with Calcein being satisfactory but the fluorometric end-point being better.

EXPERIMENTAL

Apparatus and reagents

Dowex A-1 *chelating resin column:* Seal together two lengths of borosilicate tubing, one of 15-mm inside diameter and 15 cm long and the other of 6-mm inside diameter and 10 cm long. Draw down the smaller end somewhat so that it will retain a small plug of borosilicate wool to support the resin. Connect a borosilicate nozzle of small bore to the bottom of the column by means of a piece of surgical rubber tubing so that the flow-rate can be adjusted with a screw clamp. Transfer to the column 2·0 to 2·5 ml of Dowex A-1 chelating resin in the water-swollen, salt form. The upper, larger-diameter portion of the column serves as a reservoir.

Calcein: Dissolve 0·1 g of Calcein W (the sodium salt of Calcein, available from the G. Frederick Smith Chemical Company, Columbus, Ohio) in 100 ml of water. This solution is satisfactory for several weeks. Alternatively prepare this stock solution from Calcein (the free acid, also available from the same company) by dissolving 0·1 g in 100 ml of water containing 0·5 ml of 2*N* potassium hydroxide; a solution prepared in this way is stable for only 3 or 4 days, presumably because of the excess alkali. From this stock solution prepare daily a 0·0033% solution by diluting 1 ml of the 0·1% solution to 30 ml with de-ionized water.

Water and other reagents. Use only demineralized water (passage through Amberlite MB-1) in making up the various solutions and in the analysis. Use hydrochloric acid and potassium hydroxide which are low in calcium as determined by running through the entire procedure but omitting the lithium chloride. Use potassium hydroxide rather than sodium hydroxide as it gives less fluorescence with Calcein.[3]

Preparation of calcium-free lithium chloride: Filter a hot, concentrated solution of lithium chloride through a sintered-glass filter of fine or medium porosity. Filter paper has no strength in hot, concentrated solutions of lithium chloride and invariably breaks under the weight of the liquid. Cool the solution to room temperature and filter off the crystals of lithium chloride which form using a sintered-glass filter. Prepare a saturated solution (about 43%) of this lithium chloride in water and store the solution in a polyethylene bottle.

Prepare an ion-exchange column containing about 20 ml of Dowex A-1 chelating resin in the salt form. Pass 100 ml of 2*N* hydrochloric acid through the column and then 50 ml of water. Pass through the column 60 ml of 2*N* lithium hydroxide to which disodium dihydrogen ethylenediaminetetra-acetate equivalent to 6 mg of calcium has been added. Wash the column very thoroughly with water. The column is now in the lithium form and free of calcium.

Dilute the saturated lithium chloride solution to a concentration of about 100 mg per ml. Make the solution basic by the addition of 5 ml of 2*N* lithium hydroxide per litre of lithium chloride solution. Pass up to 4 litres of this solution through the column at the rate of 10 ml per min. Store the resulting calcium-free solution in a polyethylene bottle or concentrate to recover crystalline lithium chloride.

Calcium-free potassium hydroxide solution: This may be prepared with a Dowex A-1 resin column, by a procedure similar to that described for the preparation of calcium-free lithium chloride.

Photofluorometer. Two different photofluorometers were used at the two laboratories where this work was done, a Coleman Model 12 Electronic Photofluorometer provided with filters No. 12–223 (exciting beam) and No. PC-2 (fluorescent beam) and a non-commercial instrument constructed from a Sylvania 4-watt Black Lite, a Wratten K3 filter, a Weston 856RR, helium-filled Photronic photoelectric cell, and a General Electric galvanometer, 0·001 μA./mm. Pyrex test-tubes were used as cells in both instruments.

Recommended procedure for the determination of calcium in lithium salts with preliminary separation of calcium

Throughout this determination, when liquid is being passed through the column of Dowex A-1, use a flow-rate of not more than 2 ml per min. Prepare the resin column by passing through it 10 ml of 2*N* hydrochloric acid. Wash the column with 10 ml of water added in small portions. Pass 3 ml of 2*N* potassium hydroxide through the column and follow with 10 ml of water. Avoid an excess of potassium hydroxide as any calcium in it is retained by the resin. The resin approximately doubles in size on passing from the hydrogen to the potassium form. The resin should not be stored in the hydrogen form because this causes a decrease in its capacity.

Weigh 2 g of the lithium salt (chloride, bromide or sulphate) to be analysed. Dissolve it in 25 ml of water and make the solution basic with 2 or 3 drops of 2*N* potassium hydroxide. Pass the solution through the column. Wash the column with 5 ml of water. Discard the liquid which has passed through the column. Elute the calcium with 4 ml of 2*N* hydrochloric acid. Wash the column with two 3-ml portions of water. Neutralise the eluate with 2*N* potassium hydroxide and add an excess of 1 ml. Add 1 drop of 0·1% solution of Calcein and titrate with 0·005*M* disodium dihydrogen ethylenediaminetetra-acetate, observing the end-point visually. The end-point is marked by a sharp decrease in the fluorescent colour. The change is somewhat more easily observed under ultraviolet light. Alternatively, and with better results, the titration may be carried out as a fluorometric titration as described below.

Standardise the EDTA solution by titrating a suitable aliquot of a standard calcium solution prepared by dissolving calcium carbonate in hydrochloric acid; use Calcein as indicator.

Samples larger than 2 g may be used and as little as 0·0002% of calcium detected in lithium chloride. With larger samples use a correspondingly greater volume of water and a slightly lower flow-rate.

Procedure for the determination of calcium in lithium salts by the EDTA-Calcein-fluorometric method without prior separation

Employ procedure (A) or (B) or a slight modification thereof depending on the characteristics of the fluorometer.

(A) *Using the Coleman Model* 12 *electronic photofluorometer.* Weigh directly into a fluorometer cuvette a sample of 100 mg of the lithium salt (chloride, bromide or sulphate) to be analysed. Dissolve the sample in about 10 ml of water and make the solution basic by the addition of 1·0 ml of 2*N* potassium hydroxide. Add 5 drops of 0·0033% Calcein. Titrate with 0·00025*M* disodium dihydrogen ethylenediaminetetra-acetate.

After the addition of each increment of EDTA stir the solution by bubbling through it a stream of air introduced through a length of very small-bore polyethylene tubing. Measure the fluorescence after each addition. Plot the fluorescence intensities found against the volume of EDTA added and draw straight lines through the vertical and horizontal portions of the results. From the end-point, as indicated by the intersection of the lines, calculate the calcium in the sample.

(B) *Using the locally constructed photofluorometer with Wratten K*3 *filter.* Weigh a sample of 1 g of the lithium salt (chloride, bromide or sulphate) to be analysed directly into the fluorometer cell. Dissolve the sample in about 27 ml of water and make the solution basic by the addition of 3·0 ml of 2*N* potassium hydroxide. Add 5 drops of a 0·1% solution of Calcein. Titrate with 0·0005*M* disodium dihydrogen ethylenediaminetetra-acetate. Continue as given in the second paragraph of procedure (A) above.

RESULTS AND DISCUSSION

Several samples of lithium chloride were analysed according to the recommended procedure involving the prior separation of the calcium on the Dowex A-1 resin. Additional calcium was added to some of the samples. The results of some of the analyses are summarised in Tables I and II. It was found that owing to the very large ratio of lithium to calcium in the samples, the resin would only take up about 1% of its theoretical capacity for calcium (theoretical capacity: 15 mg of calcium for 2·5 ml of resin; limit: 1% of this or 0·15 mg of calcium). This puts a limitation on the size of the sample and the amount of calcium which can be handled in one determination. Although the method does not possess the simplicity that might be desired, it does permit the detection of as little as 0·0002% calcium.

The fluorometric titration procedure, Procedure (A), was tested on 100-mg samples of lithium chloride, purified by the ion-exchange procedure given above, to which 2–20 μg of calcium were added. The results are given in Table III. A typical titration curve for a sample containing 5 μg of calcium is shown in Fig. 1. Procedure (B) was tested on 1-g samples of various lithium salts "spiked" with various amounts of calcium; the results are given in Table III and a typical titration curve, for a sample containing 50 μg of calcium, is shown in Fig. 2.

The fluorometric titration method without prior concentration of the calcium with the Dowex A-1 resin is the more rapid of the two procedures. The precision is satisfactory, but 0·001% of calcium is the least amount that can be determined in lithium chloride by this method. Concentration of the calcium by the ion-exchange

TABLE I.—DETERMINATION OF CALCIUM IN LITHIUM SALTS BY THE RECOMMENDED PROCEDURE INVOLVING PRELIMINARY SEPARATION OF CALCIUM WITH DOWEX A-1

Lithium salt taken,	Calcium found,	
g	*μg*	%*
Visual end-point		
LiCl (Lot A)		
15·0	34	0·00022
20·0	34	0·00016
LiCl (Lot B)		
2·0	26	0·0011
LiCl (Lot C)		
2·0	35	0·0016
10·0	120	0·0012
Fluorometric end-point		
LiCl (Lot A)		
2·0	6·8	0·00019
2·0	6·4	0·00017
2·0	7·4	0·00022
LiCl (Lot D)		
2·0	7·1	0·00020
2·0	6·4	0·00017
2·0	6·7	0·00018
LiBr (Lot E)		
2·0	48·5	0·0023
2·0	47·5	0·0022
2·0	46·5	0·0021
Li_2SO_4 (Lot F)		
2·0	10·0	0·00035
2·0	9·7	0·00033
2·0	9·8	0·00034
Blank		
0·0	3·0	—
0·0	2·8	—
0·0	3·1	—

Lot A. Purified by Dowex A-1 method described above; average = 0·00020% calcium.

Lot B. Purified by simple recrystallisation; average = 0·0011% calcium.

Lot C. As received from Lithium Corporation of America; average = 0·0014% calcium.

Lot D. Purified by Dowex A-1 method described above; average = 0·00019% calcium.

Lot E. Commercial material, Lithium Corporation of America: average = 0·0022% calcium.

Lot F. Commercial material, Lithium Corporation of America; average = 0·00034% calcium.

* % Calcium found is calculated after subtracting the average blank, 3·0 μg, from the calcium found.

TABLE II.—DETERMINATION OF CALCIUM IN LITHIUM CHLORIDE BY THE RECOMMENDED PROCEDURE INVOLVING PRELIMINARY SEPARATION OF THE CALCIUM WITH DOWEX A-1

Lithium chloride taken, *g*	Calcium added, *μg*	Total calcium* present, *μg*	Calcium found, *μg*	Error, *μg*
Visual end-point				
Lot A. 20·0	200	243	196	−47
Lot B. 2·0	50	75	74	−1
2·0	100	125	120	−5
Fluorometric end-point				
Lot A. 2·0	20	26·9	28·3	+1·4
2·0	20	26·9	27·8	+0·9
2·0	20	26·9	27·6	+0·7

Lot A. Purified by Dowex A-1 method described above; value of 0.00020 % calcium (from Table 1) used in calculating total calcium present.

Lot B. Purified by simple recrystallisation; value of 0·0011 % calcium (from Table 1) used in calculating the total calcium present.

* Total calcium values include 2·9 μg added with reagents.

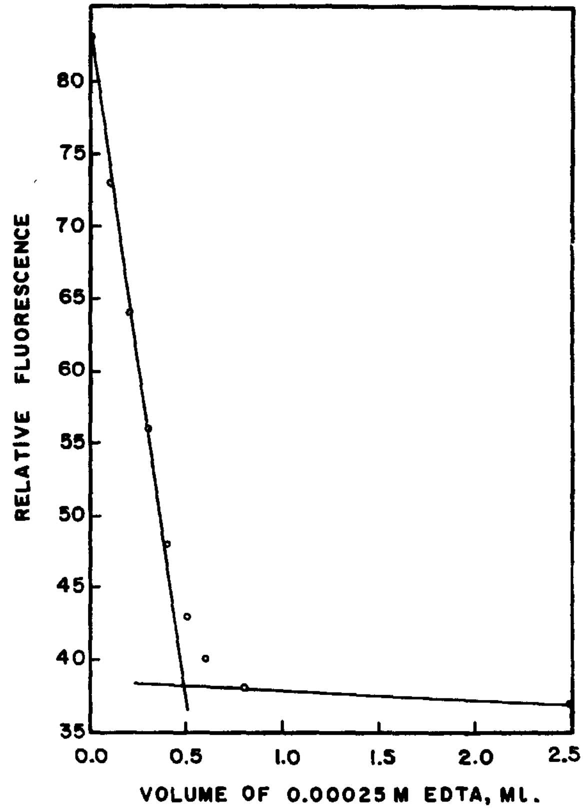

FIG. 1.—Fluorometric titration of 5 μg of calcium in 100 mg of lithium chloride with EDTA using Calcein indicator [Procedure (A), Coleman Model 12 Fluorometer].

procedure followed by the fluorometric titration extends the sensitivity to 0·0002% of calcium. The precision is good unless too large a sample is taken. The visual titration following concentration also permits the detection of as little as 0·0002% of calcium but does not possess the precision of the fluorometric titration and generally requires the use of larger samples. This, in turn, requires proportionately longer time.

The methods are applicable to lithium chloride, bromide and sulphate and undoubtedly to other lithium salts.

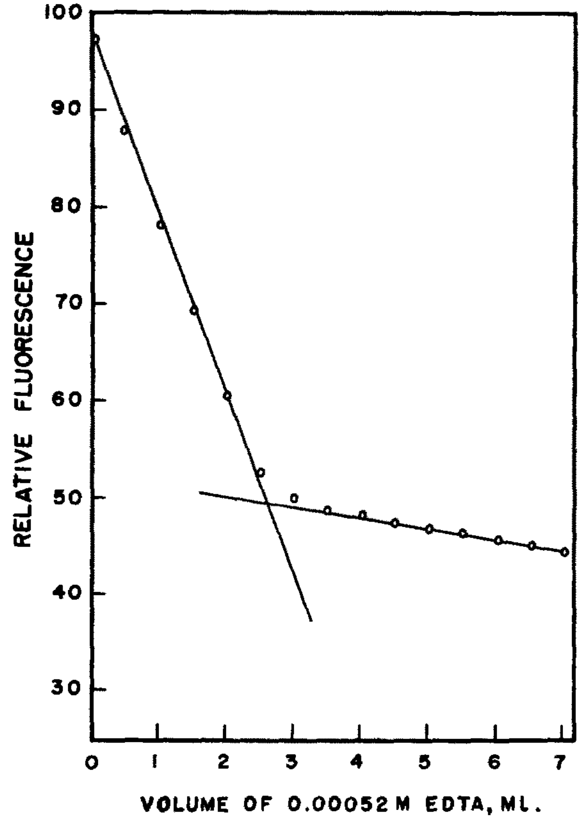

FIG. 2.—Fluorometric titration of 50 μg of calcium in 1 g of lithium chloride with EDTA using Calcein indicator [Procedure (B), Collins Fluorometer].

Magnesium, provided it is not a major constituent, does not interfere with the determination of calcium. Aluminium, up to at least 0·1%, causes no interference. Iron above 0·1% does cause interference.

Although it was reported by Diehl and Ellingboe[1] that strontium and barium are titrated together with calcium at pH 12 by EDTA using Calcein as indicator, barium was found not to interfere in the procedures described here. Thus, using 1-g samples of lithium chloride containing 26 μg of calcium (as determined by fluorometric titration) to which were added 276 μg and 552 μg of barium, 27·8 and 27·2 μg of calcium were found [Procedure (*B*)]. Also, in the presence of lithium bromide, barium is not titrated. It may be that the potassium hydroxide contained sufficient carbonate to precipitate all the barium; sodium hydroxide was used in the original procedure of

TABLE III.—DETERMINATION OF CALCIUM IN LITHIUM SALTS BY THE FLUOROMETRIC TITRATION PROCEDURE WITHOUT PRELIMINARY SEPARATION

Calcium added, µg		Total calcium present, µg	Total calcium found, µg	Error, µg
0·100-g Sample [Procedure (A) Coleman Fluorometer]				
LiCl (Lot A)*	2·0	2·2	1·5	−0·7
	2·0	2·2	2·0	−0·2
	2·0	2·2	2·2	0·0
	5·0	5·2	4·6	−0·6
	5·0	5·2	4·9	−0·3
	5·0	5·2	5·1	−0·1
	10·0	10·2	9·5	−0·7
	10·0	10·2	9·9	−0·3
	10·0	10·2	9·7	−0·5
	20·0	20·2	19·7	−0·5
	20·0	20·2	19·8	−0·4
	20·0	20·2	20·1	−0·1
1·00-g Sample [Procedure (B), Collins Fluorometer]				
LiCl (Lot D)	0·0	1·9	7·3	+5·4
	10·0	11·9	14·0	+2·1
	10·0	11·9	11·5	−0·4
	10·0	11·9	14·3	+2·4
	10·0	11·9	15·4	+3·5
	20·0	21·9	23·6	+1·7
	20·0	21·9	25·8	+3·9
	20·0	21·9	23·7	+1·8
	20·0	21·9	24·1	+2·2
	25·0	26·9	28·1	+1·2
	25·0	26·9	27·4	+0·5
	50·0	51·9	52·3	+0·4
	50·0	51·9	53·1	+1·2
	50·0	51·9	52·9	+1·0
	50·0	51·9	52·7	+0·8
	50·0	51·9	55·0	+3·1
	50·0	51·9	53·5	+1·6
	50·0	51·9	54·4	+2·5
	50·0	51·9	54·1	+2·2
	50·0	51·9	52·9	+1·0
	50·0	51·9	56·2	+4·3
	50·0	51·9	54·7	+2·8
	100·0	101·9	103·7	+1·8
	100·0	101·9	100·8	−1·1
	100·0	101·9	103·1	+1·2
	100·0	101·9	101·2	−0·7
	100·0	101·9	103·1	+1·2

Table III (*contd.*)

	Calcium added, μg	Total calcium present, μg	Total calcium found, μg	Error, μg
LiBr (Lot E)	0·0	22·2	23·1	+0·9
	50·0	72·2	71·6	−0·6
	50·0	72·2	73·5	+1·3
	100·0	122·2	122·8	+0·6
Li_2SO_4 (Lot F)	10·0	13·4	21·4	+8·0
	50·0	53·4	56·7	+3·3
	50·0	53·4	55·6	+2·2
	100·0	103·4	104·1	+0·7
	100.0	103·4	104·0	+0·6
	50·0	53·4	56·3	+2·9

* Lot designations same as in Table I.

Diehl and Ellingboe but is supplanted here by potassium hydroxide because of the significantly lower fluorescence of potassium with Calcein. Strontium is not titrated in the procedure here described but does render the end-point less distinct. Zinc does not interfere at all.

Zusammenfassung—Zwei Methoden zur Bestimmung von Calcium in Lithiumsalzen werden beschrieben. In beiden Verfahren wird Calcium mit sehr verdünnter ÄDTA-Lösung titriert unter Verwendung von Calcein als Fluorescenzindicator. Bei einer Methode wird das Calcium in Anwesenheit der Lithiumsalze titriert, in der anderen wird das Calciumzverst mittels des chelierenden Ionenaustauschers DOWEX A-1 abgetrennt.

Résumé—Les auteurs décrivent deux méthodes de dosage du calcium dans les sels de lithium. Dans les 2 méthodes, le calcium est dosé avec de l'EDTA très dilué et le point équivalent est déterminé par fluorimétrie avec la calcéïne comme indicateur. Le titrage est réalisé en présence du sel de lithium dans une méthode; dans l'autre, on fait une séparation préliminaire du calcium sur une résine échangeuse d'ions Dowex A-1.

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CO-PRECIPITATION IN SOME BINARY SULPHATE SYSTEMS

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Summary—Studies have been made of the distribution behaviour of tracers with alkaline earth sulphates, using the technique of precipitation from homogeneous solution. The co-precipitation of strontium with barium sulphate and of lead, lanthanum, and yttrium, separately, with barium sulphate, and with strontium sulphate, were investigated. Although there was qualitative correlation between the observed values of the distribution coefficient and the theoretical solubility product ratios for each of the binary systems studied, the divergence between theory and observation was so great that it seems unlikely that there is any quantitative correlation.

I—CO-PRECIPITATION OF STRONTIUM WITH BARIUM SULPHATE

THE co-precipitation of trace impurities with barium salts as carriers has been the object of many studies, a number of which have been concerned with the application and significance of the homogeneous and logarithmic distribution equations.[1]

Several investigators have considered the effect of the fractional rate of precipitation on the logarithmic distribution coefficient.[2,3] For example, Hermann[3] precipitated lanthanum oxalate from homogeneous solution in the presence of actinium. Where the fractional rate of precipitation was constant, Hermann obtained a rate constant from a plot of "log of the carrier concentration in solution" versus "time". In experiments designed to obtain *varying* fractional rates, a plot of rate constant versus the observed distribution coefficient, extrapolated to zero rate of precipitation, gave a value of λ which Hermann designated as the "maximum (or minimum) limiting distribution coefficients". Hermann attributed the change in the distribution coefficient, *i.e.* variable co-precipitation results, to differing states of supersaturation.

Riehl[4] has also considered the effect of supersaturation on the distribution coefficient with systems in which barium chloride, with radium tracer present, was crystallised from initially quite supersaturated solutions. In Riehl's experiments, the fractional supersaturation‡ varied from nearly 1 at the beginning of precipitation to zero at the end; in contrast, Hermann has postulated that the fractional supersaturation should be constant for the process of precipitation from homogeneous solution.

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‡ Defined as (a − b)/a, where a is the concentration of the barium in the supersaturated solution and b is the concentration of the barium in the final saturated solution.

Hermann derived a modification of the logarithmic distribution equation from Riehl's equation, assuming S′ (fractional supersaturation) to be constant:

$$\log \frac{t_f}{t_i} = \frac{\lambda}{1 + (\lambda - 1)S'} \log \frac{c_f}{c_i} \tag{1}$$

where t_f, t_i, c_f, and c_i refer to the final and initial concentrations of the tracer and carrier respectively. Where S' is zero, then the usual form of the logarithmic distribution equation, *i.e.*

$$\log \frac{t_f}{t_i} = \lambda \log \frac{c_f}{c_i} \tag{2}$$

is obtained. If the value of λ calculated from equation (2) is dependent upon supersaturation (or on the fractional rate of precipitation), this could then explain the inability to relate distribution coefficient and solubility products.[2]

Studies of the distribution behaviour of tracers with alkaline earth sulphates, using the technique of precipitation from homogeneous solution, are described in this paper. The co-precipitation of strontium with barium sulphate and of lead, lanthanum, and yttrium, separately, with barium sulphate, and with strontium sulphate, were investigated

EXPERIMENTAL

Reagents

All chemicals were reagent-grade. Barium nitrate was purified by recrystallisation from water. To prepare barium-free strontium solutions, a strontium nitrate solution was slowly evaporated and fifteen consecutive 5-g portions of the crystals were discarded; because barium nitrate is less soluble than strontium nitrate, it should concentrate in the discarded solid. The supernatant solution was then diluted to the desired concentration. The solutions of barium and strontium were also used in the later co-precipitation studies involving lead, lanthanum, and yttrium as tracers.

Sulphamic acid was purified[5] and stored in a desiccator until ready for use.

Radioactive Tracers

Both γ- and β-emitting isotopes were used. Strontium-90, from the Oak Ridge National Laboratories, was initially used as a source of carrier-free strontium. The sample was over 2 years old and it was assumed that there was no other activity present but that of strontium and its daughter yttrium-90. However, for a greater part of the study, carrier-free strontium-85, obtained from Nuclear Science and Engineering Corporation, was used because of the convenience of measuring γ activity. The half-life was found experimentally to be 65 days.[6]

High specific activity barium-133 from Oak Ridge National Laboratories was used as a source of γ activity. Barium-140, Oak Ridge National Laboratories, 12·6-day half-life, a γ- and β-emitter, was used when carrier-free barium was required.

Apparatus

A conventional single channel scintillation spectrometer with stabilised high voltage source was used both for γ-ray spectroscopy and for regular γ counting. The γ activity was determined as described by Gordon and Ginsburg.[7] The β activity was measured with an end-window proportional counter flushed with 90% argon-10% methane gas. Precipitations were carried out in the reaction vessel described by Gordon and Rowley.[8] Photometric titrations were performed in an Evelyn colorimeter and pH measurements were taken with a Beckman model H-2 line-operated pH meter.

Method of precipitation of barium sulphate

Barium sulphate was precipitated with sulphamic acid as previously described.[8] In most instances, 40 mg of sulphamic acid per 21 ml of reaction mixture were used. In all cases, 400 mg of ammonium chloride were also added to increase the particle size of the precipitate.[8] Reactions were carried out at 80°. In a few experiments the barium was precipitated for comparison purposes by direct mixing with a solution containing sulphate; in some instances, pre-formed barium sulphate was used. In experiments where the amount of strontium was made so large that the carrier in effect became strontium sulphate, the amount of added sulphamic acid was also made larger than that used in the precipitation of barium in order to decrease the time of initial precipitation of strontium sulphate; however, other conditions were essentially the same as for the precipitation of barium sulphate.

Methods of Analysis

Barium was determined either by photometric titration with EDTA[9] or by radio-assay with previously added barium-133. Strontium was determined either by photometric titration or by radio-assay with strontium-85. Carrier-free strontium-85 was determined by scintillation methods, and carrier-free strontium-90 was determined, in the presence of its daughter, by applying the unmodified form of the Kirby equation.[10] A modified equation, $a_1/A_1 = C_4/C_2$, was employed when the samples were allowed to stand for more than 2 months, where a_1 is the activity of the parent in the unknown, A_1 is the activity of the parent in the standard, C_4 is the counting rate of the mixture, and C_2 is the counting rate of the standard. Two-ml aliquots of the filtrate or of the dissolved precipitate were evaporated, then counted. The efficiency of β counting was determined with Ra-DEF standards of known activity; the concentration of the strontium-90 was thus determined to be approximately 10^{-9} *M*.

Procedure

The following were added to a 100-ml volumetric flask: an aliquot of stock barium (or strontium) nitrate solution, tracer isotope, carrier tracer if the carrier was to be determined by radio-assay, sulphamic acid, and ammonium chloride. The solution was diluted to volume and a 20-ml aliquot pipetted into the reaction cell. One ml of rinse water was used and the cells were then sealed and reacted in an oil bath at 80° ± 0·4° for a desired period of time. When the cell was opened, the filtrate and precipitate were separated by centrifugation.[8] The filtrate was then transferred to a 100-ml volumetric flask and 10 ml of concentrated ammonium hydroxide added to the solution which was then diluted to volume. The resulting solution was analysed for the appropriate alkaline earth cation either by photometric titration, by scintillation counting, or by spectroscopy. The filter frit and its solid contents were placed in a beaker to which was added 50 ml of solution which was 0·02*M* in EDTA and 6·4*M* in ammonium hydroxide. The contents were heated to 80° for several hr to dissolve the precipitate. In cases where the carrier concentration in the precipitate was determined by photometric titration, a known excess of ammoniacal EDTA solution was added and back-titrated with a standard magnesium solution. However, in most cases radio-assay was used.

RESULTS AND DISCUSSION

Precipitation of Barium in the Presence of Trace Quantities of Strontium

Experimental data and results for the co-precipitation of carrier-free strontium-90 and of strontium-85 with barium sulphate are summarised in Tables I and II. The average value of λ in Table I is 0·0143 and in Table II it is 0·0120. A much closer adherence to the logarithmic than the homogeneous distribution equation is definitely indicated. A least squares plot of the results of Table II yielded the equation, $\lambda = 0{\cdot}0114 + 0{\cdot}0009f$ where f is the fraction of barium precipitated; a least squares analysis was made only for the results of Table II because of the greater agreement among the results, which was probably due to the greater reliability of the methods of analysis.

The co-precipitation values of the two tables are plotted in Fig. 1 along with the theoretical curves for λ equal to 0·0143 and to 0·0120. The difference in the two distribution coefficients could easily be due to differences in pH and hence in the fractional rates of precipitation of the barium sulphate. Rate constants (arbitrary units) were determined in a manner analogous to that of Hermann. For the results of Table I, where the experiments were conducted at pH 0·65, the rate constant for the precipitation of barium sulphate was $-(3{\cdot}11 \times 2{\cdot}3) \times 10^{-3}$ per min. For the results of Table II, the rate constants were calculated to be $-(0{\cdot}35 \times 2{\cdot}3) \times 10^{-3}$ per min for pH 1·60,

$-(0\cdot58 \times 2\cdot3) \times 10^{-3}$ per min for pH 1·30, and $-(1\cdot08 \times 2\cdot3) \times 10^{-3}$ per min for pH 1·25. These values are in qualitative agreement with the previously published results[11] for the hydrolysis of sulphamic acid; with the fractional hydrolysis rate increasing with decreasing pH, presumably the fractional rate of precipitation of barium sulphate would also increase. At pH 0·65, the increased fractional rate of precipitation of barium sulphate would be expected, as was found, to result in a larger value of the distribution coefficient.

The fractional rate of precipitation was also increased by increasing the concentration of sulphamic acid, *i.e.* using 150 mg rather than 40 mg of sulphamic acid. The rate constant was determined to be $-(5\cdot95 \times 2\cdot3) \times 10^{-3}$ per min at pH 1·1.

TABLE I. CO-PRECIPITATION OF CARRIER-FREE STRONTIUM-90 WITH BARIUM SULPHATE[a]

Reaction time, *min*	Barium precipitated, %	Strontium co-precipitated, %	λ $\times 10^2$	D $\times 10^2$
255	26·7	0·28 (0·37)	0·95 (1·25)	0·71 (1·06)
475	57·1	0·88 (0·92)	1·00 (1·09)	0·70 (0·70)
597	70·2	1·20 (1·23)	1·00 (1·02)	0·52 (0·53)
701	80·3	1·64 (1·66)	0·97 (1·03)	0·39 (0·42)
816	90·26	2·55 (2·41)	1·09 (1·05)	0·27 (0·27)
649	91·2	4·28 (4·19)	1·80 (1·76)	0·43 (0·42)
723	96·57	5·73 (5·74)	1·75 (1·75)	0·22 (0·22)
780	97·21	4·35 (4·34)	1·27 (1·24)	0·13 (0·13)
942	97·90	4·46	1·18	0·10
780	97·92	6·93 (7·17)	1·85 (1·93)	0·16 (0·16)
1000	98·64	3·82	0·91	0·052
1100	98·91	7·73	1·78	0·092
1315	99·02	6·72 (6·55)	1·50 (1·46)	0·074 (0·069)
1184	99·09	5·47 (5·37)	1·20 (1·19)	0·053 (0·052)
2750	99·25	11·37 (10·80)	2·47 (2·34)	0·090 (0·092)
1318	99·26	8·25 (8·21)	1·80 (1·75)	0·067 (0·067)
1392	99·35	7·43 (7·21)	1·53 (1·49)	0·053 (0·051)
1946	99·50	9·13 (8·97)	1·81 (1·77)	0·050 (0·050)
1987	99·56	9·60 (9·46)	1·88 (1·85)	0·049 (0·049)

[a] 40 mg of sulphamic acid, 19·80 mg of barium, and 400 mg of ammonium chloride in 21-ml volume; final concentration of strontium-90, 2×10^{-9} *M*; pH = 0·65; reaction temperature, 80°.

[b] The results in parentheses were obtained by use of the modified Kirby equation as described in text.

The values of the distribution coefficients are given in Table III. The single experiment in the table in which only 14 mg of sulphamic acid were used gave a distribution coefficient of 0·0106 which is qualitatively correct for the much slower fractional rate of precipitation obtained. The approximately linear relationship of λ with the fractional rate of precipitation (using previously described rate constants) is shown in Fig. 2.

The value of the distribution coefficient obtained by Gordon, Reimer, and Burtt[12]

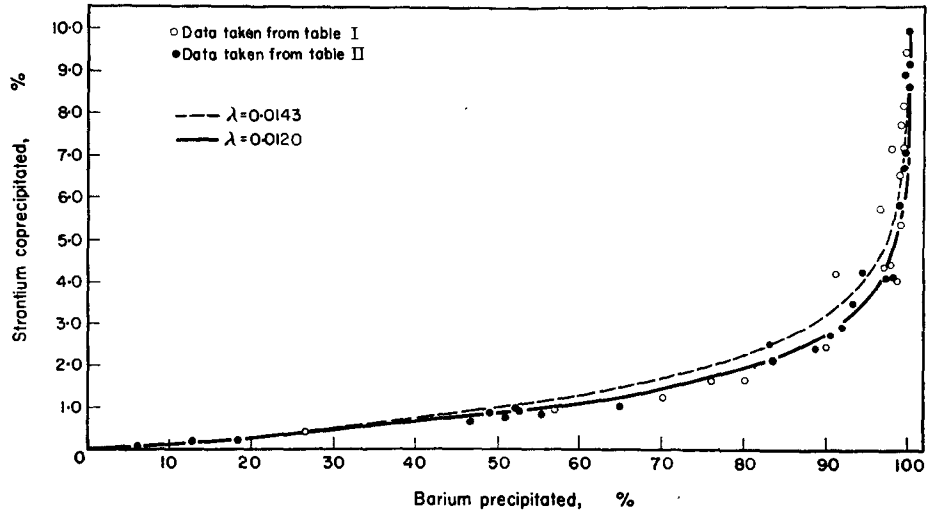

FIG. 1.—Co-precipitation of carrier-free strontium with barium sulphate.

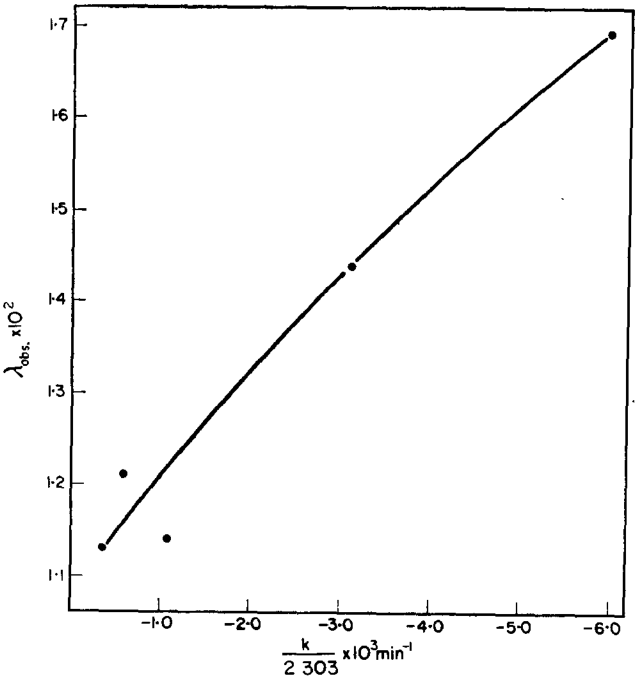

FIG. 2.—Distribution coefficient as a function of fractional rate of precipitation.

TABLE II. CO-PRECIPITATION OF CARRIER-FREE STRONTIUM-85 WITH BARIUM SULPHATE[a]

Reaction time, *min*	pH	Method of analysis of barium[b]	Barium precipitated, %	Strontium co-precipitated, %	$\lambda \times 10^2$	$D \times 10^2$
106	1·60	T	6·2	0·071	1·30	1·08
204	1·60	T	12·8	0·18	1·31	1·23
306	1·60	T	18·4	0·18	0·88	0·80
639	1·60	T	46·7	0·63	1·00	0·72
850	1·60	T	49·1	0·84	1·25	0·88
898	1·60	T	51·0	0·74	1·04	0·72
587	1·60	T	52·2	0·93	1·28	0·87
950	1·60	T	52·7	0·87	1·17	0·79
1104	1·60	T	55·6	0·81	1·00	0·65
1232	1·60	T	65·0	0·99	0·94	0·54
1089	1·60	T	76·1	1·65	1·16	0·54
839	1·25	G	83·2	2·47	1·40	0·51
1596	1·60	T	83·5	2·12	1·19	0·43
1726	1·60	T	88·9	2·40	1·10	0·31
1906	1·60	T	90·78	2·74	1·17	0·29
1814	1·60	T	91·89	2·91	1·18	0·27
1438	1·60	T	91·90	3·10	1·25	0·28
971	1·25	G	93·28	3·49	1·32	0·26
615	1·25	G	94·46	4·26	1·50	0·26
1675	1·60	T	97·40	4·10	1·15	0·11
2185	1·60	T	98·21	4·10	1·04	0·078
1141	1·25	G	98·82	5·86	1·36	0·074
2466	1·60	T	99·37	6·71	1·37	0·046
2151	1·60	T	99·37	7·11	1·46	0·049
898	1·30	G	99·83	7·74	1·23	0·014
3619	1·60	T	99·85	9·96	1·61	0·017
1295	1·25	G	99·90	6·78	1·02	0·0073
1053	1·30	G	99·90	9·16	1·39	0·048
2713	1·60	T	99·90	8·62	1·31	0·0094
759	1·30	G	99·91	7·31	1·10	0·0079

[a] 40 mg of sulphamic acid, 19·80 mg of barium, 400 mg of ammonium chloride, 1 microcurie of barium-133 (where used), and 20 microcuries of strontium-85; reaction temperature, 80°.

[b] T indicates determination of barium by photometric titration with EDTA; G indicates determination of barium by γ counting of barium-133; determination of strontium was by γ counting of strontium-85.

in 20% methanol solutions by the hydrolysis of methyl sulphate at 83° was 0·03 for several different ratios of carrier to tracer concentrations. The differences between this value and those obtained in the present study may be attributed either to a significant difference in the fractional rate of precipitation, or to variation in the carrier to tracer ratios, or to the media used. For example, in their study, 15 hr were required to precipitate 94% of the barium while in the present study the time necessary to precipitate 92% of the barium was approximately 32 hr, which could easily account for the larger constant obtained, *i.e.* 0·03.

Experiments were performed in which there was direct mixing of solutions of barium and sulphate, where the fractional rate of precipitation would be considerably increased. The results are shown in Table IV. The value of λ was approximately 1·0 (for the first two experiments of the table conducted at the lower temperature of 25°).

It is somewhat difficult to compare this value of λ obtained at 25° with previous values of λ ($\simeq$0·01) obtained at 80° because of the temperature dependence of the distribution coefficient. However, a value of λ approaching unity would be expected for rapid precipitation regardless of temperature. Perhaps more striking are the results for the last two experiments of Table IV in which λ was determined to be 0·027 for the slower method of precipitation and to be 0·22 for the rapid method, after a long period of digestion which could only have served to reduce the latter value from some previously greater value.

TABLE III. EFFECT OF CHANGE OF FRACTIONAL RATE OF PRECIPITATION UPON CO-PRECIPITATION[a]

Reaction time, *min*	Sulphamic acid, *mg*	Barium precipitated, %	Strontium co-precipitated, %	$\lambda \times 10^2$	$D \times 10^2$
5839	14·0	86·3	2·09	1·06	0·34
105	150·0	54·3	1·26	1·62	1·08
156	150·0	85·8	3·40	1·77	0·58
201	150·0	87·8	3·47	1·68	0·45
429	150·0	99·50	15·25	3·54	0·095
255	150·0	99·83	10·20	1·69	0·019
480	150·0	99·80	15·62	2·73	0·37
375	150·0	99·86	12·67	2·09	0·021

[a] 19·80 mg of barium, 400 mg of ammonium chloride, 1 microcurie of barium-133, and 10 microcuries of strontium-85; pH = 1·1; reaction temperature, 80°; analyses of barium and strontium were performed by scintillation spectrometry.

TABLE IV. EFFECT OF METHOD OF PRECIPITATION ON DISTRIBUTION COEFFICIENT[a]

Reaction time, *min*	pH	Reaction temperature, °*C*	Method of precipitation	Method of analysis		Barium precipitated, %	Strontium co-precipitated, %	λ	D
				Carrier	Tracer				
120	0·65	25	Direct mixing	b	c	98·82	98·69	0·98	0·90
120	0·65	25	Direct mixing	b	c	98·82	98·41	0·97	0·84
14490	1·25	80	Homogeneous[d]	e	e	99·91	16·30	0·027	0·0002
14490	1·25	80	Direct mixing	e	e	99·83	75·40	0·22	0·005

[a] 19·80 mg of barium, 54 mg of ammonium sulphate, 1 microcurie of barium-133 (where used), and 20 microcuries of strontium-85.

[b] Barium determined by photometric titration with EDTA.

[c] Strontium determined by β counting (Kirby method).

[d] 40 mg of sulphamic acid used in place of ammonium sulphate.

[e] Barium and strontium both determined by scintillation spectroscopy.

Variation of the Mole Fraction Ratio of Barium to Strontium

Several experiments were performed in which the mole fraction of barium in the initial barium-strontium mixture (0·144 millimoles total) ranged from 0·896 to virtually zero, *i.e.* for the precipitation of strontium sulphate in the presence of a trace quantity of carrier-free barium-140. In general, conditions were employed similar to those of the previous experiments where barium was precipitated in the presence of carrier-free strontium (*cf.* Table II) with the exception that the pH was made 1·25 in all cases.

Analysis of the various mixtures was usually made by utilising both barium-133 and strontium-85 in the reaction mixtures; where barium-140 was used, the strontium present was determined by photometric titration with EDTA and Phthalein Purple as indicator. In those instances involving the precipitation of carrier-free barium with strontium it was also necessary to use a quantity of sulphamic acid larger than 40 mg (either 60 or 400 mg were employed) because strontium sulphate did not begin to precipitate even after more than 1·5 days when a quantity of 40 mg of sulphamic acid was used.

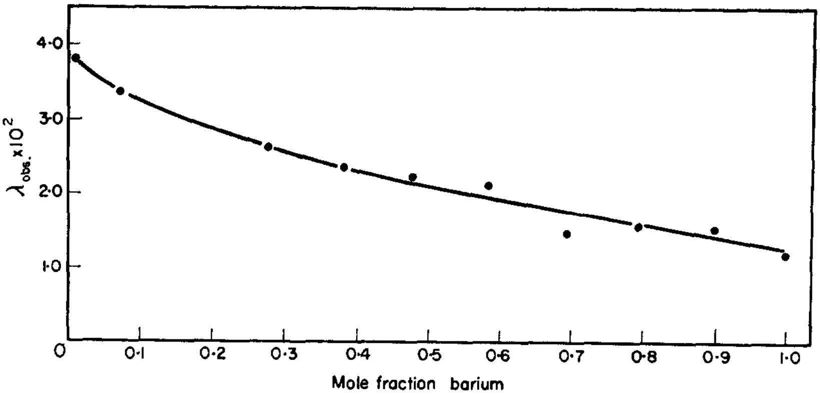

FIG. 3.—Change in distribution coefficient with mole fraction of barium. The value of $\lambda = 1·2$ (mole fraction of barium = 1) is taken from Table II.

In Fig. 3 are plotted the average values of λ for each experiment to show the variation of the distribution coefficient with mole fraction (except for the values for the co-precipitation of carrier-free barium-140 with strontium sulphate). Each point on the curve represents the average in most instances of four separate precipitations. Because 1 microcurie, 0·24 mg of barium, of high specific activity barium-133 used in these experiments, could by itself be precipitated with 40 mg of sulphamic acid, it must be assumed that the barium has in all cases acted as the carrier for strontium, except where carrier-free barium-140 was used; the latter, in the quantity normally used could not be precipitated in any appreciable quantity.

TABLE V. CO-PRECIPITATION OF CARRIER-FREE BARIUM WITH STRONTIUM SULPHATE[a, b]

Reaction time, *min*	pH	Sulphamic acid added, *mg*	Barium co-precipitated, %	Strontium precipitated, %	$\lambda \times 10^2$	D $\times 10^3$
1373	1·20	60·0	33·85	5·87	14·6	12·2
1790	1·20	60·0	98·89	55·14	17·8	1·38
1473	1·20	60·0	91·61	20·05	8·59	2·30
1540	1·20	60·0	99·94	29·28	4·67	0·0249
298	1·10	400·0	26·60	9·33	31·6	28·4
347	1·10	400·0	68·8	12·6	11·5	6·52
405	1·10	400·0	96·75	21·1	6·92	0·90

[a] 0·144 millimoles of strontium, 400 mg of ammonium chloride, 1 microcurie of varium-133, and 2 microcuries of strontium-85; reaction temperature, 80°.

[b] Carrier and tracer analyses were made by scintillation spectrometry.

The results for the co-precipitation of carrier-free barium with strontium sulphate, shown in Table V, are quite erratic; no explanation can be given for the lack of agreement within these results.

Effect of Digestion on the Co-precipitation of Strontium with Excess Barium Present

By using 14 mg of sulphamic acid it was possible to precipitate only 95% of the barium present as is shown in Table VI. The extent of co-precipitation of the added strontium-85 increased only very slightly with time, the increase being of the order of 0·06% per 1000 min over the approximately 7000 min digestion period.

TABLE VI. EFFECT OF DIGESTION ON CO-PRECIPITATION OF STRONTIUM WITH BARIUM SULPHATE[a,b]

Reaction time, *min*	Barium precipitated, %	Strontium co-precipitated, %	λ $\times 10^2$	D $\times 10^2$
9246	95·29	2·40	0·88	0·13
13022	95·29	2·60	0·86	0·13
16427	95·19	2·83	0·95	0·15

[a] 19·80 mg of barium, 14 mg of sulphamic acid, 1 microcurie of barium-133, 2·0 microcuries of strontium 85, 400 mg of ammonium chloride; pH = 1·1; reaction temperature, 80°.

[b] Carrier and tracer analyses were made by scintillation spectrometry.

Co-precipitation of Strontium upon Pre-formed Barium Sulphate

Pre-formed barium sulphate was prepared by precipitating stable barium, with barium-133 present, from homogeneous solution. This resulted in a precipitate containing about 1 microcurie of activity per 34 mg of barium sulphate. Twenty ml of solution containing 0·4 g of ammonium chloride and carrier-free strontium-85 were added to the 34 mg of active barium sulphate in the reaction cell, along with 1 ml of rinse water, and allowed to react for various periods of time at 80°. The results of several experiments are shown in Table VII and indicate that the co-precipitation is about the same as that obtained when the barium is precipitated from homogeneous solution.

TABLE VII. CO-PRECIPITATION OF CARRIER-FREE STRONTIUM UPON PREFORMED BARIUM SULPHATE IN ABSENCE OF EXCESS SULPHATE[a]

Reaction time, *min*	Barium precipitated, %	Strontium co-precipitated, %
33	100	1·72
70	98·94	2·94
90	97·34	2·80
92	98·20	2·72
160	98·31	3·18
2668	98·29	5·28
4080	99·63	6·42
5305	99·16	6·02
10170	98·93	5·98
18748	99·15	5·43
34500	98·60	6·57

[a] Carrier and tracer analyses made by scintillation spectrometry.

Similar experiments were performed in which 32·6 mg of ammonium sulphate were added to determine the effect of excess sulphate. As shown in Table VIII, the co-precipitation of strontium is quite extensive and increased with time of digestion.

Effect of Temperature on the Co-precipitation of Strontium

Barium sulphate was precipitated from homogeneous solution at 90°; the results are shown in Table IX. Although the distribution coefficient is greater (*cf.* 2×10^{-2} at 90° with $1{\cdot}4 \times 10^{-2}$ at 80°), it is difficult to determine the exact cause of the increased co-precipitation. This might be attributed to the increase in the fractional hydrolysis rate of the sulphamic acid, hence an increase in fractional precipitation rate. Distribution coefficients at various temperatures should be compared only at identical fractional precipitation rates.

TABLE VIII. CO-PRECIPITATION OF CARRIER-FREE STRONTIUM UPON PREFORMED BARIUM SULPHATE IN PRESENCE OF EXCESS SULPHATE[a]

Reaction time, *min*	Barium precipitated, %	Strontium co-precipitated, %
40	100	16·5
407	100	31·5
786	100	36·6
1455	100	49·7

[a] Carrier and tracer analyses made by scintillation spectrometry.

TABLE IX. CO-PRECIPITATION OF CARRIER-FREE STRONTIUM WITH BARIUM SULPHATE AT 90°[a,b]

Reaction time, *min*	Barium precipitated, %	Strontium co-precipitated %	$\lambda \times 10^2$	D $\times 10^3$
175	57·4	1·72	2·04	1·30
257	97·76	7·62	2·09	0·19
328	99·30	10·66	2·27	0·054
384	99·87	11·43	1·83	0·017

[a] 19·80 mg of barium, 1 microcurie of barium-133, 2·0 microcuries of strontium-85, 40 mg of sulphamic acid, and 400 mg of ammonium chloride; pH = 1·3.
[b] Carrier and tracer analyses made by scintillation spectrometry.

II—CO-PRECIPITATION OF LEAD WITH (A) BARIUM SULPHATE AND WITH (B) STRONTIUM SULPHATE

ALTHOUGH Popov[13] has reported that lead is co-precipitated only on the surface of barium sulphate crystals, other workers[14] have considered that the co-precipitation of lead for this system follows the homogeneous distribution law. These conflicting claims warranted a further study of this system by the present techniques.

From the solubility products, it would be predicted that lead would co-precipitate with barium sulphate by derichment in the crystal, *i.e.* a distribution coefficient less than 1. In the other case, the co-precipitation of lead with strontium sulphate should occur by enrichment in the crystal.

EXPERIMENTAL

Radioactive tracers

(*a*) *Lead with barium sulphate.* Barium-133 was employed as the carrier isotope. Lead-210 (Radium D), half-life 19·4 years, Atomic Energy of Canada Ltd., was used as tracer. Lead-210 is the parent in the decay scheme of bismuth-210, half-life 5 days, and polonium-210, half-life 138 days.[6] Fresh samples were used because they showed no high-energy γ peak, whereas aged samples indicated the presence of polonium-210.

(*b*) *Lead with strontium sulphate.* Strontium-85 was used as carrier isotope and lead-210 as tracer.

Procedures

(*a*) *Lead with barium sulphate.* The general procedure used in the study of the co-precipitation of strontium with barium sulphate was employed except for the substitution of 2·0 g of ammonium nitrate for ammonium chloride; 40 mg of sulphamic acid were used in all cases. The maximum concentration of lead present was calculated to be $1 \cdot 4 \times 10^{-6}$ *M*. Analyses were performed by scintillation spectrometry to determine both carrier and tracer concentrations.

(*b*) *Lead with strontium sulphate.* The procedure used in the precipitation of lead was identical with that for the co-precipitation of lead with barium sulphate except for the use of 60 mg of sulphamic acid. Analyses were performed by scintillation spectrometry.

RESULTS AND DISCUSSION

The results of Table X and Fig. 4 indicate co-precipitation by derichment of lead with barium sulphate and a much closer adherence to the logarithmic than to the homogeneous distribution equation. The average value of λ is equal to 0·188. In a separate experiment, it was found that considerably more lead co-precipitated with the barium when the latter was precipitated by the direct addition of sulphate.

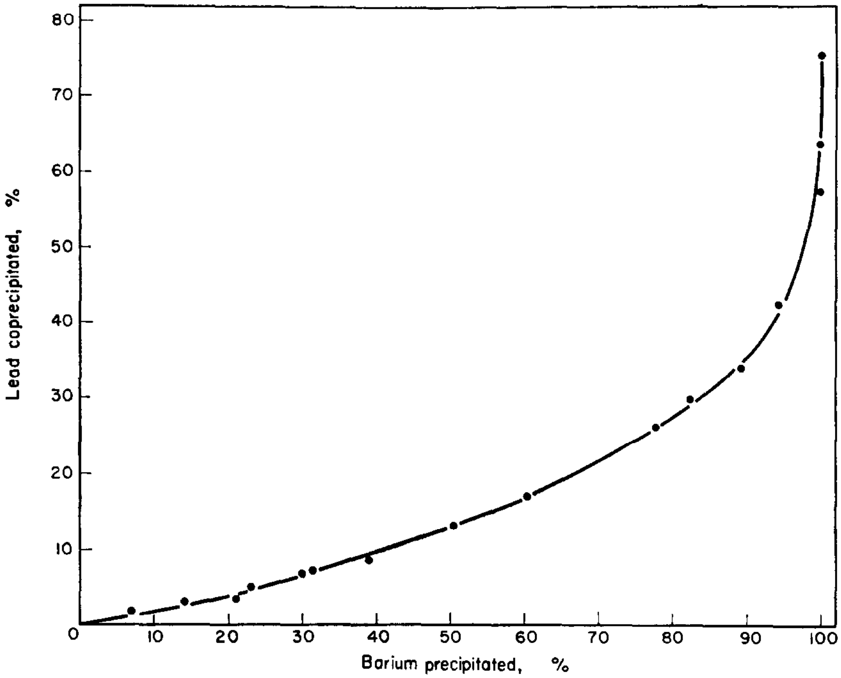

FIG. 4.—Co-precipitation of lead with barium sulphate.

The results of Table XI and Fig. 5 confirm co-precipitation by enrichment of lead in the strontium sulphate. Adherence of the results to the logarithmic distribution equation is only slightly better than to the homogeneous distribution equation.

III—CO-PRECIPITATION OF LANTHANUM AND OF YTTRIUM WITH (A) BARIUM SULPHATE AND WITH (B) STRONTIUM SULPHATE

CO-PRECIPITATION studies similar to the preceding have usually involved tracer and carrier ions of similar charge, *e.g.* radium and barium. However, there have been a few studies involving dissimilarly charged ions, *e.g.* zinc with iron^{III} periodate,[7] manganese^{II} with basic tin^{IV} sulphate,[15] rare earths with thorium iodate,[16] and yttrium with barium sulphate[12]

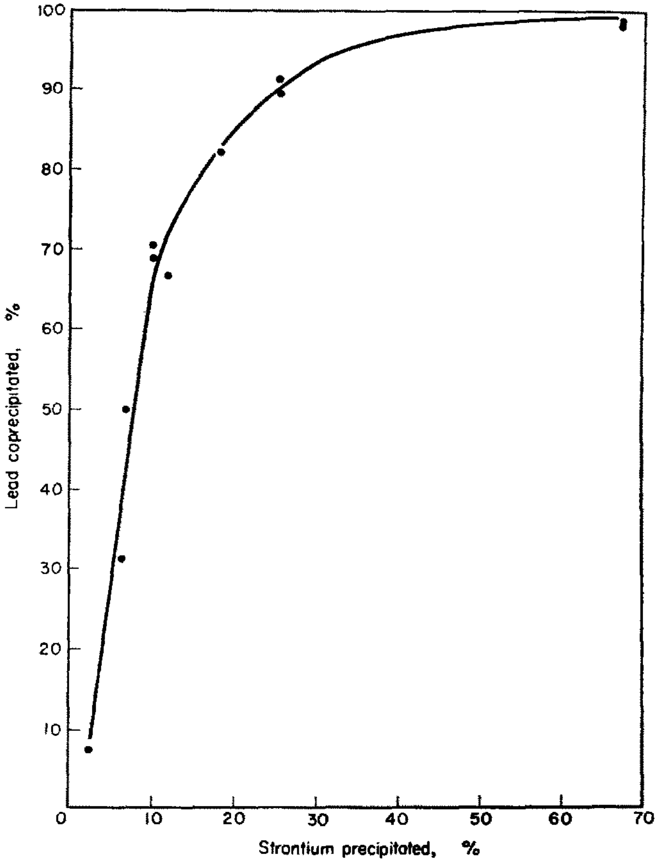

FIG. 5.—Co-precipitation of lead with strontium sulphate.

EXPERIMENTAL

Radioactive tracers

Barium-133 and strontium-85 from the previous investigations were used. Lanthanum-140 was prepared by separating it from barium-140 by precipitation of barium nitrate in fuming nitric acid;[17] the half-life of the lanthanum-140 was determined to be 40 hr. Yttrium-90 was separated from its parent, strontium-90, in a similar manner. Its half-life was determined to be the same as the reported value, *i.e.* 64 hr.

Procedure

The procedures used for the co-precipitation of lanthanum were similar to those for the co-precipitation of strontium with barium sulphate and lead with strontium sulphate. Analyses were by scintillation spectrometry.

The procedure used with yttrium in the case of barium sulphate was that of direct precipitation with ammonium sulphate in order to provide a comparison with a previous study in which barium sulphate was precipitated from homogeneous solution.[12] To a 21-ml volume of solution (containing 0·144 millimole of strontium or barium, 400 mg of ammonium chloride, and yttrium isotope) 47 mg of ammonium sulphate were added. The reaction mixture was allowed to stand for 60 min at 25°, the phases separated by centrifugation and analysed. Yttrium-90 was assayed by scintillation spectroscopy. Its high-energy β-rays were converted to bremsstrahlung (X-ray photons), through interaction of the β-rays with 0·6-cm aluminium absorbers placed between the sample and the scintillation crystal. Yttrium-90, through the resultant 55 Kev radiation, could thus be assayed by scintillation spectrometry in the presence of the other γ-emitters.

TABLE X. CO-PRECIPITATION OF LEAD WITH BARIUM SULPHATE

Reaction time, *min*	Barium precipitated, %	Lead co-precipitated, %	λ	D
80	5·87	1·47	0·245	0·239
145	14·1	2·86	0·192	0·179
117	21·0	3·18	0·137	0·124
200	23·0	4·76	0·187	0·167
180	30·0	6·59	0·191	0·165
270	31·2	7·02	0·195	0·166
169	39·0	8·51	0·131	0·145
450	50·4	13·1	0·200	0·148
259	60·3	15·92	0·188	0·125
720	77·7	26·3	0·203	0·102
312	82·4	29·8	0·204	0·0907
873	89·1	33·9	0·187	0·0626
496	94·12	42·39	0·195	0·0460
600	99·60	57·1	0·153	0·00534
1156	99·66	63·5	0·177	0·00593
1099	99·81	75·33	0·223	0·000581

TABLE XI. CO-PRECIPITATION OF LEAD WITH STRONTIUM SULPHATE

Reaction time, *min*	Strontium precipitated, %	Lead co-precipitated, %	λ	D
365	2·44	7·68	3·23	3·33
368	7·02	49·9	9·50	13·2
482	6·49	31·3	5·60	6·57
435	10·0	70·6	11·6	2·16
389	10·6	69·0	10·4	18·8
345	11·9	66·8	8·70	14·9
482	18·3	82·2	8·54	20·6
413	25·4	89·7	7·76	25·6
451	25·4	91·4	8·37	31·2
482	54·0	98·67	5·56	63·3
540	67·3	98·58	3·80	33·7
575	67·3	97·95	3·48	23·2
[a]	74·1	94·47	2·14	5·97

[a] Strontium precipitated by direct addition of sulphate.

When strontium was used as the carrier (0·144 millimole), it was precipitated from homogeneous solution by the addition of ten times the stoichiometric amount of sulphamic acid (t = 80°).

RESULTS AND DISCUSSION

Co-precipitation of lanthanum with barium sulphate is by derichment in the crystal and is appreciable only in the range where 95 to 100% of the barium sulphate is precipitated as is indicated by Fig. 6 and Table XII. Although calculations (not shown) indicated that the system did not adhere very closely to either distribution equation, this should not preclude actual conformity to either type of distribution because of the

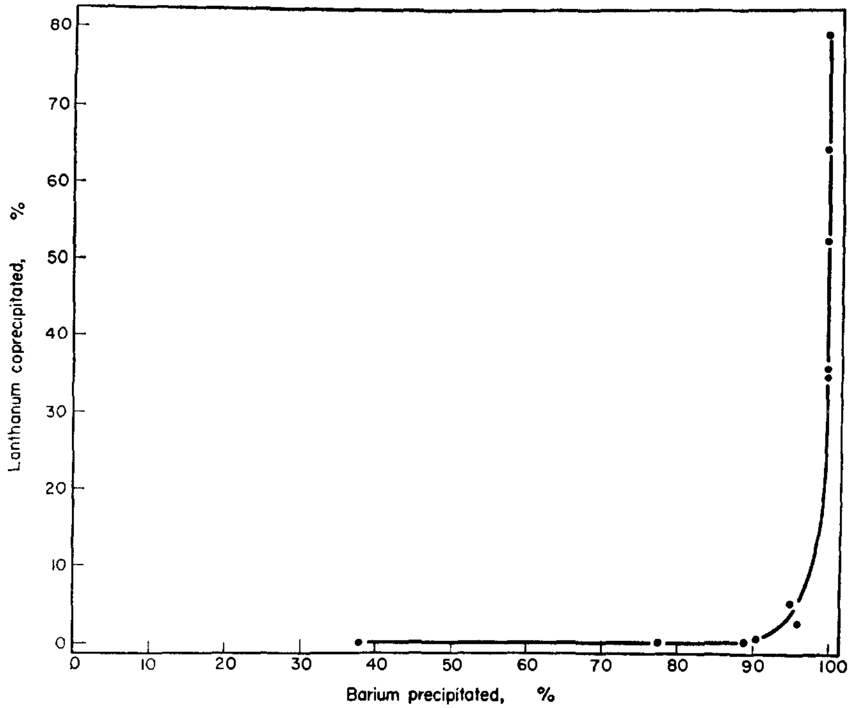

FIG. 6.—Co-precipitation of lanthanum with barium sulphate.

TABLE XII. CO-PRECIPITATION OF LANTHANUM WITH BARIUM SULPHATE

Reaction time, *min*	Barium precipitated, %	Lanthanum co-precipitated, %
431	77·5	0·17
539	88·5	0·69
568	90·76	1·23
636	95·91	2·66
760	95·40	5·35
846	98·94	9·0
1070	99·25	21·5
1132	99·25	25·3
1262	99·51	36·0
1341	99·53	35·0
1745	99·47	64·3
1310	99·53	52·2
1950	99·50	79·3
a	99·9	87·5

[a] Barium precipitated by direct addition of sulphate; precipitate digested for 60 min.

experimental uncertainties of analysis in the present case and particularly because of the limited range over which the data were obtained.

Co-precipitation of lanthanum with strontium sulphate is by enrichment in the crystal. The results are shown in Table XIII. Calculations of the distribution coefficients, λ and D, show that the logarithmic distribution equation is more closely obeyed than is the homogeneous distribution equation. Modified distribution equations[18] have been derived which show a functional dependence of distribution coefficient upon initial concentration of carrier ion if the carrier and tracer ions are of dissimilar charge. The two initial concentrations of strontium used in the present case were so slightly different that it was not possible to determine this functional dependence. The values of λ and D in Table XIII were calculated from the unmodified equations.

TABLE XIII. CO-PRECIPITATION OF LANTHANUM WITH STRONTIUM SULPHATE

Reaction time, *min*	Strontium precipitated, %	Lanthanum precipitated, %	λ	D
Sulphamic acid added: 400 mg; initial concentration of strontium: 8·2 × 10^{-3} *M*				
265	1·74	2·92	1·69	1·70
343	47·8	74·9	2·13	3·26
445	47·7	81·1	2·57	4·70
373	60·4	85·7	2·10	3·93
392	64·9	86·7	1·93	3·53
491	71·9	92·06	2·00	4·53
543	76·2	96·47	2·33	8·54
Sulphamic acid added: 400 mg; initial concentration of strontium: 8·7 × 10^{-3} *M*				
300	11·8	13·0	1·11	1·12
360	44·0	56·4	1·43	1·65
425	74·1	90·0	1·71	3·15
570	82·9	98·3	2·31	11·9
Sulphamic acid added: 60 mg; initial concentration of strontium: 8·2 × 10^{-3} *M*				
1277	1·11	0·96	0·351	0·86
1544	10·9	12·4	1·15	1·16
1650	22·4	37·8	1·87	2·11
Direct addition of sulphate				
0	84·6	85·8	1·04	1·10

The co-precipitation of yttrium with barium sulphate precipitated from homogeneous solution with dimethyl sulphate has been shown[12] to be negligible up to 95% of the barium precipitated. In the present case, even though a conventional procedure was employed, the quantity of yttrium co-precipitated with barium sulphate or with strontium sulphate was also found to be negligible. For example, when the barium was virtually completely precipitated, only 0·8% of the yttrium co-precipitated; when 75·3% of the strontium was precipitated, only 1·04% of the yttrium co-precipitated.

The result obtained with the rare earths indicate the possibility of fractionation of rare earth isotopes. For example, yttrium did not co-precipitate with barium sulphate whereas lanthanum could be made to co-precipitate extensively. Thus, a considerable fractional separation of these rare earth isotopes could be attained. From the results obtained, it would appear that strontium sulphate could be used in a similar manner.

CONCLUSIONS

The systems studied generally showed a much closer adherence to the logarithmic distribution equation than to the homogeneous equation. The characteristic slight change[19] of distribution coefficient with change in the fraction of carrier precipitated is evident in varying degrees in the present systems.

The observed (average) values of the logarithmic distribution coefficients for the several systems studied are shown in Table XIV along with the theoretical values of the distribution coefficients calculated from the solubility product ratios.[20] It should be noted that only in the case of the strontium-lead system is there any close correlation between the observed and the theoretical values of the distribution coefficients; this may be a purely fortuitous case inasmuch as the other systems, and studies of some rare earth oxalate systems[2] as well, have not shown the predicted correlation. In view of the dependence of the distribution coefficient upon fractional precipitation rate, it seems unlikely that such a correlation exists. The only correlation which did hold in all of the present cases was a qualitative relationship between solubility product ratio and the experimentally observed value of the distribution coefficient, *i.e.* whether impoverishment or enrichment would occur.

TABLE XIV. COMPARISON OF $\lambda_{\text{observed}}$ AND $\lambda_{\text{theoretical}}$

Carrier	Tracer	λ_{obs}	$\lambda_{\text{calc}} = \frac{K_{sp}(\text{carrier})}{K_{sp}(\text{tracer})}$	$\frac{\lambda_{\text{calc}}}{\lambda_{\text{obs}}}$
Barium	Strontium	0·012	$8{\cdot}17 \times 10^{-4}$	$6{\cdot}81 \times 10^{-2}$
Barium	Lead	0·188	$9{\cdot}24 \times 10^{-3}$	$4{\cdot}91 \times 10^{-2}$
Barium	Radium	1·133[a]	$1{\cdot}31 \times 10^{4}$	$9{\cdot}85 \times 10^{3}$
Strontium	Barium	3·13 to 14·5	$1{\cdot}22 \times 10^{3}$	$3{\cdot}90 \times 10^{2}$ to $8{\cdot}41 \times 10^{1}$
Strontium	Lead	8·20	$1{\cdot}13 \times 10^{1}$	1·38
Strontium	Lanthanum	1·87	$1{\cdot}33 \times 10^{1}$	7·11

[a] Extrapolated from data of Gordon and Rowley.[8]

Although the theoretical significance of the coefficient in the logarithmic distribution equation remains unknown, the equation itself can be used empirically to predict the extent of co-precipitation (for various fractions of the carrier precipitated) under a prescribed set of reaction conditions if the average value of the distribution coefficient has been obtained experimentally. This would have practical application in separation processes in which precipitation from homogeneous solution is employed.

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Zusammenfassung—Unter Heranziehung der Methode der Fällung aus homogener Lösung wurden die verteillungseigenschaften von "Tracern" mit Erdalkalisulfaten studiert. Die Mitfällung von Strontium mit Bariumsulfat sowie von Blei, Lanthan und Yttrium (jedes für sich) mit Barium und Strontiumsulfat wurde untersucht. Wenn auch eine qualitative Beziehung zwischen den beobachteten Verteillungskoeffizienten und den theoretischen Werten der Löslichkeitsprodukte für jedes der Studierten binären Systeme festgestellt werden konnte, so war die Abweichungen zwischen Theorie und beobachteten Werten so gross, dass eine quantitative Beziehung als unwarhscheinlich angenommen werden musste.

Résumé—Les auteurs ont étudié le fonctionnement au point de vue partage des traceurs avec des sulfates alcalino-terreux, en utilisant la méthode de précipitation en solution homogène. Les co-précipitations du strontium avec le sulfate de baryum, et du plomb, du lauthane et de l'yttrium, séparèment avec le sulfate de baryum et avec le sulfate de strontium, ont été étudiées. Bien qu'il y ait une relation qualitative entre les valeurs observées du coefficient de partage et les rapports théoriques des produits de solubilité pour chacun des systèmes binaires étudiés, la divergence entre la théorie et l'expérience est si grande qu'il semble improbable qu'il existe une relation quantitative.

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A NEW PROCEDURE FOR PREPARATION OF ANHYDROUS PERCHLORIC ACID EMPLOYING ANHYDROUS MAGNESIUM PERCHLORATE

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Summary—The dehydration of hydrated perchloric acid to yield anhydrous acid is described. Anhydrous (5·5% water content) magnesium perchlorate is employed as desiccant followed by distillation under reduced pressure. The new procedure is less complicated than previously described processes, and is convenient for the preparation of small amounts to be employed in studies of the preparation of anhydrous metallic perchlorates from reactions with suitable selected reagents, and for convenient lecture demonstrations.

INTRODUCTION

THE earliest investigation of anhydrous perchloric acid was made by Roscoe in 1863.[1] The first study of the preparation of oxonium perchlorate, OH_3ClO_4, as well as of other perchloric acid hydrates, was included, namely, $OH_3ClO_4 \cdot H_2O$, which was later shown to exist in two forms, α and β, with distinctive melting points. More extensive studies of these and higher hydrates were made by van Wyk[2] and by van Emster.[3] A more thorough study of these perchloric acid hydrates was provided by Smith and Goehler.[4] The anhydride of perchloric acid, chlorine heptoxide, Cl_2O_7, was first prepared by Michael and Cohn,[5] (b.p. at ordinary pressures 82°).

The multiple simultaneous separation by distillation of anhydrous perchloric acid, oxonium perchlorate and higher perchloric acid hydrates, was described by Goehler and Smith.[6] Distillation of dioxonium perchlorate at 8 to 18 mm pressure was employed for this separation. The large scale preparation of anhydrous perchloric acid by reduced pressure distillation of mixtures of fuming sulphuric acid and dioxonium perchlorate was described by Smith.[7]

The preparation of crystalline oxonium (perchlorate m.p. 49·905°)[8] is best performed by the reaction of anhydrous perchloric acid with dioxonium perchlorate by use of the following reaction:

$$HClO_4 + O_2H_5ClO_4 \rightarrow 2OH_3ClO_4.$$

The present work provides a dry distillation of aqueous perchloric acid by reaction with anhydrous magnesium perchlorate, and it is a convenient procedure for lecture demonstration as well as for the preparation of small samples of the anhydrous acid for immediate usage. Since the anhydrous perchloric acid is not stable upon long storage, the above reaction is always followed and provides a product which may be readily employed in reconversion to the anhydrous acid by distillation at reduced pressure and at 110° by the reaction:

$$OH_3ClO_4\ (110^\circ \text{ in vacuo}) \rightarrow HClO_4 + O_2H_5ClO_4.$$

The anhydrous acid forms the distillate and the 73·6% perchloric acid remains in the still pot.

EXPERIMENTAL

Reagents

Partially dehydrated magnesium perchlorate dihydrate, (app. 5% H_2O): commercially available.

Hydrated perchloric acid, 72·5% to 85%, the water azeotropic composition or stronger acid: *dioxonium perchlorate* or acid of lower water content such as oxonium perchlorate. These items are commercially available.

Dry ice for refrigeration of the cold finger distillation receiver.

Apparatus

A description, with line drawing, of the apparatus has been given by Smith.[7]

Procedure

The chilled perchloric acid for dehydration is added to the still pot in small increments and is mixed well after the addition of the anhydrous magnesium perchlorate. The proportions employed are 17–20 g of acid to 100 g of the desiccant. The latter is added in 10- to 20-g increments to 4- to5-g portions of acid, with stirring to ensure effective contact between acid and desiccant.

The still pot is then connected to the cold finger in a Dewar flask chilled by use of finely-divided dry ice. The cold finger distillate receiver is connected to the vacuum pump with an intermediate acid absorbing scrubbing tower containing Ascarite or Mikohbite to prevent any passage into the vacuum pump of acid vapours not condensed in the cold finger. The distillation is started at room temperature and the still pot is slowly heated to a maximum of 70° employing an electrically energised Glas-Col heating mantle with variable voltage energy source. A reduced pressure of 0·25 to 0·5 mm is required and the time of the distillation is 8 to 10 hr for most complete accumulation of anhydrous acid formed. A yield of 85% or better is thus provided.

If the preparation of anhydrous perchloric acid is not for use within a few hrs (12–24), there is, at room temperature, the gradual accumulation of decomposition products which gradually colour the acid yellow, then brown, and finally black at which point after 10–14 days at room temperature an explosion ensues. Storage at liquid air temperatures materially extends this time limit. The impurity thus accumulated is postulated to be ozone.

A minor contaminant of the distilled anhydrous acid is found to be the anhydride of perchloric acid, chlorine heptoxide. It is formed by dehydration in greater proportion if the reaction mixture is not distilled immediately after the preparation is provided. Its presence is shown by the fact that dilution of the anhydrous perchloric acid with sufficient water to form oxonium perchlorate leaves the chlorine heptoxide content unchanged for 72 to 96 hr before it reacts with water to form, first anhydrous perchloric acid, followed by conversion to oxonium perchlorate.

In all of the manipulations herein described it is well to keep in mind that anhydrous perchloric acid in contact with organic material produces violent explosions. If the ground-glass joints require some material to make them more effective, use perchloric acid for this purpose. Silicone greases explode in contact with anhydrous perchloric acid. The reaction between water and anhydrous perchloric acid is extremely exothermic. For this reason the conversion to oxonium perchlorate is best made by the addition of 72·5% perchloric acid until the acid is solid at approximately 50° melting point. Oxonium perchlorate (84·8% $HClO_4$) is stable indefinitely at ordinary temperatures. Its reaction, while less likely to produce explosions in contact with organic matter than the anhydrous acid, is still a hazard in contact with carbonaceous products. Chlorine heptoxide is known to be explosive when heated or subject to shock.

On the other hand 70·0 to 73·6% perchloric acid is a remarkably stable product. It may be distilled at ordinary pressure at 200–203° with but slight decomposition and this process may be employed in its purification. Dioxonium perchlorate, $O_2H_5ClO_4$ (73·605% $HClO_4$), has been described in preparation as a standard of reference in acidimetry.[9] Assuming that 10 ml of 70–72·5% perchloric acid are employed in a routine control laboratory analysis in the steel industry, cement, leather, and agricultural feed industries, there are one hundred and fifty million individual analyses carried out annually which owe their outstanding effectiveness to the use of this acid. Such widespread applicability belies the implication that reactions employing perchloric acid are hazardous. Chemists thoroughly familiar with the chemistry of perchloric acid and its salts are richly rewarded in its multiplicity of productive applications.

Zusammenfassung—Die Dehydration hydrierter Perchlorsäure zu wasserfreier Säure wird beschrieben. Wasserfreies (5·5% Wassergehalt) Magnesiumperchlorat wird als wasserentziehendes Mittel verwendet, mit anschliessender Destillation unter vermindertem Druck. Die Methode ist weniger kompliziert als früher beschriebene Verfahren und bequem um kleine Mengen wasserfreier Säure herzustellen, wie sie in den Studien zur Bereitung von wasserfreien Metallperchloraten oder für Demonstrationszwecke gebraucht werden.

Résumé—L'auteur décrit la déshydration de l'acide perchlorique hydraté pour obtenir de l'acide anhydre. Du perchlorate de magnésium anhydre (contenant 5,5 pour cent d'eau) est employé comme desséchant; une distillation sous pression réduite suit cette première opération. Cette nouvelle méthode est moins compliquée que celles décrites précèdemment; elle convient pour la préparation de faibles quantités à employer dans l'étude de la préparation des perchlorates métalliques anhydres à partir de réactions utilisant des réactifs convenablement choisis; elle convient aussi pour des démonstrations commodes de conférence.

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INFRARED SPECTRA OF SOME ORGANO-PHOSPHORUS EXTRACTANTS*

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Summary—The infrared spectra of a group of organo-phosphorus compounds useful for extraction of metals from acidic aqueous solutions are presented and discussed. The spectra of a few organo-phosphorus degradation products or probable impurities are also included. Many of the organic groups responsible for some of the absorption bands are identified.

IN this paper the infrared spectra of a number of organo-phosphorus compounds which are under consideration for the extraction of various metal ions from aqueous solution are presented and discussed. The spectra of a few of the phosphorus compounds expected to occur as impurities in such extractants are also included. An attempt is made to assign some of the absorption bands to vibrations caused by specific functional groups. Other infrared investigations of less pure samples of these compounds and the spectral changes observed during various purification steps will be discussed in a subsequent report.

The functional group assignments of the bands are based on prior general correlations of the spectra of typical organo-phosphorus compounds.[4,6,7,10,11,15,17,18,19,24,27,29,31,33,37,42] Also, spectra of compounds located in catalogues by use of the A.S.T.M.-Wyandotte I.B.M. cards, and spectral reports concerning butyl phosphates,[2,11,14,15,33,35] cyclic ethers,[16] di-*n*-butyl hydrogen phosphate,[1,5,11,35] di-2-ethylhexylphosphoric acid,[5,38] dialkylphosphonates and phosphine oxides,[15,34] phosphates and phosphonates,[15] tri-*n*-butyl phosphate,[2,3,4,6,9,12,13,15,21,23,30,35,36,40] and trimethylphosphine[28] proved of value for this investigation. Discussions of hydrogen or phosphoryl inter- or intra-molecular bonding and shifts in frequency of absorption bands with changes in other substituents[8,12,25,26,32,34,39,41,43] were also helpful.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Infracord, Model 137, spectrometer with sodium chloride optics was used to record the infrared spectra for most of the compounds. A Perkin-Elmer Model 21 spectrometer was used to obtain spectra of the remaining compounds. Sodium chloride window cells of nominal path lengths of 0·05, 0·2, and 1·0 mm were used for recording spectra of solutions and sodium chloride windows were used for film spectra.

Reagents

All materials used for preparing solutions or drying them were of reagent grade. The organo-phosphorus compounds investigated were commerical grade, purified commercial grade, or synthesised and purified in this laboratory.

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Procedure

Solutions containing about 20% (w/v) or 1 mole/litre of the organo-phosphorus compound to be investigated were prepared in carbon tetrachloride or carbon disulphide. These were diluted by volume as necessary to ascertain the position and relative intensity of strong absorption peaks. Where traces of water were expected or solutions were turbid, the solutions were dried with anhydrous calcium or sodium sulphate, or potassium carbonate before recording the spectra. Spectra were recorded in cells of various path lengths, using reference cells of the same path lengths filled with pure solvent. In a few cases spectra of thin films on sodium chloride plates were recorded. Regions of very high absorbance for the solvents are omitted in the figures.

RESULTS

In Table I are listed the spectra presented in the figures with notes concerning the source or treatment of the samples.

TABLE I. COMPOUNDS INVESTIGATED BY INFRARED SPECTRA

Fig. No.	Name of compound	Source*	% in CCl_4	Treatment
1	Tricaprylphosphate	A	18·4	
2	Octanol-2	E	16·9	
3	Caprylphenylphosphonic acid	A	27·0 5·4	
4	Di-*sec*-butylphenylphosphonate	A	20·2	Dried anhyd. Al_2O_3
5	Di-*n*-butylhydrogenphosphonate	A	19·8	
6	Tri-*n*-butylphosphite	G	25·0	
7	Tris-*iso*propylphosphite	G	20·8 8·3	 Treated 1 pellet KOH
8	Tri-*n*-octylphosphine oxide	B	19·3	
9	Tri-*n*-octylphosphine oxide	A	†	
10	Tris-(2-ethylhexyl)-phosphine oxide	A	6·7	
11	Tris-(*iso*-octyl)-thiophosphate	C	†	
12	1-Phenyl-3-*iso*hexenyl-1-phospha-3-cyclopentene-P-oxide	D	20·3	
13	Di-*n*-butylphosphoric acid	G	21·0	
14	Tri-*n*-butylphosphate (impure)	F		Distillation residue
15	Tri-*n*-butylphosphate (purer)	F		Purified by solvent washing treatments

* A Synthesised or purified at ORNL
B Eastman
C Penninsular Chemical Co.
D DuPont
E Reagent grade
F Obtained during purification treatments
G Commercial, technical grade of unknown purity
† Films, not solution

DISCUSSION

The spectra of the solvents recorded versus air were similar to previously published spectra.[3] Carbon tetrachloride spectra in the 6·4 μ (1560 cm^{-1}) and 12 to 14 μ (715 to 835 cm^{-1}) regions were unsuitable for use owing to over-compensation of a band and very high absorbance, respectively. Although carbon disulphide is usually used only for the 7·5 to 15 μ (655 to 1335 cm^{-1}) region, spectra obtained between 2·3 to 3·3, 3·7 to 4·2 and 4·9 to 5·9 μ were useful in this study and bands observed for the organo-phosphorus extractants in these regions confirmed those observed using carbon tetrachloride as solvent. Since neither of these solvents contain C-H groups, solute-solvent hydrogen bonding effects were minimal in the spectra.

Although cyclohexane, xylene, or saturated aliphatic hydrocarbons are generally preferable to carbon tetrachloride or carbon disulphide as diluents for extractions, their complex spectra made the former solvents unsuitable for this infrared study.

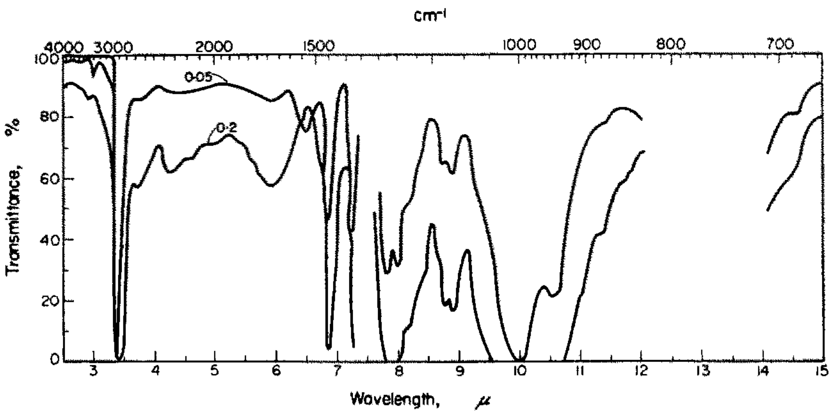


Fig. 1.—Tricaprylphosphate

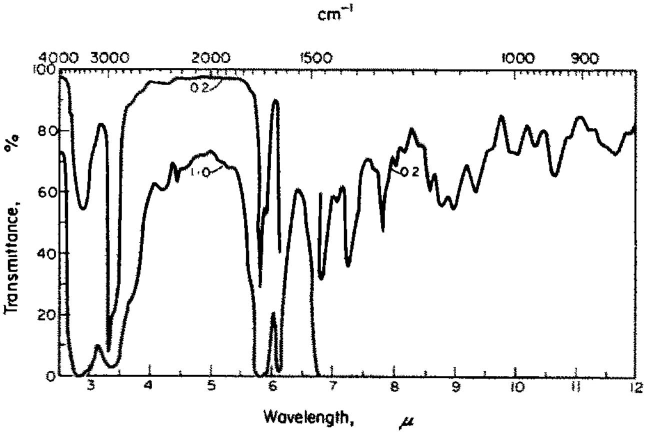
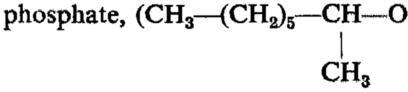


Fig. 2.—Octanol-2



A. *Tricaprylphosphate.* The infrared spectrum of our purest sample of tricaprylphosphate, $(CH_3\text{—}(CH_2)_5\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}O\text{—})_3\ P \rightarrow O$, is presented in Fig. 1. This may be compared to the spectrum of octanol-2 (capryl alcohol), Fig. 2. The alcohol shows a band at 3355 cm^{-1} attributable to an —OH vibration of a loose polymer hydrogen-bonded type, while the phosphate has a band at 3560 cm^{-1} attributable to a single-bridged intermolecular hydrogen-bonded type —OH vibration. The CH_3- and CH_2-stretching (2960 and 2920 cm^{-1}), —CH_2 scissor (1465 cm^{-1}), C-H bending (1380), and methyl rocking (1140) vibrations are at the same positions for both compounds. In Fig. 1, the strong band at 1255 cm^{-1} is due to the phosphoryl, P → O, stretching vibration, calculated to appear at 1176 cm^{-1};[8] whereas the 1160 and strong 1000 cm^{-1} bands are due to C—O—(P—) or (C)—O—P vibrations and the 970 and 940 cm^{-1} bands to vibrations of the C—O—P type.

Like other samples of this phosphorus compound, a trace of acidic impurity is indicated by the shoulder at 2700 cm^{-1}, typical of P—OH type compounds. The band at 2380 cm^{-1} is indicative of some unreacted alcohol in the phosphate rather than a P—H type impurity, inasmuch as the alcohol has a strong band at 2380 cm^{-1}.

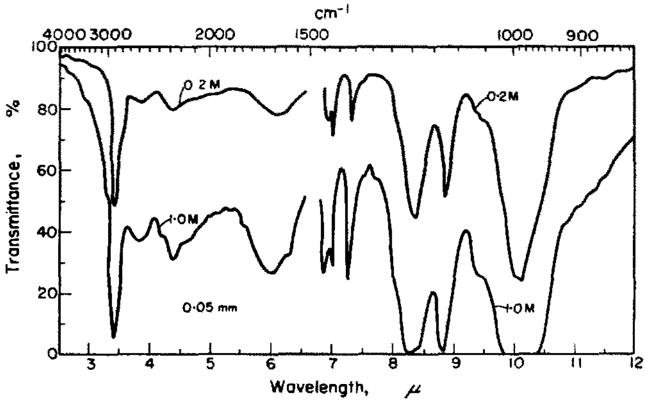
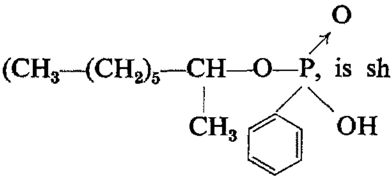
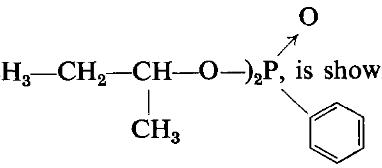


FIG. 3.—Caprylphenylphosphonic acid

B. *Caprylphenylphosphonic acid.* The spectrum of caprylphenylphosphonic acid,


$(CH_3-(CH_2)_5-CH(CH_3)-O-P(\rightarrow O)(C_6H_5)-OH$

is shown in Fig. 3. It is a composite of the spectra of octanol-2, phosphonic acid, and mono-substituted benzene except for the absence of the 3355 cm^{-1} band of the alcohol, Fig. 2. The P—OH group vibration band is centred at 2640 cm^{-1}, a broad band with an absorbance of only 0·42 in a 1-mm cell for a 1*M* solution. The bands in the 2200 to 2400 cm^{-1} region indicate some phosphine P—H impurities in the preparation. The broad group of partially resolved bands between 2200 and 2400 cm^{-1} are probably phenyl vibrations. The phosphoryl stretching band is the band at 1240 cm^{-1}, as calculated.[8] The strong band at 1130 cm^{-1} is the P—O-aryl vibration, and the still stronger band at 985 cm^{-1} is due to P—O—R group vibrations. Another strong band at 685 cm^{-1}, not shown in Fig. 3, is due to the mono-substituted aromatic group. The bands at about 2900, 1450, and 1350 cm^{-1} are also noted in the alcohol spectrum; the 1060 cm^{-1} shoulder is due to a P—O—C (alkyl) vibration; the 1430 cm^{-1} band is probably attributable to an aromatic type vibration.



C. *Di-sec-butylphenylphosphonate.* The spectrum of di-*sec*-butylphenylphosphonate, $(CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—O—)_2\overset{\displaystyle O}{\overset{\nearrow}{P}}\diagdown C_6H_5$, is shown in Fig. 4. Several bands present are also noted in the spectra of 2-butanol given in the N.B.S. catalogue, Serial Nos. 431 and 750,[36] as well as bands typical of mono-substituted aromatic compounds. Such common bands are: the 2950, 1670, 1460, 1385, and 1250 cm^{-1} bands of the alcohol, the 3000 cm^{-1} region $\rangle$CH band, 4 typical mono-substituted aromatic bands in the 1600–2000 cm^{-1} region, and 5 more at 1460, 1175, 1130, 1070, and 1040 cm^{-1}. The bands of less definite assignment are: $\sim$2600 cm^{-1}, R—O or P—OH; 2400–2200, phenyl or P—H impurities; $\sim$1000 P—O—R (alkyl); 1327 or 1310 cm^{-1} P $\rightarrow$ O, calculated to be 1307 cm^{-1}.[8] The band at 3470 cm^{-1}, a hydrogen-bonded OH vibration, is probably due to alcohol, an impurity, and was more prominent in other samples. The bands in the 1650 to 2000 cm^{-1} and 2750 cm^{-1} regions also indicate traces of unreacted alcohol are present. The 690 cm^{-1} band is typical of mono-substituted aromatics.

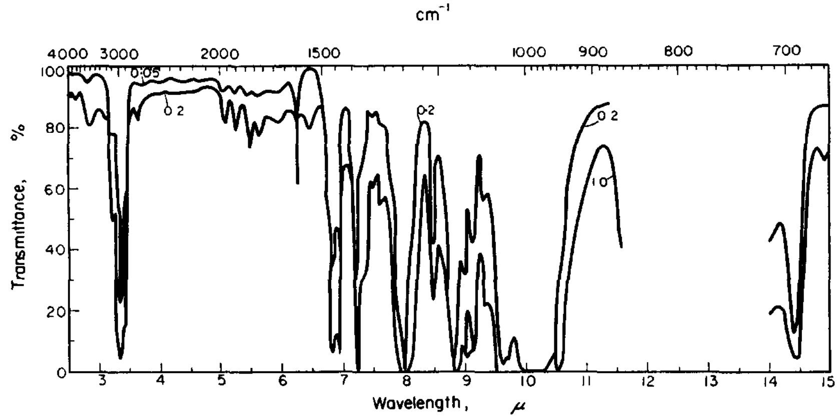
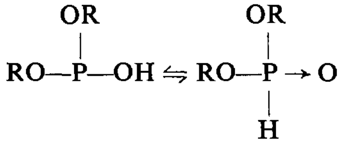


FIG. 4.—Di-*sec*-butylphenylphosphonate

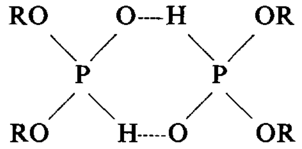
D. *Dibutylhydrogenphosphonate.* The spectrum of a sample submitted as dibutylphosphite, of empirical formula $C_8H_{19}O_3P$, is presented in Fig. 5. Examination of the absorption peaks indicates the presence of a P—H grouping at 2428 cm^{-1}, and a probable P $\rightarrow$ O phosphoryl grouping at 1247 cm^{-1}, with only a weak broad shoulder in the 2800 cm^{-1} region where P—OH bands normally occur. Thus the indicated structure approaches that of the dibutylphosphite keto isomer, dibutylhydrogenphosphonate, as shown below.



$$RO—\overset{\displaystyle OR}{\overset{|}{P}}—OH \leftrightharpoons RO—\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle OR}{\overset{|}{P}}}}\rightarrow O$$

dialkylphosphite dialkylhydrogenphosphonate

As prior discussions[39] have indicated, the actual structure of the compound submitted may be dimeric:



This structure would account for, at least in part, the hydrogen-bonded hydroxy vibration noted at 3500 cm^{-1}.

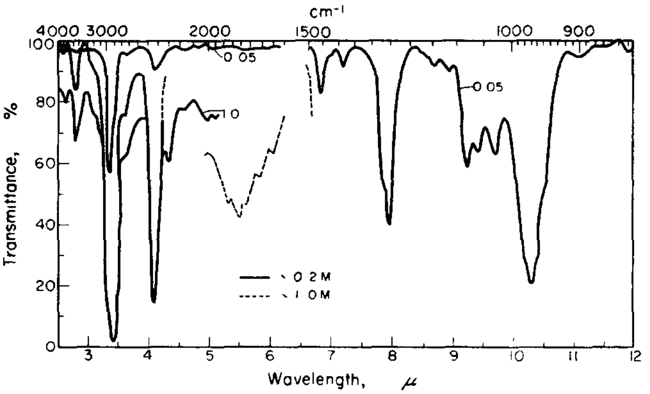


FIG. 5.—Di-*n*-butylhydrogenphosphonate

The experimental spectrum can be compared to spectra reported by others, including: Sadtler No. 9041,[40] Fox,[22] Bellamy-Beecher,[11] and also the typical bands for phosphorus compounds containing butoxy groups according to McIvor and co-workers.[33] Many bands are at about the same positions as expected and of appropriate intensity. The bands noted between 1615 and 2185 cm^{-1} (4·55 to 6·2 μ) for the 1·0-mm path spectrum were not noted in the prior studies with shorter path lengths. The band at 1375 cm^{-1} attributable to an R—O—P vibration is stronger than noted by McIvor's group. The band at 1248 or that at 1137 cm^{-1} may be the phosphoryl vibration, calculated to appear at 1254 cm^{-1}.[8] The 980 cm^{-1} band of the Sadtler spectrum was not noted in our scan, but other bands at 968 and 952 cm^{-1} in Fig. 5 were not in the Sadtler spectrum. The low frequency vibrations below 850 cm^{-1} anticipated from McIvor's work could not be observed in a carbon tetrachloride solution.

The bands in the 4·55 to 6·2 μ region cannot be assigned, owing to lack of correlations for this region. They may be harmonics, combination, or difference bands of fundamentals in lower frequency regions. Alternatively, they may be attributed in part to minor impurities. Similar bands appear in Fox's spectrum.[22]

The spectrum of Fig. 5 can also be compared to Daasch's most recent spectrum of this compound[20] which is likewise similar in most respects. However, the band at 1080 cm^{-1} in Fig. 5 is stronger than that at 1020 cm^{-1} whereas the situation is reversed in Daasch's spectrum. The bands for the Sadtler spectrum in this region are too intense for comparison. The intensity ratio for these bands in Fig. 5 is similar to that observed by Bellamy and Beecher.[12]

E. *Trialkylphosphites.* The spectra of samples of tri-*n*-butyl- and tris-*iso*propylphosphites, respectively, are presented in Figs. 6 and 7. The spectrum of the former can be compared to a spectrum published previously by Daasch and Smith,[19] and butoxy group positions indicated by McIvor and coworkers.[33] The bands of Fig. 7 can be compared with other isopropoxy group assignments.[33] Each spectrum can be also compared with the other and the general organo-phosphorus group vibrational

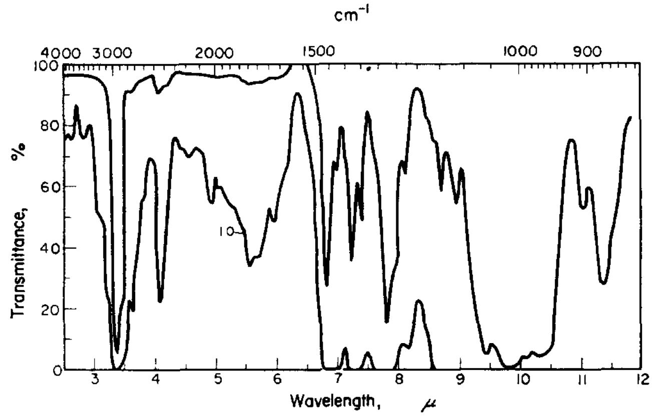


Fig. 6.—Tri-*n*-butylphosphite

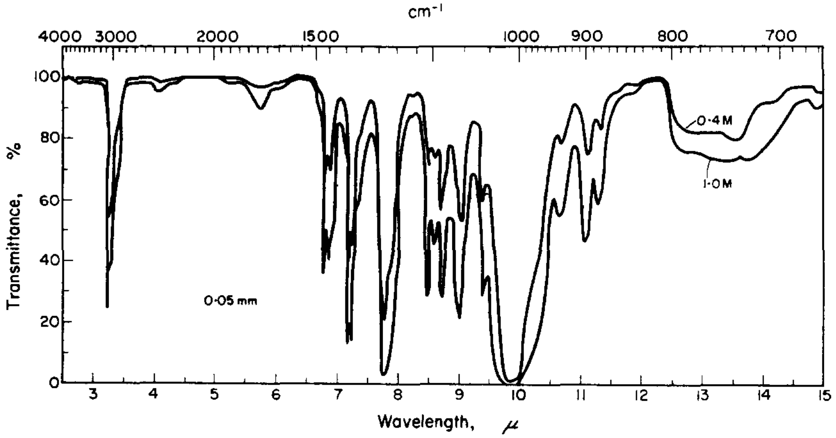


Fig. 7.—Tri-*iso*propylphosphite

correlations. Both of these phosphite samples show slight absorption in the 3400–3550 cm^{-1} region typical of hydrogen-bonded OH. This absorption is assumed to be due to impurities in the samples.

For the tributyl phosphite, Fig. 6, the C—H stretching vibration is at 2950 cm^{-1} compared to 2940 cm^{-1} estimated from the literature.[20] Bands occur at 2910, 2750, 2440, 1990, 1905, 1795, 1685, 1625, 1430, 1265, and 880 cm^{-1} which were not observed in the spectrum reported previously, while the early spectrum has bands at 2780, 2380, 2335, 1490, and 955 cm^{-1} not noted in our spectrum. All the bands typical of butoxy groups[33] are apparent in both spectra.

For the tris-*iso*propylphosphite, Fig. 7, bands are noted at approximately all the positions typical of the *iso*propoxy, $(CH_3)_2CHO$, group[33] except that the weak band at 1184 cm^{-1} was not noted and the 1108 to 1114 cm^{-1} band is replaced by either the 1136 or 1096 cm^{-1} bands.

The 1·0-mm spectrum of the tributyl compound has a band shoulder near 2750 cm^{-1} typical of P—OH bands, probably indicating the presence of some type of impurity in the sample.

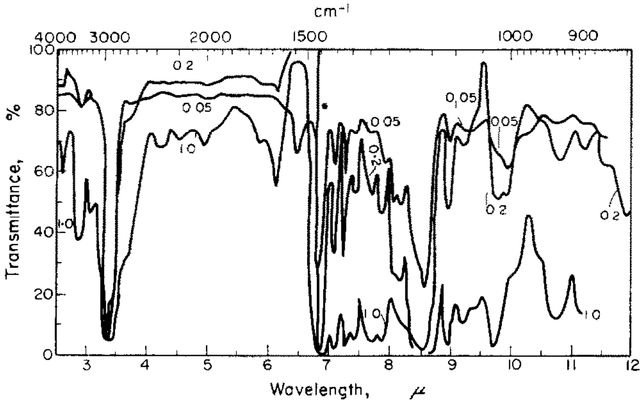


FIG. 8.—Tri-*n*-octylphosphine oxide

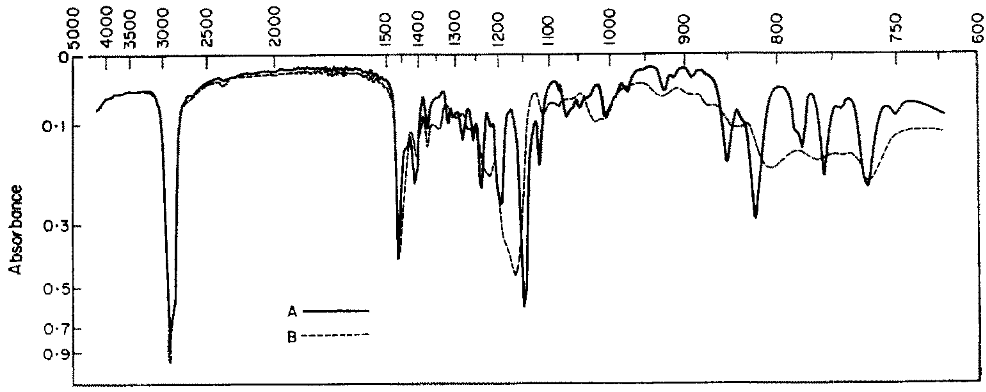


FIG. 9.—Tri-*n*-octylphosphine oxide A: solid (film) B: Liquid (film)

It is somewhat surprising how weak the absorption is near 2400 cm^{-1} due to the P—H grouping in both phosphites.

F. *Tri-n-octylphosphine oxide.* The spectrum of tri-*n*-octylphosphine oxide (TOPO) is shown in Figs. 8 and 9. This compound now has wide use as an analytical extractant. The complete spectrum has not previously been published. One study[34] reports that the phosphoryl stretching frequency occurs at 1142 cm^{-1} as a solid and at 1170 cm^{-1} in carbon disulphide solution. From our studies the frequencies for this $P \rightarrow O$ grouping are as shown in Table II.

This band is calculated to appear at 1177 cm^{-1},[8] or 1167 cm^{-1}.[43]

The spectrum was compared to the spectra given in the literature for *n*-octane and octanol-1. Several of the bands noted for the phosphine oxide occur at the same position as in the comparison spectra. Others appear which are typical of organo-phosphorus compounds.

The ~2900 cm^{-1}, 1460, 1140, 1116, 821, 760, and 720 cm^{-1} bands in the TOPO spectra correspond to similar bands in the hydrocarbon, alcohol, or both. The first three of these are the C—H stretching, bending, and skeletal frequencies; while the last, 720 cm^{-1}, is the CH_2 rocking vibration which appears in linear hydrocarbon derivatives containing 4 or more methylene groups.

TABLE II. PHOSPHORYL VIBRATION POSITIONS FOR TOPO

State	$P \rightarrow 0$, *cm*$^{-1}$
Solid film	1143
Liquid film	1165
CCl_4 solution	1154
Cyclohexane solution	1192 or 1171

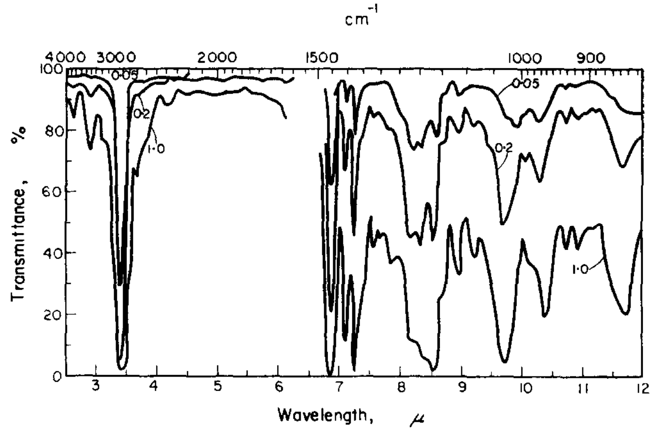


FIG. 10.—Tris-(2-ethylhexyl)-phosphine oxide (purified) (in CCl_4)

Unfortunately, no good correlation occurs for P—C compounds in the literature. Although bands in the 715 to 770 cm^{-1} region have been attributed to this vibration,[42] other work,[11,12] as well as the similar bands of hydrocarbon derivatives noted in the previous paragraph, indicate a band in this region may be due to other types of vibrations.

G. *Tris-(2-ethylhexyl)-phosphine oxide.* The spectrum of a sample of tris-(2-ethylhexyl)-phosphine oxide in carbon tetrachloride is displayed in Fig. 10. In the spectrum several absorption bands can be identified. These include: 3345 cm^{-1} H-bonded OH impurity, 2915 and 2865 C—H stretching, 1447 CH_3 deformation and C—H_2 scissor, 1390 CH_3 sym. deformation, 1155 phosphoryl stretching (1160 in CS_2, 1150 as solid film) and, not shown, the ~720 cm^{-1} CH_2 rocking vibrations. The band at 2780 cm^{-1} may be a tertiary carbon stretching vibration. The phosphoryl frequency tris-(*iso*-octyl)-thiophosphate is calculated to appear at 1177 cm^{-1}.[8]

H. *Tris-(iso-octyl)-thiophosphate.* The spectrum of a commercial sample of tris-*iso*-octylthiophosphate, $(C_8H_{16}O)_3\ P \rightarrow (S)$, is presented in Fig. 11. Hooge and Cristen[28] cite bands in the 550 to 750 cm^{-1} regions as due to the P → S group; Nyquist,[37] 715 to 760 cm^{-1}; and Bellamy,[10] 850 to 600 cm^{-1}. Bellamy remarks that this absorption usually is weak. Thomas, as cited by Bellamy, assigns a narrower range of 800 to

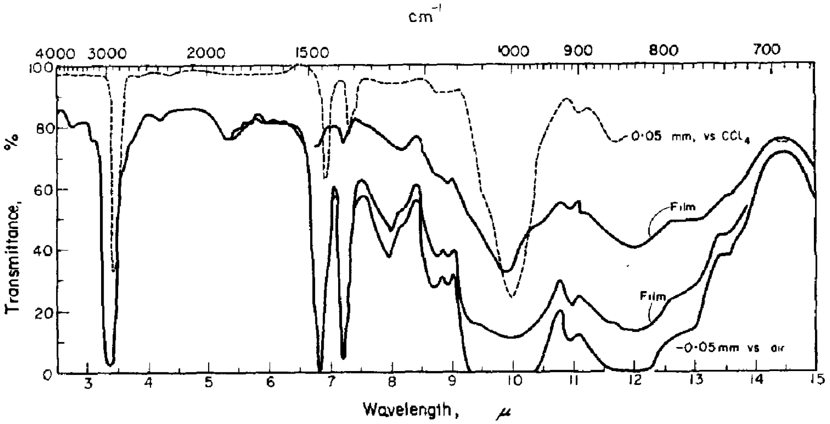


FIG. 11.—Tris-(*iso*-octyl)-thiophosphate

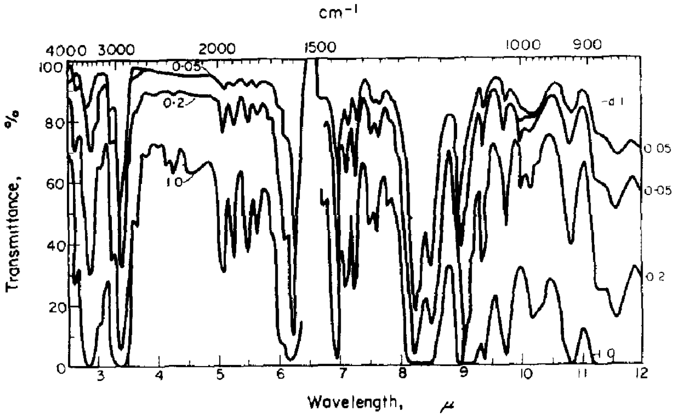
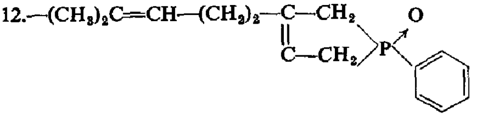
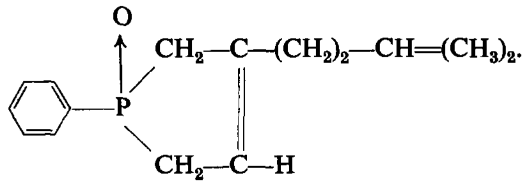


FIG. 12.—



845 cm^{-1} for trialkylthiophosphates. In Fig. 11 a very broad absorption band is shown with maximum intensity at 820 cm^{-1}, probably due to the P → S group. Other bands identifiable are the CH bands at ~2900 and 1450, and the 1000 cm^{-1} P—O—C (alkyl) bands. The shoulder near 2650 cm^{-1} indicates the presence of P—OH as an impurity; the band at 2350 cm^{-1}, P—H as an impurity; and the band near 1870 cm^{-1}, an unidentified impurity.

I. 1-*Phenyl*-3-*isohexenyl*-1-*phospha*-3-*cyclopentene*-*P*-*oxide*. The spectrum of an unsaturated cyclic phenyl-substituted phosphine oxide is shown in Fig. 12. The structure of this compound is:



Perhaps one of the most complicated of the spectra recorded, it is nevertheless possible

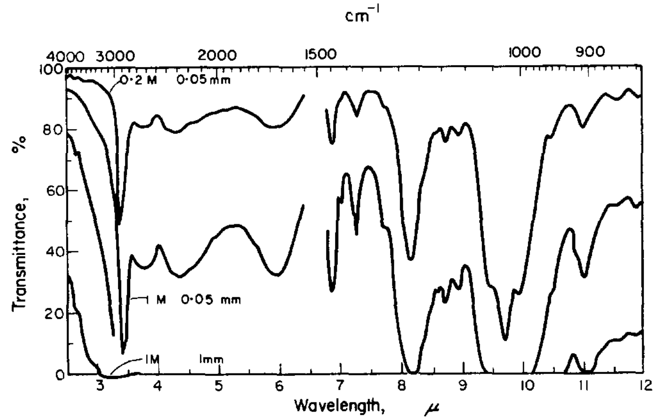


FIG. 13.—Di-*n*-butylphosphoric acid

to assign many of the observed bands to certain groupings of this compound, or possible impurities, as listed in Table III.

Impurities indicated are hydrogen-bonded types containing an OH group and lesser amounts of phosphine P—H and P—OH acidic impurities. The assignment of the phosphoryl frequency, calculated as 1183 cm^{-1} without consideration of the ring, is somewhat in doubt because of the strong doublet at 1215 and 1205 cm^{-1}. Tertiary phosphine oxides sometimes have a doublet phosphoryl vibration. The 1165 cm^{-1} band assigned to a phenyl vibration or the 1107 cm^{-1} band could also be due to the phosphoryl group. The 926 cm^{-1} band is assigned to the P-cyclic grouping by analogy to the observation of Cason and co-workers[16] who investigated some cyclic phosphorus esters.

J. *Dibutylphosphoric acid.* The spectrum of a sample of dibutylphosphoric acid is displayed in Fig. 13. This spectrum can be compared to the published spectra of this compound: Sadtler No. 9041,[40] and Peppard and co-workers.[38] In general, all three spectra are quite similar; however, the ~1230 cm^{-1} band of the Sadtler spectrum is less intense than in the other two. In our spectra, bands are resolved at 1058, 1030, and 1005 cm^{-1} whereas the spectrum reported by Sadtler has a shoulder at ~1060 and a broad band centred at 1030 and the 1030 cm^{-1} band is observed only in the spectrum presented by Peppard.

Gaunt and Meaburn[23] also show a spectrum of dibutylphosphoric acid which is very similar to all of the other spectra below 1450 cm^{-1} but differs slightly above this frequency.

TABLE III. BAND ASSIGNMENTS FOR UNSATURATED CYCLIC PHOSPHINE OXIDE

Band, approx.		Intensity*	Assignment
μ	cm⁻¹		
2·62	3815	mw sh	
2·88	3470	s	—OH polymer
3·04	3290	m sh	—OH polymer
3·22	3105	ms	$\mathrm{CH{=}C}<$ olefin
3·41	2930	vs	CH stretch
3·45	2900	ms sh	CH stretch
3·62	2760	w	P—OH
4·27	2340	w	P—H
4·49	2230	w	
4·65	2150	w	
5·06	1975	w	
5·24	1910	w	
5·47	1830	w	
5·61	1785	w	
5·83	1715	w	
5·99	1670	mw sh	$\mathrm{HC{=}C}<$ olefin
6·09	1640	m	$\mathrm{HC{=}C}<$ olefin
6·22	1605	s	Phenyl
6·77	1475	mw	Phenyl
6·91	1445	m sh	CH_3—C bend
6·96–8	1435	vs	CH_3—C bend, P—ø
7·10	1410	sh	
7·12	1405	m	CH_3—C bend
7·27	1375	m	CH_3—C bend
7·51	1330	mw	
7·64	1310	m	HC=C olefin
8·22	1215	vs	P → 0 stretch
8·30	1205		P → 0 stretch
8·59	1165	vs	Phenyl
9·02	1108	vs	—M bonded P → 0 stretch
9·36–9	1070	m	Phenyl
9·72	1030	mw	Phenyl
10·0	1000	m	
10·17	982	mw sh	
10·26	974	mw sh	
10·80	926	m	P—cyclic ring
11·3	885	ms	
11·55	866	ms	$>\mathrm{C{=}CH}$ olefin
12·2	820	m	
13·1	764	ms sh	
13·5	740	vs	Phenyl
14·48	690	vs	Phenyl

* w = weak, m = medium, s = strong, v = very, sh = shoulder.

K. *Tributylphosphate.* The infrared spectra of tributylphosphate available in the published literature, reports, and infrared catalogues are rather sparse. This is somewhat surprising since the compound is widely used as an extractant in atomic energy work. Reports have shown that the extraction of uranium and of other undesired elements by tributylphosphate is often affected by the presence of small proportions of impurities. The nature of the separation processes tends to promote the accumulation of degradation products of both the organo-phosphorus ester extractant and the diluent.

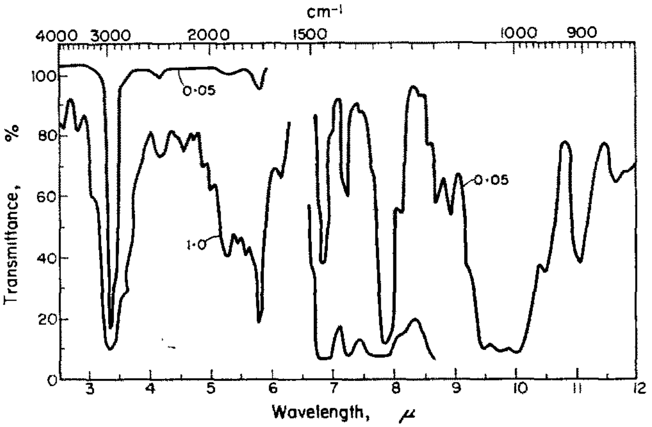


FIG. 14.—Tri-*n*-butylphosphate distillation residue

The approximate positions of the infrared absorptions bands of tributylphosphate as reported by various investigators are shown on Fig. 16.

Examination of these compiled spectra of tributylphosphate show there are many discrepancies in the position and relative intensity of some of the bands.

In the Kendall,[30] Daasch and Smith,[19] Gaunt and Meaburn, crude,[23] and, perhaps, in the Sadtler[40] spectra, bands occur in the 1550 to 2000 cm^{-1} region, which, with one exception, are absent in the Gaunt-Meaburn spectrum of a sample of purified material. Unfortunately, the path length used in most cases was insufficient to reveal bands due to weak absorbing overtone, combination vibrations or the absorption due to minor impurities. Our spectra, discussed later, show that many of these bands are noted only if samples in cells of longer path length are used in the absorbance measurement.

The purified sample studied by Gaunt, the Sadtler spectrum for a longer path length, and the Kendall spectra have too great an absorption in the 975 to 1100 cm^{-1} region for resolution of the individual absorption vibrational modes. Several differences in the spectra are also noted in the 700 to 920 cm^{-1} region.

Besides these spectra, several individual absorption bands for tributylphosphate have been reported as listed in Table IV.

Some of the typical positions for bands expected for various possible impurities are listed in Table V.

Figures to be published in a separate report show the spectra of varied samples of tributylphosphate investigated during this work. Shown here are Fig. 14, the spectrum

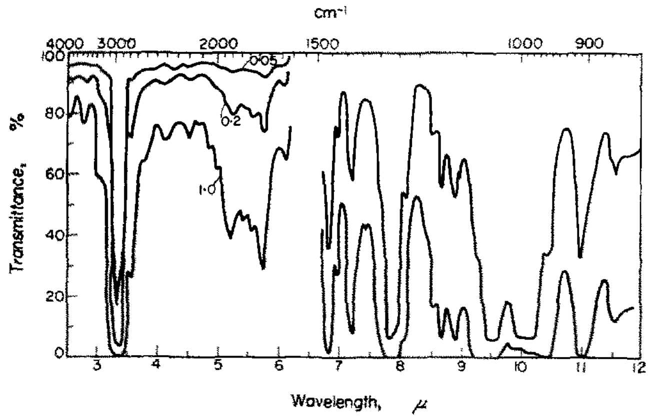


FIG. 15.—Tri-*n*-butylphosphate

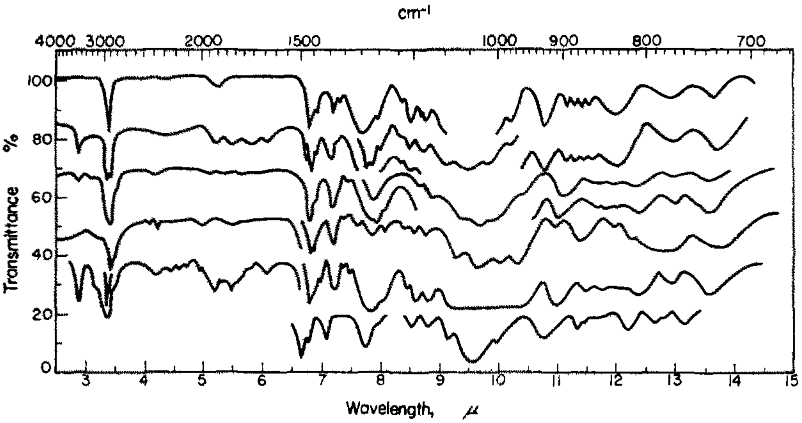


FIG. 16.—Literature spectra of tri-*n*-butylphosphate

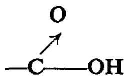
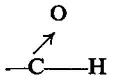
TABLE IV. SELECTED ABSORPTION PEAKS REPORTED FOR TRIBUTYLPHOSPHATE

Bands, *cm*$^{-1}$	Reference
1233, 1275, 1290	5
931, 991, 1026	14
1269 (P → 0)	15
1015, 1031, 1061, 1129, 1157, 1280	35
989–93, 1250, 1290	24

of a very impure compound, and Fig. 15, the spectrum of fairly pure tributylphosphate. By use of thicker cells and up to 27% of the compound in the carbon tetrachloride diluent, many bands appear in the 2·7 to 6·3 μ (1600 to 3700 cm^{-1}) region which are often absent in the spectra of films or those for solutions in 0·05-mm cells or at lower concentrations. The use of thin cells or lower concentrations or both is necessary, however, to determine the location of absorption peaks beyond 6·5 μ (under 1540 cm^{-1}).

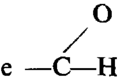
From a study of the absorbancies of both major and minor infrared absorption peaks using cells of three different path lengths and two or three concentrations of tributylphosphate, it was shown that, in general, both Beer's and Lambert's laws apply to all absorption peaks investigated. It was also indicated that the intensity of bands in the 2·7 to 6·3-μ region are rather sensitive to the concentration of tributylphosphate. Consequently, for comparison of the intensities of peaks in this region all absorbancies were adjusted numerically to that expected for 25% (w/v) solutions, based on Beer's law.

TABLE V. EXPECTED IMPURITY BAND POSITIONS

Group	Bands, *cm*$^{-1}$
P—OH	2500–2640
C—O—C	1145
(C)—NO	1645
(C)—NO_2	1550, 1355
 $-\overset{O\nearrow}{C}-OH$	1695–1725, 2500–3450
C=C	1740–55
(R)—OH	3200–3550
 $-\overset{O\nearrow}{C}-H$	1720–40, 2720, 825–975 (w–m)
H—O—H	3095, 1715, 673
P—H	2350–2450

The residue from the flask following a vacuum distillation of commercial tributylphosphate was used in recording the spectrum shown in Fig. 14. The functional groups responsible for some of the bands can be identified as follows: 3500 hydrogen-bonded hydroxy; 2950 C—H stretching; 2600 (shoulder) acidic P—OH-type impurity; 2400 phosphine P—H-type impurity; 1900 to 1700, due partly to unidentified impurities; 1270 phosphoryl stretching mode; 1145 and 1110 cm^{-1} typical for several butyl-substituted compounds.

The spectrum of the purer sample, Fig. 15, can be discussed and compared to that of the impure sample. The 2950 cm^{-1} band due to a C—H stretching mode is expected; the ~2600 partially resolved shoulder attributable to —P—O-type impurities is less pronounced than in Fig. 14; the ~2600 band attributed to phosphine-type impurities is of about the same intensity as in the less pure product; the 1900 to 1700 cm^{-1} bands are of far lesser intensity than in the impure tributylphosphate, especially the unidentified 1725 cm^{-1} band. These changes on purification indicate that at least a portion of the absorbancy of the bands, in all but the first case, are due to impurities not removed during purification. The unexplained bands could not be confidently assigned from examination of the spectra of mixtures of a purer tributylphosphate with known amounts of butanol, mono- or dibutyl-phosphoric acids, nor tributylphosphine. Among the types of groups which can have bands in the 1900 to 1700



cm^{-1} region are: carboxylic acid —C(O)OH, olefin C=C, and aldehyde $-\overset{\overset{O}{/}}{C}-H$.

The spectrum of the purer sample of tributylphosphate compares fairly well with some of the spectral bands shown in the literature, especially where varied authors agree as to the position and intensity of the infrared absorption bands,.

Acknowledgements—The authors are indebted to W. J. Ross and R. E. Feathers for synthesis or purification of some of the organo-phosphorus compounds, J. M. Schreyer for the loan of an Infracord, and T. G. Burke for assistance in obtaining some of the spectra.

Zusammenfassung—Die IR-Spektren von einigen für die Extraktion von Metallionen wichtigen organischen Phosphorverbindungen werden mitgeteilt und diskutiert. Spektra einiger wichtiger Abbauprodukte und Verunreinigungen sind ebenfalls gezeigt. Viele der für die Absorbtionsbanden verantwortlichen organischen Gruppen werden identifiziert.

Résumé—Les auteurs présentent et discutent les spectres infra-rouges d'un groupe de composés organiques du phosphore utilisés pour l'extraction des métaux en solutions aqueuses acides. Les spectres de quelques produits de dégradation organiques du phosphore ou des impuretés probables sont aussi présentés. Plusieurs groupes organiques responsables de certaines vandes d'absorption sont identifiés.

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THE QUANTITATIVE DETERMINATION OF URANYL ION BY MEANS OF THE URANYL-SENSITISED PHOTODECOMPOSITION OF OXALIC ACID

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Summary—The uranyl-sensitised photodecomposition of oxalic acid is followed by the use of a modified Warburg constant-volume micro-manometric apparatus. The minimum concentration of uranyl ion determined was 100 μM.

INTRODUCTION

OXALIC acid, in aqueous solution, decomposes very slightly when irradiated with ultraviolet light to give at least one gaseous product.[1,2,3] Uranyl ion sensitises this photodecomposition.[1] Furthermore, the rate of gas production for a solution of given oxalic acid concentration is a function of the uranyl ion concentration of the solution.[4] The amount of gas produced from an oxalic acid solution also containing uranyl ions, during an irradiation of time t, may, therefore, be used to determine the amount of uranyl ion present. However, the actual amount of gas may be determined by means of the change of pressure in a system of given volume.[5]

An apparatus well suited to the measurement of small pressure changes in systems of given volumes at constant temperature is the Warburg constant-volume respirometer.[6] By placing properly prepared samples containing oxalic acid and uranyl ion in Warburg flasks, irradiating the samples for a time t, and measuring the change in pressure, it is possible to determine from a previously prepared standard curve and the measured pressure changes, the concentrations of uranyl ion in the samples.

EXPERIMENTAL

Apparatus

A rectangular Warburg apparatus, model USL, accommodating fourteen flask-manometer assemblies was used. The necessary modification required instalment of two General Electric G 36 T 6 germicidal lamps in place of the fluorescent lamps supplied with the apparatus. General Electric 89 G 693 ballasts were used externally in place of the original ones. The G 36 T 6 lamps are instant starting and, according to the manufacturer's specifications, emit 11·6 W of power at 2537 Å at a lamp voltage of 105 V and a current of 420 mA. Quartz Warburg vessels with centre cups and single side arms were substituted for the ordinary Pyrex vessels. A shield for protecting the eyes of workers from ultraviolet radiation was constructed and placed over the top of the constant temperature water bath of the Warburg during operation. A Beckman Model G pH meter was used for all pH measurements.

Reagents

"Baker's Analysed" $H_2C_2O_4 . 2H_2O$, $UO_2(NO_3)_2 . 6H_2O$, hydrochloric acid and sodium hydroxide were used in the investigation. A master solution of uranyl chloride was prepared in the following manner: $UO_2(NO_3)_2 . 6H_2O$ was carefully heated to give UO_3 which was washed and digested in water at 70–80°, then dried at 110° for several hr.[7,8] The molecular weight of the UO_3 hydrate was determined by igniting weighed samples at 800° to U_3O_8.[8] After determining the molecular weight of the UO_3 hydrate, the amount necessary to give the desired uranyl chloride concentration was weighed out and dissolved in dilute hydrochloric acid.

Procedure

Standard solutions of uranyl chloride were prepared by diluting appropriate volumes of the master uranyl chloride solution. Standard solutions of oxalic acid, hydrochloric acid and sodium hydroxide were also prepared. The pH of the oxalic acid solution was adjusted to 2·75 with sodium hydroxide. This oxalic acid-binoxalate mixture was 0·025M in oxalate.

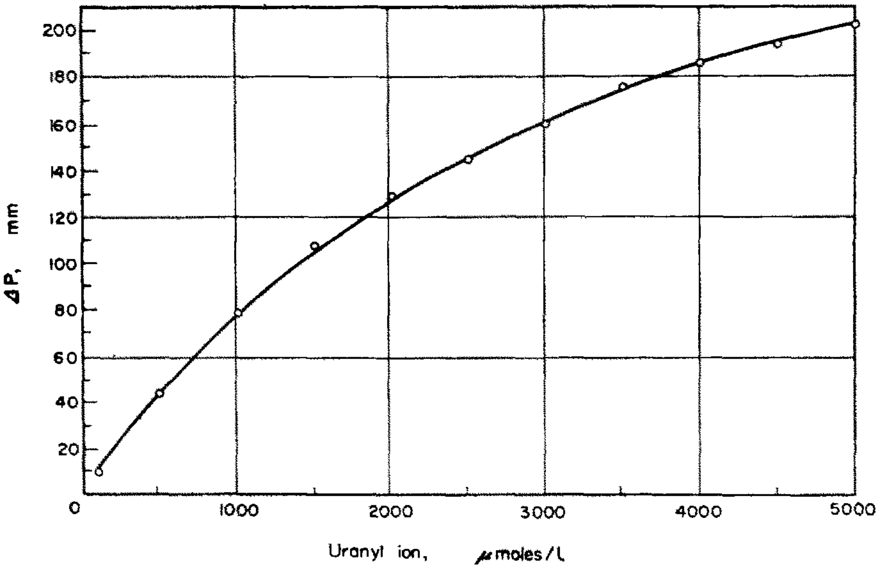

FIG. 1.—Standard curve for pressure change *vs.* uranyl concentration

In preparing the samples for analysis, the pH of each standard uranyl chloride solution was measured. Five ml of the standard solution were then diluted to 10 ml with dilute hydrochloric acid (or sodium hydroxide) and water; the amount of acid or base added being such that the pH of the diluted sample was 2·75 ± 0·25. Ten ml of the oxalic acid-binoxalate mixture (pH 2·75) were placed in a 25-ml volumetric flask and to this were added 5 ml of the prepared uranyl chloride sample. This was then diluted to volume with $1{\cdot}78 \times 10^{-3}M$ hydrochloric acid (pH 2·75). Three ml of the samples, as prepared in the foregoing manner, were then placed in each of five Warburg flasks. After introduction of the sample, each numbered flask was attached to the manometer of corresponding number. The ground glass joints of the flasks and manometers were sealed first with a water seal, then by coating with a paraffin-vaseline mixture. The ground glass joints of the side arms and side arm stoppers were sealed with a thin film of vaseline. The flask-manometer assemblies were then placed in position on the Warburg apparatus. The protective shield was placed over the top of the water bath and the pressure in the flasks was reduced by decreasing the compression on the manometer reservoirs. The shaking motor was started (frequency-75) and the flask-manometer assemblies were allowed to come to equilibrium at the temperature of the water bath (30°). After equilibrium had been reached, as indicated by relatively constant Brodie solution levels in the manometers, the flasks were irradiated for 2 min. Ten min were allowed to pass after irradiation before the final manometer readings were made. The average of the corrected pressure changes in the five flasks for a 2-min irradiation period was plotted against the concentration of uranyl ion in the original standard sample. Fig. 1 shows the curve obtained when various uranyl ion concentrations are plotted against Δp in 2 min. The standard curve may be used to determine the concentration of uranyl ion in solutions of unknown uranyl chloride concentrations provided that the compositions of the standard and unknown match in other respects.

DISCUSSION

Three factors affect the pressure changes observed in flasks containing equal volumes of an identical solution. These factors are:

(1) slight changes in the temperature of the water bath and in atmospheric pressure,

(2) small differences in the free volumes of the various flask-manometer assemblies,

(3) differences in the amount of ultraviolet radiation actually entering the solutions in the flasks.

The first factor is compensated for by means of thermobarometers as described by Umbreit *et al.*[5] The second and third factors may be accounted for by what have been termed pressure constants. From a theoretical standpoint, all flask-manometer assemblies of equal free volume containing equal volumes of identical oxalic acid-uranyl solutions into which is passing an equal amount of ultraviolet light should exhibit equal pressure changes for an irradiation of time t. Since not all flask-manometer assemblies have identical free volumes and the amount of light entering each flask is slightly different, pressure changes (after having been corrected for thermobarometer fluctuations) are not the same for all flasks containing equal volumes of identical solutions. For this reason a reference flask-manometer assembly was chosen to which pressure changes in other flask-manometer assemblies could be related in order to obtain corresponding results from all flasks. An empirical constant was obtained for each of the other flasks which, when multiplied by the pressure change in each such flask, gave a result equal to the pressure change in the reference flask. Solutions of identical composition were irradiated for a specific time interval in determining these constants for each cell in a definite position above the light source.

In addition to the thermal barometers, two standard flask-manometer assemblies were chosen for the purpose of maintaining a check on the reproducibility of the system. Before each experiment, equal volumes of a freshly prepared oxalic acid-uranyl solution were placed in the two flasks. The standard manometers were read along with the other manometers during the course of an experiment. These readings were compared from one experiment to the next and were generally found to agree to within 6 mm. The two thermobarometers were placed at diagonally opposite corners of the water bath, the standard flask-manometer assemblies occupying the two remaining corners.

As shown in Fig. 2, the change of pressure for a given irradiation period is dependent upon the pH of the system; the effect of pH being much more pronounced for the $0{\cdot}1M$ than for the $0{\cdot}01M$ oxalic-uranyl systems. In the range 2·5 to 3·0, pH has little effect on the pressure changes exhibited by $0{\cdot}01M$ oxalic acid-uranyl systems. Furthermore, the pressure change in this pH range is not greatly different from the maximum which occurs at pH 1·2–1·3. The points of Fig. 2 represent the average experimental results. The standard error for the upper portion of the curve for $0{\cdot}01\ M$ oxalic acid is ± 2 mm.

The points of Fig. 1 were found to be reproducible to within 4 mm at the lower and 8 mm at the upper uranyl ion concentration limits. In the determination of uranyl ion concentration these variations cause a relative error of 25% and 6% respectively. However, in the range $400\mu M$ to $5000\mu M$ uranyl ion the maximum relative error to be expected is 6%.

Increasing the irradiation period might make possible the determination of uranyl ion below a concentration of 100 μM. It is advisable, however, to limit irradiation periods to those which do not cause pressure changes greater than 250 mm of Brodie solution at the highest uranyl ion concentration since this is approximately the maximum pressure change which can be measured by one reading of a manometer. Thus, an increase of irradiation period would require a corresponding decrease in the upper concentration limit of uranyl ion.

Any ion which is capable of complexing with uranyl ion, sensitising the oxalic acid photodecomposition, or altering the over-all photolysis reaction in any way will, of course, be a source of interference to the method. Of the common ions studied, K^+, Na^+ and Cl^- have been found to have no observable effect on the rate of gas production. Sulphate causes a slight reduction while PO_4^{3-}, F^- and Al^{3+} greatly reduce the rate. Nitrate interferes by oxidation of organic materials. Iron^{III} sensitises the oxalic acid photodecomposition, thus increasing the rate. Any organic acid such as malonic, tartaric, lactic, succinic, glutaric, valeric and propionic, whose anions complex with uranyl ion, interferes.

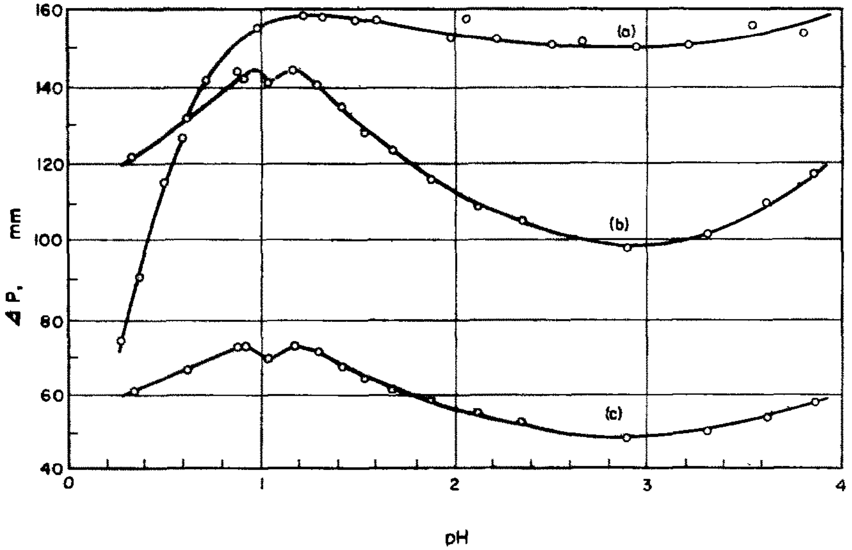

FIG. 2.—A, B and C—2500 μM uryanl ion.
A—0.01 M oxalic acid; 2 min irradiation
B—0.1 M oxalic acid; 4 min irradiation
C—0.1 M oxalic acid; 2 min irradiation

It is important that the amount of light entering the solutions in each Warburg flask be kept constant. It is necessary, therefore, to make certain that the flasks, surfaces of the ultraviolet lamps, and water in the water bath are kept clean. Several methods for cleaning the flasks are discussed by Umbreit *et al.*[5] An efficient method of removing the paraffin-vaseline sealing mixture from the flasks consists of soaking them in white gasoline followed by several rinsings in ethyl alcohol. The surfaces of the ultraviolet lamps were washed with a mild detergent solution before each run. After thorough rinsing of the lamp and water bath surfaces, the water bath was filled with distilled water to a point such that the water level was within 1/8 to 1/4 in. of the tops of the side arms on the flasks.

CONCLUSION

This method is new and its practical application requires considerable care. Further investigation is necessary for the application of the method to a specific problem. The fact that many common ions interfere restricts its use at the present time to the determination of uranyl ion in solutions of known composition. The shape of the standard curve (Fig. 1) is not ideal for the purpose of making quantitative determinations. Furthermore, the cost of the equipment involved is a deterrent.

Despite the limitations of the method, it illustrates what the authors believe to be a new analytical technique for the quantitative determination of uranyl ion.

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Zusammenfassung—Die durch Uranlyionen sensitivierte Photozersetzung von Oxalsäure wird mittels eines Modifizierten Warburgschen Mikromanometrischen Apparates (Konstantes Volum) verfolgt. Die bestimmte Mindestkonzentration an Uranyl war 100 Mikromolar.

Résumé—La photodécomposition de l'acide oxalique excitée par l'uranyle est suive par l'utilisation d'un appareil micro-manométrique de Warburg modifié à volume constant. La concentration minimale d'uranyle dosé était 100 micro-molaire.

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SPECTROPHOTOMETRIC DETERMINATION OF COPPER, NICKEL, COBALT, IRON AND MANGANESE AS THEIR PYRIDINE THIOCYANATES

SIMULTANEOUS DETERMINATION IN MIXTURES*

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Summary—Spectrophotometric determinations of copper, nickel, cobalt, iron, and manganese, based on the chloroform extraction of the metal pyridine thiocyanates, have been investigated. Optimum conditions require the pH of the aqueous solution to be in the range about 5–8; tartaric acid is used to prevent precipitation of hydrous oxides. An excess of pyridine must be used because chloroform readily extracts pyridine from the aqueous solution. Results are improved by making the extraction from a solution of high ionic strength (2 or above), which is provided by magnesium nitrate. Perchlorate decreases the absorbance, but the effect is essentially constant over a perchlorate concentration range of 0·8 to 2*M*. Although the metal pyridine thiocyanates are extracted by benzene, substituted benzenes, and halogenated hydrocarbons, chloroform is superior to other solvents in extraction efficiency and in colour stability of the extracted species. An example is given of the simultaneous determination of copper, nickel, cobalt, and iron in the same solution. Anions that also form metal pyridine compounds must be absent.

INTRODUCTION

IN 1922 Spacu[1] reported a "sensitive reaction for copper, thiocyanates and pyridine" based upon the formation of an insoluble product by reaction of the three substances in neutral solution. For use in the detection of copper, Spacu warned against the addition of an excess of pyridine, in which the precipitate is soluble. He also reported that the sensitivity for the detection of copper could be increased by shaking the mixed solutions with chloroform, which acquires an emerald green colour. The reaction was later reported[2] as a microchemical method for copper, in which the chloroform extract was evaporated to dryness and the copper was weighed as $Cu(C_5H_5N)_2(CNS)_2$, or converted to CuS for weighing. Spacu and coworkers applied the pyridine thiocyanate reaction to the gravimetric determination of copper,[3–5] nickel,[6] cobalt,[7] cadmium,[8] mercury,[9] and zinc.[10] Cuny[11] first applied the reaction to the determination of thiocyanate. Cuny, and later Golse[12] devised indirect titrimetric methods for copper, based upon the titrimetric determination of the excess of thiocyanate in the filtrate after precipitation and filtration of the copper pyridine thiocyanate.

The precipitates formed by reaction with thiocyanate and pyridine were used by Martini[13] for the microchemical detection of nickel, copper, cobalt, cadmium, and zinc; similar precipitates were obtained by the use of aniline instead of pyridine. The

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* Condensed from a dissertation submitted by Stephen S. Baird to the faculty of the Graduate School of The University of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1958. Part of the work on copper pyridine thiocyanate was presented at a joint meeting of the Southeast and Southwest Regions, American Chemical Society, in New Orleans, Louisiana, December, 1953.

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pyridine thiocyanate reaction has been widely used for the determination of copper in organic materials.[14–22]

There are but few literature references to the instrumental measurement of the chloroform extract of copper pyridine thiocyanate. Jean[23] used the method for the determination of copper, cobalt, and nickel, although the instrumental details (including any optical filters used) were not given. Moeller and Zogg[24] recorded the spectrum of the chloroform extract of copper pyridine thiocyanate, and reported an absorption maximum at 415 mμ. They claimed that so long as stoichiometric quantities of pyridine and thiocyanate were present, the coloured compound was extracted by chloroform; on the contrary, we have found that an excess of pyridine is essential for the extraction.

Kruse and Mellon[25] used the chloroform extract of copper pyridine thiocyanate for the determination of thiocyanate; the absorbance was measured at 410 mμ. They reported that the colour was found to vary with the volume of aqueous phase in the extraction, and claimed that the colour "does not follow Beer's law." Only solvents "with some dipole" were reported to extract the coloured species.

Recently, Forsythe, Magee and Wilson[26] have fractionally precipitated nickel and cobalt as their pyridine thiocyanates by pH control. The nickel precipitate was extracted into chloroform and the cobalt precipitate was extracted into methyl *iso*butyl ketone for spectrophotometric determination.

The pyridine thiocyanates of twelve bivalent cations have been prepared in this laboratory, and many of their properties have been measured.[27] The present report deals with the spectrophotometric determination of copper, nickel, cobalt, iron, and manganese. Because these elements are frequently found together in various alloys, simultaneous spectrophotometric determination can prove to be useful. An illustration is given of the simultaneous determination of copper, nickel, cobalt, and iron.

EXPERIMENTAL

Apparatus

A Beckman Model DK-2 Recording Spectrophotometer was used for scanning to obtain the absorption spectra. A Beckman Model DU Spectrophotometer was used for quantitative absorbance measurements. Silica cells of 1·00-cm optical path were used with both instruments. A Leeds and Northrup Stabilised pH Indicator was used for the pH measurements, and a Beckman Model K Automatic Titrator was used for rapid adjustment of the pH of solutions before extraction.

Reagents

Unless otherwise specified, all reagents were of A.C.S. specification reagent purity. The water used was purified to a specific resistance of 200,000 Ω or more.

Standard solutions

Where convenient to do so, 0·10*M* stock solutions were prepared; solutions of lower concentration were prepared, as needed, by volumetric dilution of the stock.

Copper nitrate: 6·354 g of pure electrolytic copper were dissolved in nitric acid; the solution was evaporated nearly to dryness, then diluted to exactly 1 litre; concentration, 0·1000*M*.

Cobalt nitrate: approximately 30 g of cobalt nitrate hexahydrate were dissolved to make 1 litre of solution, which was standardised against standard EDTA and standard magnesium chloride solutions, using Eriochrome Black T indicator screened with methyl orange in the presence of diethanolamine.

Nickel nitrate: 5·869 g of pure nickel foil were dissolved in nitric acid; the solution was evaporated nearly to dryness, then diluted to exactly 1 litre; concentration, 0·1000*M*.

Iron^{II} chloride: 0·0559 g of pure iron wire for standardising was dissolved in iron-free hydrochloric acid; the solution was evaporated to about 5 ml, then diluted with water, and 10 ml of 20% hydroxylamine hydrochloride were added. Dilution to exactly 1 litre gave a 0·00100*M* solution. Solutions prepared in this way were stable for several months.

Manganese sulphate: 16·90 g of manganese sulphate monohydrate were made to 1 litre; concentration, 0·100*M*.

Buffer solutions

These were prepared to contain, per litre, 50 ml of pyridine, 2·0 g of potassium thiocyanate, and 30 g of magnesium nitrate, along with the buffer constituent. Hydrochloric acid or sodium hydroxide, as appropriate, was added to give the desired pH, which was measured with a pH meter. Buffer constituents for the various pH regions were as follows: pH about 2, saturated potassium chloride and hydrochloric acid; pH 3 to 6, potassium acid phthalate; pH 7 to 8, pyridine; pH 9 to 11, borate.

Other reagents and solvents

Percentage composition of solutions is given on a weight/volume basis.

Acetic acid: 1*M*.

Chloroform: reagent grade.

Citric acid: 1%.

Hydroxylamine hydrochloride: 20%.

Magnesium nitrate hexahydrate: 50%.

Potassium thiocyanate: 10%

Pyridine: clear, water-white; Coleman and Bell or J. T. Baker.

Tartaric acid: 10% and 20%.

Determination of Copper

Procedure

To approximately 100 ml of solution, containing about 0·2 to 0·5 mg of copper, add 25 ml of 10% tartaric acid (or 25 ml of 1% citric acid), 6 ml of 50% magnesium nitrate, 8 ml of pyridine, 8 ml of 10% potassium thiocyanate, and adjust the solution to pH 5–7 with sodium hydroxide. Extract with three 10-ml portions of chloroform. Drain the extracts into a 50-ml volumetric flask and dilute to about 40 ml with fresh chloroform. Add 1 ml (or more if necessary) of acetone to clear the extract, and complete the dilution to volume with fresh chloroform. Measure the absorbance, against a reagent blank, at 405 mμ in a 1·00-cm cell. (Obviously, the concentration range can be proportionately decreased by the use of cells of longer optical path.)

The absorption spectrum of the chloroform extract of copper pyridine thiocyanate is shown in Fig. 1, Curve A. A plot of absorbance against copper concentration is a straight line, the slope of which corresponds to a specific absorptivity of 27·4 ml per mg-cm.

If perchlorate is present in the original copper solution, adjust the perchlorate concentration to 0·8 to 2*M* (using sodium perchlorate), and proceed as described above. In this case the specific absorptivity is 22·8 ml per mg-cm.

Effect of variables

Effect of pH. A series of buffer solutions covering the pH range 2 to 11 was prepared; the buffers contained the pyridine and potassium thiocyanate reagents to develop the copper product, and magnesium nitrate to increase the ionic strength. Equal volumes of buffer solution and a standard copper solution were mixed, and the pH was measured. The mixture was transferred to a separatory funnel, and extracted with one 5-ml portion of chloroform. (A single extraction was used so as not to "smear out" the pH effect.) The extract was diluted to 10 ml with chloroform, and its absorption spectrum determined. The spectral curves are shown in Fig. 2. Fig. 3, in which absorbance (at 405 mμ) is plotted against pH of the aqueous solution before extraction, shows that there is a considerable pH range over which extraction is nearly constant.

The pH of the residual aqueous layer, after extraction with chloroform, was measured. Results are shown in Table I. The change in pH was always in the direction towards the neutral point (pH 7) which suggests that the change in pH was due to extraction of the buffer components by chloroform. The change of pH in the region used in the standard procedure (pH 5–7) is not significant. If ammonium thiocyanate is used as reagent, the decline in extractability begins at pH about 7, instead of 8, and

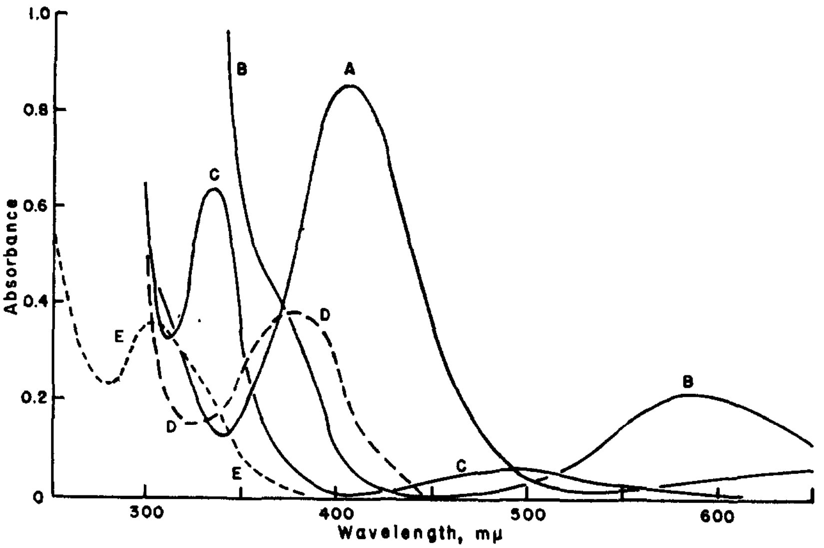

FIG. 1.—Spectral curves for chloroform solutions of metal pryidine thiocyanates. A: Copper, 31 μg/ml. B: Nickel, 1·1 mg/ml. C: Cobalt, 11·9 μg/ml. D: Iron^{II}, 11·2 μg/ml. E: Manganese, 0·30 mg/ml.

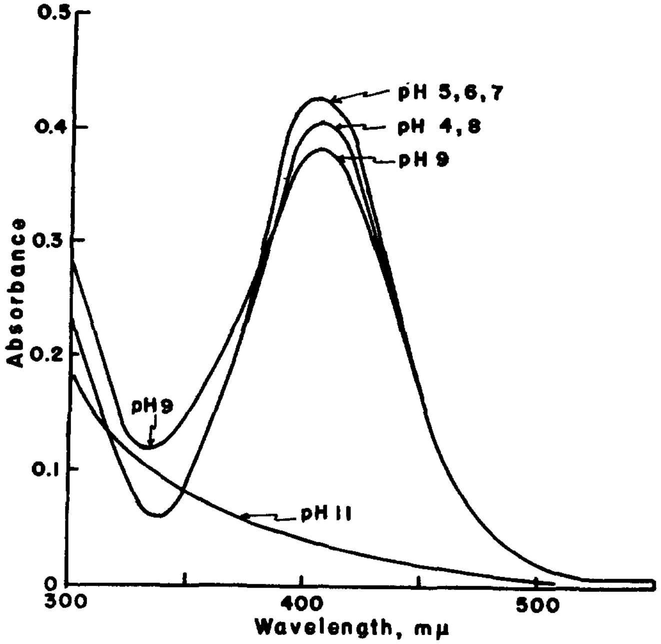

FIG. 2.—Absorption spectra of chloroform extract of copper pyridine thiocyanate as a function of initial pH of aqueous solution.

for a given pH above 7 the extractability is much less than when potassium thiocyanate is used. This difference is probably due to the competition between pyridine and ammonia in the solution for the complexation of the copper. It should be remarked that at high pH (above 11), different solute species are present; the aqueous solution and the chloroform extract are yellow-brown.

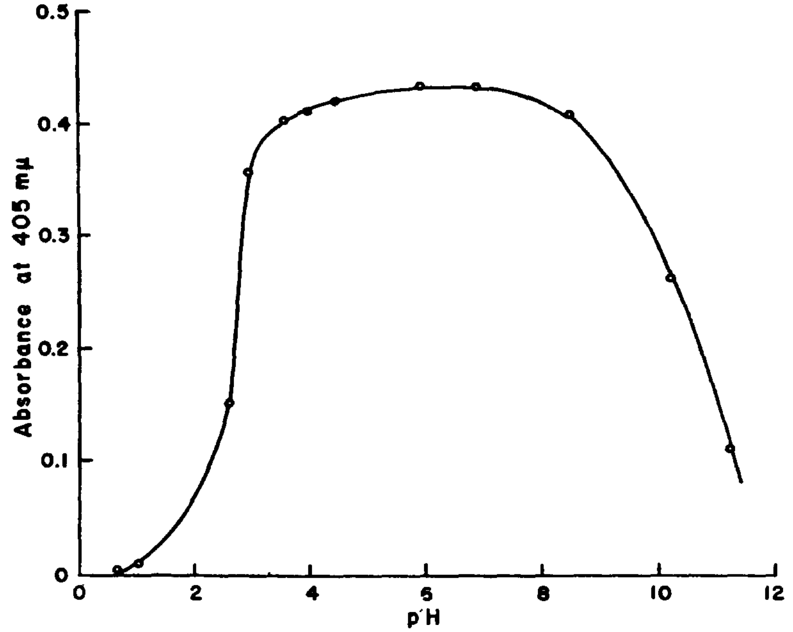

Fig. 3.—Effect of pH on chloroform extraction of copper pyridine thiocyanate. Copper, 16 μg/ml.

Table I.—Change of pH of aqueous solution due to extraction of copper pyridine thiocyanate with chloroform.

Initial pH	Final pH
3·30	3·95
3·52	4·15
4·03	4·92
5·00	5·08
5·98	6·30
6·67	6·98
6·88	7·12
7·88	7·70
8·88	8·52
10·04	9·25
10·9	9·6

Effect of tartaric acid. With a view to the possible use of tartaric acid as a sequestering agent to prevent the precipitation of various hydroxides, a study was made of the effect of tartaric acid on the extraction of the copper pyridine thiocyanate. When sufficient magnesium nitrate is added to give an ionic strength of 2 or greater, the colour (absorbance) of the extract, for a given amount of copper, is independent of the concentration of tartaric acid.

Effect of ionic strength. Magnesium nitrate was used to vary the ionic strength of the solutions. To 25·0 ml of copper solution (60 μg per ml) were added, in order, 10 ml of 20% tartaric acid, 2 ml of

10% potassium thiocyanate, 2 ml of pyridine, and various volumes of 50% magnesium nitrate. The mixture was adjusted to pH 5 with sodium hydroxide; all solutions were brought to the same volume, then extracted twice with 10-ml portions of chloroform. The extracts were diluted to 25·0 ml in volumetric flasks, and cleared by shaking with about 50 mg of ammonium chloride. The absorbance was measured at 405 mμ. A plot of absorbance against ionic strength of the solution is shown in Fig. 4. The initial point represents the ionic strength of the solution used in the pH studies. The conditions chosen for the standardised procedure are such that the ionic strength will always exceed 2.

Jean[23] reported that acetate is necessary for adequate extraction of copper pyridine thiocyanate from solutions containing iron^{III}. The effect observed by Jean may be an ionic strength effect. Chalk[28] states that acetate must be absent. When the ionic strength and the concentrations of pyridine and thiocyanate are adequate, no detrimental effect of acetate has been observed.

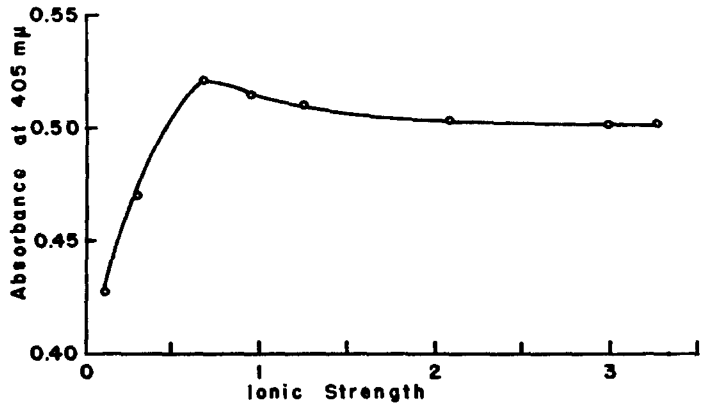

FIG. 4.—Effect of ionic strength on extraction of copper pyridine thiocyanate.

Effect of perchlorate. Fixed amounts of copper (10·0 ml of solution containing 60 μg per ml) were treated with various volumes of 8*M* perchloric acid, and tartaric acid, pyridine, and potassium thiocyanate as in the standard procedure. After adjustment to pH 5, the mixtures were extracted with two 10-ml portions of chloroform; the extracts were cleared with a small amount of solid ammonium chloride, diluted to 25·0 ml, and the absorbance measured at 405 mμ. A plot of absorbance against concentration of perchlorate is shown in Fig. 5. It was determined that perchlorate adversely affected the distribution of pyridine between the aqueous and the chloroform phases. If perchlorate is present, its concentration should be adjusted to 0·8–2*M* (the plateau region in Fig. 5) before proceeding with the analysis. Because of the lower absorptivity in the presence of perchlorate, the standardisation of the photometric method would, of course, have to be made under the same conditions.

Solvent effects. It was found that aliphatic hydrocarbons, alicyclic hydrocarbons, aliphatic ethers and esters did not extract copper pyridine thiocyanate. This was believed to be due to the unfavourable distribution of pyridine between water and the organic solvent under the conditions of formation of copper pyridine thiocyanate. In order to test this point, aqueous solutions of pyridine (1*M*) were adjusted to ionic strength 2 and pH 7, and extracted with an equal volume of organic solvent: chloroform, carbon tetrachloride, or di-*iso*propyl ether. Pyridine in the chloroform extract was determined spectrophotometrically by its absorbance at the 10·09 μ peak in the infrared. Pyridine in the aqueous layer was determined by adding water to about a volume of 125 ml, followed by 20 ml of 6*M* sodium hydroxide and distillation until 80 ml had passed over; the distillate was titrated with hydrochloric acid (about 0·1*N*) to a pH of 4·0. The distribution ratio found for pyridine between the organic and the aqueous phase was as follows: chloroform, 10·7; carbon tetrachloride, 3·8; di-*iso*propyl ether, 0·1.

Table II shows some spectral data for a chloroform and for a carbon tetrachloride extract of copper pyridine thiocyanate, under identical conditions of preparation.

Benzene and substituted benzenes extracted the copper pyridine thiocyanate. The time-stability of the colour decreased with increase in complexity and number of substituents; as judged visually, the colour-stability decreased in the order: benzene $\geq$ toluene > xylene > bromobenzene, chlorobenzene, ethylbenzene > diethylbenzene $\gg$ cumene (*iso*propylbenzene) > triethylbenzene. In the latter two cases the colour was obviously changed within 1 hr, and had completely disappeared in 24 hr. By contrast, the colour in chloroform was stable indefinitely. The reason for the fading was not investigated. All of the tested halogenated hydrocarbons extracted copper pyridine thiocyanate to a greater or lesser extent; chloroform was superior to carbon tetrachloride, 1:1:2:2-tetrachlorethane (perchloroethylene), and 1:1:2-trichloroethane (trichloroethylene), in absorbance of the copper complex and in colour stability. Although the absorption curves in the various solvents were all of the same general shape, the absorption maximum occurred at somewhat different wavelengths; in chloroform, benzene, and bromobenzene, maximum absorption occurred at 405–410 mμ; in carbon tetrachloride, toluene, xylene, ethylbenzene and diethylbenzene, maximum absorption occurred at 425–430 mμ. This effect is possibly due to some interaction of the solvent with the pyridine of the complex.

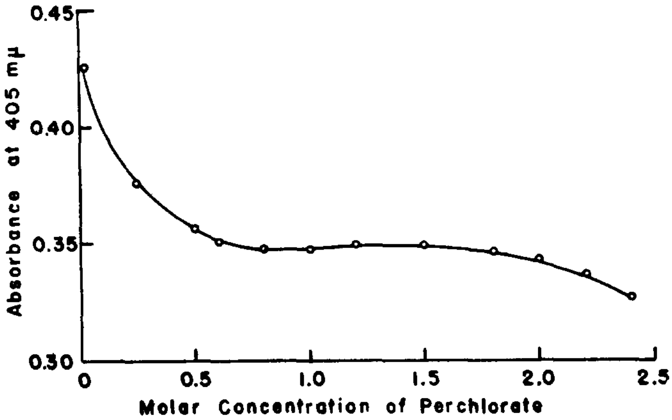

FIG. 5.—Effect of perchlorate concentration on the absorbance of chloroform extract of copper pyridine thiocyanate.

TABLE II.—RESULTS FOR COPPER PYRIDINE THIOCYANATE EXTRACTED INTO CHLOROFORM AND INTO CARBON TETRACHLORIDE

Wavelength, mμ	Absorbance in CHCl$_3$	Absorbance in CCl$_4$
350	0·197	0·013
375	0·503	0·051
400	0·835	0·143
410	0·835	0·177
425	0·722	0·209
440	0·501	0·199
475	0·113	0·072
500	0·034	0·025

A disadvantage in the use of chloroform is that below 400 mμ the absorbance of the pyridine-chloroform mixture increases quite rapidly with time (approximately quadruples in the first 50 hr). For any system that is to be measured below 400 mμ, this would require making the absorbance measurement without undue delay after the extraction, and for measurements below about 320 mμ (*e.g.* manganese pyridine thiocyanate, with absorbance peak at 300 mμ) it may be impossible to balance the spectrophotometer for zero absorbance reading of the blank.

Determination of Nickel

For the pyridine thiocyanates of nickel and the other cations reported herein, the effect of the different variables was investigated and found to be essentially the same as for copper. The same general procedure can therefore be followed for the determination of these cations.

Procedure

To approximately 100 ml of solution, containing about 20 to 60 mg of nickel, add the reagents and carry out the extraction as described for copper. If necessary, adjust the pH of the aqueous layer, between extractions, by the addition of pyridine.

The spectral curve for the chloroform extract of nickel pyridine thiocyanate is shown in Fig. 1, Curve B. Measure the absorbance, against a reagent blank, at 360 mμ; care must be taken to set the wavelength accurately because the measurement is made on a shoulder band. The absorbance is linear with concentration of nickel; at 360 mμ the specific absorptivity is 0·408 ml per mg-cm. Reduced sensitivity is obtained by measurement at 580 mμ; at this wavelength the absorbance is also linear with concentration, the specific absorptivity is 0·185 ml per mg-cm., and the optimum range is about 50 to 170 mg of nickel in the original solution.

Determination of Cobalt

Procedure

With approximately 100 ml of solution, containing 0·2 to 0·65 mg of cobalt, proceed as in the determination of copper. The spectral curve for the chloroform extract of cobalt pyridine thiocyanate is shown in Fig. 1, Curve C. Measure the absorbance at 335 mμ. Absorbance is linear with concentration of cobalt, and the specific absorptivity is 53.8 ml per mg-cm. At the 492 mμ absorption peak, the specific absorptivity is 0·415 ml per mg-cm., the absorbance is linear with concentration, and the optimum range for cobalt is about 25 to 85 mg in the original solution.

Determination of Iron

Procedure

For the determination of total iron, use a solution containing about 0·3 to 1 mg of iron. Add 20 ml of 20% hydroxylamine hydrochloride, allow the solution to stand for about 1 min, then proceed as in the determination of copper. The spectral curve for the chloroform extract of iron^{II} pyridine thiocyanate is shown in Fig. 1, Curve D. Measure the absorbance at 375 mμ. Absorbance is linear with concentration of iron, and the specific absorptivity is 35·1 ml per mg-cm. The solution has two very weak absorption regions centring at 585 and at 850 mμ; the absorptivities (0·096 and 0·173 ml per mg-cm., respectively) at these wavelengths are so small as to make the classical oxidimetric titration preferred as a completion procedure for the amounts of iron that would be required for optimum results by the spectrophotometric method.

Determination of Manganese

Procedure

Treat a solution containing about 0·8 to 3 mg of manganese^{II} as described for the determination of copper. The spectral curve is shown in Fig. 1, Curve E. Measure the absorbance at 300 mμ. Absorbance is linear with concentration of manganese, and the specific absorptivity is 12·1 ml per mg-cm. If too long a time (more than about 1 hr) has elapsed after extraction, it may not be possible to balance the spectrophotometer due to the high opacity of the reagent blank at 300 mμ.

Simultaneous Determinations

In order to apply the spectrophotometric method (matrix calculations) to the simultaneous determination of two or more constituents, it is necessary for the absorbances of the constituents to be additive. The conditions of additive absorbances are satisfied for the chloroform extracts of the pyridine thiocyanates of bivalent copper, nickel, cobalt, and iron, if sufficient pyridine and potassium thiocyanate are added to give concentrations, in the aqueous layer after extraction, of at least 40 ml and 6 g, respectively, per litre. Because some pyridine is removed with each extraction, additional pyridine may have to be added between extractions.

Table III summarises the spectrophotometric information for the different cations. With the conditions of additive absorbances satisfied, as indicated above, the absorptivites shown in Table IV apply for the simultaneous determination of the cations. Obviously, if a certain cation is known to be absent, measurement at its analytical wavelength may be omitted. The determination of manganese cannot be performed in the presence of moderate amounts of nickel, cobalt, or iron because of the opacity of the solution of their pyridine thiocyanates at 300 mμ.

TABLE III.—SUMMARY OF SPECTRAL RESULTS.

Cation	Wavelength, *mμ*	Specific Absorptivity, *ml/mg-cm*	Optimum Range, *mg/ml* in Extract
Copper	405	27·4	0·003–0·01
	705	2·30	0·03–0·12
Nickel	360	0·408	0·4–1·5
	580	0·185	1–4
Cobalt	335	53·8	0·004–0·015
	492	0·415	0·5–2
Iron	375	35·1	0·006–0·02
	525	0·096	2–7
Manganese	300	12·1	0·02–0·06

TABLE IV.—ABSORPTIVITIES OF PYRIDINE THIOCYANATES.
Tabular values in ml per mg-cm.

Wavelength, *mμ*	Cu^{++}	Ni^{++}	Co^{++}	Fe^{++}	Mn^{++}
300	10·4	21·0	50·1	40·3	12·1
335*	2·36	1·27	53·8	16·2	0·660
360*	9·53	0·408	5·90	30·8	0·136
375*	17·5	0·306	0·143	35·1	0·004
405*	27·4	0·065	0·031	20·2	0·001
492	0·97	0·028	0·415	0·080	—
525	0·21	0·047	0·331	0·096	—
580	0·68	0·185	0·039	0·037	—
705	2·30	0·019	0·006	0·057	—

* These wavelengths used for the simultaneous determination of nickel, cobalt, iron, and copper.

The simultaneous determination was tested as follows: Approximately 500 ml of a solution containing copper, nickel, cobalt, and iron were acidified with hydrochloric acid and treated with 20 ml of 20% hydroxylamine hydrochloride. After allowing the solution to stand for about 1 min, 100 ml of 50% magnesium nitrate solution were added, followed by 80 ml each of pyridine and 10% potassium thiocyanate. The solution was adjusted to pH 6–7 by addition of 50% sodium hydroxide. The mixture was transferred to a 2-litre separatory funnel and diluted to about 1 litre with water. Five extractions with 10-ml portions of chloroform were necessary before the extracts were colourless; two additional extractions were made. The extracts, drained into a 100-ml volumetric flask, were cleared by the addition of 4 ml of acetone and the solution was diluted to the mark with fresh chloroform. The absorbances, measured at 335, 360, 375, and 405 mμ, were 0·845, 0·580, 0·597, and 0·385, respectively. The matrix solution of the four simultaneous equations gave the results shown in Table V. The calculations for the simultaneous determination of more than three components are laborious, even by the matrix method.

DISCUSSION

The optimum conditions for the extraction of the metal pyridine thiocyanates are high ionic strength of the aqueous solution, adjusted to pH 5–8, and containing an excess of pyridine. Because pyridine is much more soluble in chloroform than it is in water, when equilibrated between the two solvents, the extractions are made from a relatively large volume of aqueous solution. This condition, generally unfavourable for an extraction method, is required in these methods to hold some pyridine in the aqueous phase in order to obtain complete reaction and extraction. The various metal pyridine thiocyanates vary widely in extractability in chloroform. The distribution ratios of the pyridine thiocyanates between chloroform-pyridine and water-pyridine were found, in the cases of nickel, cobalt, and copper, to be approximately 10^2,10^3, and 10^4, respectively.

TABLE V.—RESULTS OF SIMULTANEOUS DETERMINATION OF COPPER, NICKEL, COBALT, AND IRON

Component	Taken, *mg*	Found, *mg*
Copper	0·55	0·50
Nickel	46	41
Cobalt	0·63	0·61
Iron	1·0	1·1

Phosphate must be absent on account of the high concentration of magnesium ion used to increase the ionic strength. Bromide, iodide, cyanate, cyanide, and peroxydisulphate should be absent, because they also give cation-pyridine reactions similar to thiocyanate.[29]

Acknowledgment—Thanks are hereby expressed to Columbia-Southern Chemical Corporation for use of facilities in the Research Department in Corpus Christi, Texas; most of the work reported was carried out in those laboratories.

Zusammenfassung—Die spektrophotometrische Bestimmung von Eisen, Kupfer, Nickel, Kobalt und Mangan, beruhend auf der Chloroformextraktion ihrer Pyridin-thiocynate-komplexe wurde untersucht. Optimale Bedingungen benötigen einen pH-Bereich von 5–8 (wässrige Phase) und die Anwesenheit von Tartrate zur Verhinderung von Hydroxydfällungen. Pyridin muss in Überschuss anwesend sein, da es von Chloroform sehr rasch extrahiert wird. Die Resultate können verbessert werden, wenn die Extraktion aus Medium mit hoher ionaler Stärke (2 und darüber) gemacht wird, was durch Zusatz von Magnesium-nitrate erzielt wird. Perchlorate reduzieren die Absorption jedoch ist der Effekt im wesentlichen konstant über einen Bereich von 0·8–2 m in Perchlorat. Die Pyridin-thiocyanatkomplexe können auch mittels Benzol, substituiertem Benzol oder halogenierten Kohlenasserstoffen ausgezogen werden, jedoch ist Chloroform deutlich überlegen in Hinblick auf Schnelligkeit, Wirkungsgrad und Stabilität der Färbung. Ein Beispiel der Simultanbestimmung von Kupfer, Nickel, Kobalt und Eisen in derselben Lösung wird beschrieben. Anionen die ebenfalls Metallpyridin-komplexe bilden müssen abwesend sein.

Résumé—Les auteurs ont étudié les dosages spectrophotométriques du cuivre, du nickel, du cobalt, du fer et du manganèse, basés sur l'extraction par le chloroforme des thiocyanates de métal-pyridine. Les conditions les meilleures nécessitent que le pH de la solution aqueuse soit à peu près dans le domaine 5–8, l'acide tartrique est utilisé pour empêcher la précipitation des hydroxydes. Un excès de pyridine doit être utilisé car le chloroforme extrait rapidement la pyridine de la solution aqueuse. Les résultats sont améliorés en faisant l'extraction d'une solution de force ionique élevée (2 ou plus)

qui est obtenue à l'aide du nitrate de magnésium. Le perchlorate diminue l'absorbance, mais l'effet ne varie pas dans le domaine de concentration du perchlorate de 0,8 à $2M$. Bien que les thiocyanates de métal-pyridine soient extraits par le benzène, les benzènes substitués et les hydrocarbures halogènés, le chloroforme est supérieur aux autres solvants pour l'efficacité de l'extraction et pour la stabilité de la couleur du composé extrait. Les auteurs donnent un exemple de dosage simultané du cuivre, du cobalt et du fer dans la même solution. Les anions qui forment aussi des complexes de métal-pyridine doivent être absents.

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DETERMINATION OF CALCIUM IN BIOLOGICAL MATERIAL*

THE USE OF CALCEIN AS AN INDICATOR IN THE EDTA TITRATION

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Summary—The EDTA titration of calcium using the change in fluorescence of Calcein indicator under ultraviolet illumination at the end-point was very satisfactory for essentially pure calcium chloride solutions. In order to use this method for biological samples, it was found best to separate the calcium by an oxalate precipitation at a pH of 4·7, convert the calcium oxalate to calcium carbonate, and dissolve the calcium carbonate in hydrochloric acid.

INTRODUCTION

IN our laboratory, the routine method for the determination of calcium is a flame photometric procedure following a separation as the oxalate. The method[1] involves careful standardisation of technique with a precision estimated to be 4 to 5%. In certain instances, however, greater precision is desired. This could be achieved with a titrimetric method, providing the end-point was sufficiently sharp. The EDTA titration of calcium at the microgram level has been made very attractive by the recent demonstration of Wilkins[2] that the indicator Calcein[3] gave a very sharp and easily detected end-point under ultraviolet illumination.

Mori[4] has described the use of Calcein for the titration of calcium using CDTA (a reagent similar to EDTA) and has reported success in the direct titration of diluted serum and other biological fluids. Our experience with EDTA titrations has not been equally successful. We have obtained erratic results whenever any direct titrations were attempted.

Because the fluorimetric end-point was so sharp in the titration of pure solutions of calcium, the present studies were undertaken to find the conditions necessary for the determination of calcium in biological samples. We have concluded that the best procedure was to use a separation of calcium, and the separation scheme has been re-investigated.

EXPERIMENTAL

Reagents

Potassium hydroxide, 4% *solution*: Prepared by dissolving 4 g of reagent-grade potassium hydroxide in 100 ml of distilled water. It was stored in a polyethylene bottle.

EDTA, 0·0005*M solution*: Prepared from the disodium salt of (ethylenedinitrilo)tetra-acetic acid (Eastman Kodak No. 6354), and standardised against a calcium solution prepared from calcite.

Calcein solution: Prepared by dissolving 4 mg of Calcein W (G. Frederick Smith Chem. Co.) in

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* This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York.

100 ml of 0·25N potassium hydroxide solution. The solution was kept in a refrigerator, but it was found best to make fresh indicator every 3 days.

Apparatus

Illumination. A black light source (George W. Gates and Co. Mil 2F–E) giving radiation of 366 mμ was directed on the titration beaker from the side at right angles to the line of vision of the observer.

Procedure

Separation of calcium. Calcium was precipitated as the oxalate from an acetate buffered solution at a pH of 4·7. Solutions containing protein should first be acidified by the addition of glacial acetic acid. The following directions for serum may be appropriately modified for other solutions:

Dilute 0·5 ml of serum with about 4 ml of distilled water and add 4 drops of glacial acetic acid in a Vycor* centrifuge tube. Add 1 drop of bromocresol green indicator, 1 ml of 4% ammonium oxalate solution and concentrated ammonia solution until the indicator just turns blue-green. Allow the solution to stand overnight in a refrigerator. Centrifuge the solution to settle the precipitate; remove the supernatnat liquid. Place the centrifuge tube in a drying oven until dry, then transfer to a muffle furnace at 500° for 1 hr. Cool the centrifuge tube, add 1 drop of dilute hydrochloric acid (1 part of concentrated acid to 3 parts of water) to dissolve the calcium carbonate, and transfer to the titration beaker with distilled water.

Titration. The titration was carried out in a 20-ml Pyrex beaker placed on a magnetic stirrer with a 0·5 in. Teflon-covered magnet inserted in the solution to supply agitation. The calcium solution was transferred to the beaker in a final volume approximating 5 ml. Careful attention was taken not to use excessive acid to dissolve the calcium salts because the subsequent addition of 1 ml of 4% potassium hydroxide solution had been calculated to maintain the pH about 12. Five hundredths (0·05) ml of Calcein solution was added and the titration was carried out in a darkened room with ultraviolet light illuminating the solution. The blank indicator solution itself fluoresces, but the end-point could be easily detected as an appreciable change in intensity of fluorescence which was very sharp.

RESULTS

Because of interest in the determination of calcium in the serum of patients who had been treated with EDTA, recoveries of calcium under exaggerated conditions were made. The precipitations were carried out at pH 4·7, and the samples with EDTA carried a quantity equimolar with the calcium present. Table I shows a series of 40-μg samples of calcium in which the presence or absence of EDTA had no effect on the quantity precipitated.

TABLE I. PRECIPITATION OF CALCIUM WITH AND WITHOUT EDTA PRESENT

Calcium recovered, μg	
EDTA absent	EDTA present
40·0	40·0
40·0	40·0
40·2	39·8
40·0	

Recoveries on pure solutions precipitated at pH 4·7 were good, so a further comparison was made on a pooled serum sample from which one series was precipitated directly as described here, and the other series was precipitated after protein

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* Vycor centrifuge tubes are not commercially available but may be made easily by drawing the end of a test tube (Corning 19800, 15 mm × 125 mm) to a point in an oxy-gas flame. While borosilicate glass will withstand the temperature of 500°, the Vycor tubes withstand much better the thermal shock of sudden insertion into and withdrawal from the muffle furnace.

removal. The deproteinised serum sample was prepared by treating 2 ml of serum with trichloroacetic acid with a final dilution to 10 ml. A 5-ml aliquot of the acid solution was taken for calcium precipitation. If the volume of the usual quantity of protein in serum were considered, the calcium content of the aliquot of the deproteinised solution would be expected to be about 1·5% higher than that of 1 ml of serum.

Table II shows that the deproteinised serum samples had, in fact, a slightly higher calcium content than the untreated serum samples.

TABLE II. COMPARISON BETWEEN PRECIPITATION FROM UNTREATED AND DEPROTEINISED SERUM

Calcium per 100 ml of serum, *mg*	
Untreated	Deproteinised
8·7	9·1
8·7	8·9
8·8	8·9
8·6	9·1
8·7	8·8
8·8	9·0
—	—
Average 8·7	9·0

Previous studies[5] had shown that a direct precipitation of calcium from aged sera or from sera of some diseased patients did not always result in complete recovery. Complete recovery from deproteinised samples was attributed to the release of calcium from proteins when the pH was lowered. In the present work, it was reasoned that acidification of the serum without precipitation of the protein could accomplish the same result. To check this supposition, a number of 1-ml portions were pipetted from a pooled serum sample on the same day and precipitation according to present directions was carried out on three successive days. The samples were kept in a refrigerator until utilised. The results are given in Table III and show that the process of acidification liberates all of the calcium from the protein. Therefore, complete precipitation was realised.

TABLE III. RECOVERY OF CALCIUM FROM AGED SERUM

Days before precipitation	Calcium per 100 ml of serum, *mg*			
	0	1	2	3
	8·6	8·6	8·5	8·5
	8·5	8·5	8·6	8·7
	8·5	8·5	8·6	8·7
	8·5	8·8		8·5

A comparison on a number of dog serum samples was made between analyses run in the usual method of this laboratory employing the flame photometer[1] and the titration method. The results in Table IV show good agreement between the two methods.

TABLE IV. COMPARISON BETWEEN FLAME PHOTOMETRIC METHOD AND TITRATION

Calcium per 100 ml of serum, *mg*	
Flame photometer	Titration
8·3	8·6
8·8	9·0
8·7	8·9
10·1	9·8
13·9	13·6
13·0	12·7

DISCUSSION

The separation of calcium as the oxalate was utilised after initial attempts to titrate diluted serum directly resulted in poor end-points. Even wet-ashed serum samples gave erratic results; some gave satisfactory end-points immediately while others took as long as 1 to 2 hr to complete because of the fleeting nature of the end-point. The same type of behaviour was observed when phosphate was added to pure calcium chloride samples, and the difficulty was attributed to the slow reaction of the calcium phosphate precipitated at the high pH necessary for the titration. Attempts to titrate a solution of calcium oxalate were likewise unsuccessful because the calcium oxalate precipitated at the high pH. By heating the calcium oxalate at 500° we converted it to calcium carbonate which dissolved in dilute hydrochloric acid to give a solution of calcium chloride for satisfactory titration.

For the EDTA titration used in this work, the oxalate separation of the calcium made possible a uniform treatment of all kinds of samples. Because of the subsequent heating at 500°, it was not necessary to wash the precipitate to get rid of excess oxalate. Small amounts of sodium or phosphate did not interfere with the titration.

Previous work[5] had shown that all of the calcium could not be precipitated in the conventional Clark-Collip[6] manner from aged sera or in the case of some diseased states. The non-availability of some of the calcium was attributed to some alteration in the protein, possibly denaturation, which prevented complete precipitation of calcium oxalate. The liberation of all of the calcium in a form which could be completely precipitated was accomplished by trichloroacetic removal of the protein. The trichloroacetic treatment served a dual purpose in releasing the protein-bound calcium by lowering the pH (Carr[7] has shown that bovine serum albumin binds no calcium below a pH of 4·5) and in removing the protein.

If the calcium were precipitated as the oxalate at a pH at which there is virtually no protein binding, the necessity for protein removal would be eliminated. In a study of the effect of pH on the precipitation of calcium oxalate in the presence of EDTA,[8] it was shown that essentially complete precipitation could be accomplished at a pH as low as 4·7 (EDTA does not complex calcium at such pH). An acetate buffer system was utilised because the phosphate and bicarbonate systems native to serum did not buffer in this pH range. The addition of the acetic acid before the addition of ammonium oxalate released all of the protein-bound calcium by reducing the pH. Precipitation of calcium oxalate at the lower pH also reduced the possibility of contamination by calcium phosphate and by precipitation of magnesium compounds.

The indicator used in this work had an appreciable fluorescence in the absence of calcium. Wallach and coworkers[9] prepared and studied 3:6′-dihydroxy-2:4-bis-[N:N′-di(carboxymethyl)aminomethyl]fluoran which gave very little fluorescence at the end-point of a calcium titration with EDTA. Körbl and coworkers[10] studied a fluorescein-complexone (bis-[N:N′-di(carboxymethyl)aminomethyl]fluorescein) and reported that their compound showed in alkaline solution only a small residual fluorescence. These compounds are undoubtedly the purer forms of the active components in Calcein and would be preferable in a fluorescence method for calcium. For the titration end-point, however, the change in intensity of the fluorescence of the commercially available Calcein was sharp and easily detected.

Zusammenfassung—Die EDTA-Titration von Calcium mittels fluorimetrischen Endpunkte unter Verwendung von UV-Licht und Calcein-indicator, verläuft in reinen Calciumlösungen sehr zufriedenstellend. Um diese Methode für biologische Proben heranzuziehen, wird Calcium erst als Oxalat gefällt, das Oxalat ins Karbonat übergeführt und letzteres in Salzsäure gelöst.

Résumé—Le titrage du calcium par L'EDTA utilisant la variation de fluorescence de l'indicateur, la calcéine, sous exposition ultra-violette au point équivalent, est tres satisfaisant pour des solutions de chlorure de calcium pures. Afin d'utiliser cette méthode pour des échantillons biologiques, les auteurs ont trouvé qu'il était préférable de séparer le calcium par précipitation de l'oxalate à pH 4,7, de transformer l'oxalate de calcium en carbonate de calcium et de dissoudre le carbonate de calcium dans l'acide chlorhydrique.

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PRECIPITATION AND DETERMINATION OF TANTALUM AND NIOBIUM FROM HOMOGENEOUS SOLUTION WITH 3:3′:4′:5:7-PENTAHYDROXYFLAVANONE

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Summary—3:3′:4′:5:7-Pentahydroxyflavanone in fairly concentrated acidic solution (6–9*N*) does not precipitate tantalum and niobium; however, on heating or boiling, in the presence of air, this flavanone is transformed into 3:3′:4′:5:7-pentahydroxyflavone, which precipitates any tantalum and niobium present in the solution. Under the precipitation conditions, racemisation of the flavanone also takes place. The racemised flavanone which is less soluble than the original *d*-form may accompany the tantalum and niobium precipitates without affecting the quantitative determination of these elements.

The precipitation of the tantalum and niobium complexes can be controlled by regulating the acidity and the duration of boiling, as well as the concentration of the flavanone. Experimental data and procedures are given for the precipitation and determination from homogeneous solution of tantalum and niobium complexes. Zirconium and molybdenum do not interfere with the determination. Titanium must be absent or present only in minute quantity.

Since the generation of the precipitating reagent, flavone, from the flavanone is comparatively slow, the precipitation of tantalum and niobium is uniform throughout the solution. By this technique, adsorption and co-precipitation of potassium and sulphate ions in the solution are shown to be negligible. This is in contrast to the less effective dropwise addition of the flavone reported by earlier investigators, in which adsorption and co-precipitation were pronounced.

In the present study, tantalum and niobium oxides were fused with potassium bisulphate. There is no necessity using hydrofluoric acid to dissolve these oxides and therefore no polyethylene apparatus is required.

INTRODUCTION

ALL investigators and authors dealing with the chemical determination of tantalum and niobium have emphasised that it is a difficult undertaking.[6,10,16,17,19] Dupraw,[6] as late as 1953, commented that current methods for the separation and determination of the oxide combinations of titanium, tantalum, niobium and tungsten, failed to qualify as acceptable analytical procedures with respect to selectivity, accuracy, reproducibility, and ease of manipulation. Among the earlier methods for the determination of niobium and tantalum, Hoffman[10] has mentioned that Schoeller's tannin method[23] is satisfactory, though laborious. Besides the elaborate separations and operations, Schoeller's method has such undesirable features as the formation of colloidal solutions and precipitates, and absorption in solution due to hydrolysis.

Moshier and Schwarberg have used N-benzoyl-N-phenylhydroxylamine for the determination of tantalum in the presence of niobium.[20] Hiskey and his associates[9] reported the use of octochloropropane with chlorinated ores containing titanium, niobium, tantalum, and zirconium. Titanium is subsequently distilled off leaving the remaining three elements. Spectrophotometric determination of tantalum and niobium has also been reported by Klinger and Koch[11] and by Pallila, Adler, and Hiskey[21] using sulphuric acid and hydrogen peroxide.

Other approaches to the determination of tantalum and niobium have been reported.[8] Among them, the X-ray fluorescence method should be mentioned. Since the second order K-lines of niobium are difficult to resolve from the $L_{\alpha 1}$-line of tantalum, Birks and Brooks[1] have made measurements at several angles and compared the integrated intensity of the unresolved tantalum-niobium lines with that of a single niobium line. Carl and Campbell[2] adopted Birks and Brooks' procedure for the analysis of combined tantalum and niobium oxides separated chemically from ores. Mortimore, Romans, and Tews[19] made use of the internal standard principle to analyse ores containing tantalum and niobium. A more recent development in X-ray fluorescence analysis of tantalum and niobium has been the introduction of silicon and germanium crystals by Lablin.[15] By using these crystals, small amounts of tantalum can be determined in the presence of large amounts of niobium.

The method for the determination of tantalum and niobium described in this paper makes use of 3:3′:4′:5:7-pentahydroxyflavanone as a precursor of the precipitation agent. 3:3′:4′:5:7-Pentahydroxyflavanone is also known as dihydroquercetin (DHQ).

DHQ was first found in small quantity in Douglas-fir heartwood by Pew.[22] It was later discovered that this compound exists in large amounts in Douglas fir bark. Kurth and Chan[12] have made an extensive study of the extraction and isolation of this compound. Barks collected from New Mexico, California, Washington and Oregon have been analysed for DHQ, wax, and tannin. Properties such as the anti-oxidant activity of DHQ and its esters have also been investigated by Kurth and Chan.[13]

Exceptionally pure DHQ has been successfully used as a reagent for the spectrophotometric determination of molybdenum in steel and other substances.[4,5]

A large number of experiments has been carried out with the sole purpose of determining whether or not DHQ forms insoluble chelates with tantalum or niobium. Results showed that DHQ does not precipitate tantalum and niobium in acidic solution stabilised with ammonium oxalate, even after standing for a period of 3 weeks at room temperature. However, upon boiling in the presence of air, DHQ in acidic solution readily changes to quercetin which forms an insoluble chelate with tantalum and niobium. Since quercetin can thus be generated from DHQ at elevated temperatures, it provides a means for their precipitation and separation from homogeneous solution, a technique originated by Willard.[3,7] Advantages of precipitation from homogeneous solution are fully explained in a book recently published.[7]

Although the detailed mechanism involving precipitation of tantalum and niobium with DHQ is under investigation in the Aeronautical Research Laboratories, it is believed[18] that the reaction involved may take place according to the scheme shown in Fig. I.

Blank runs on DHQ, sulphuric acid, and ammonium oxalate in the same proportion and under identical conditions to those used for the determination of tantalum and of niobium have been made. Besides much unreacted DHQ, quercetin and some degradation products of DHQ were found in the precipitate.

The fact that the earth acids are readily hydrolysed and that it is difficult to keep tantalum and niobium in solution requires that the precipitation of these elements with DHQ must take place in strong acid solution and in the presence of oxalate. In $6N$ or more strongly acidic solution, DHQ is readily racemised and precipitates of tantalum and of niobium may be accompanied by the racemised DHQ, especially when filtration is performed at room temperature. The racemised material does not interfere with the determination of either tantalum or niobium when these chelates are ignited and weighed as oxides. Furthermore, elements such as zirconium, which do not precipitate with either DHQ or quercetin and which remain in 6*N* or more strongly acidic solution, can be separated quantitatively from tantalum or niobium by the technique of precipitation from homogeneous solution. Separation of tantalum oxide and niobium oxide from molybdenum is also possible. Titanium is only partially precipitated by this method and therefore separation is not possible unless only a trace of it is present.

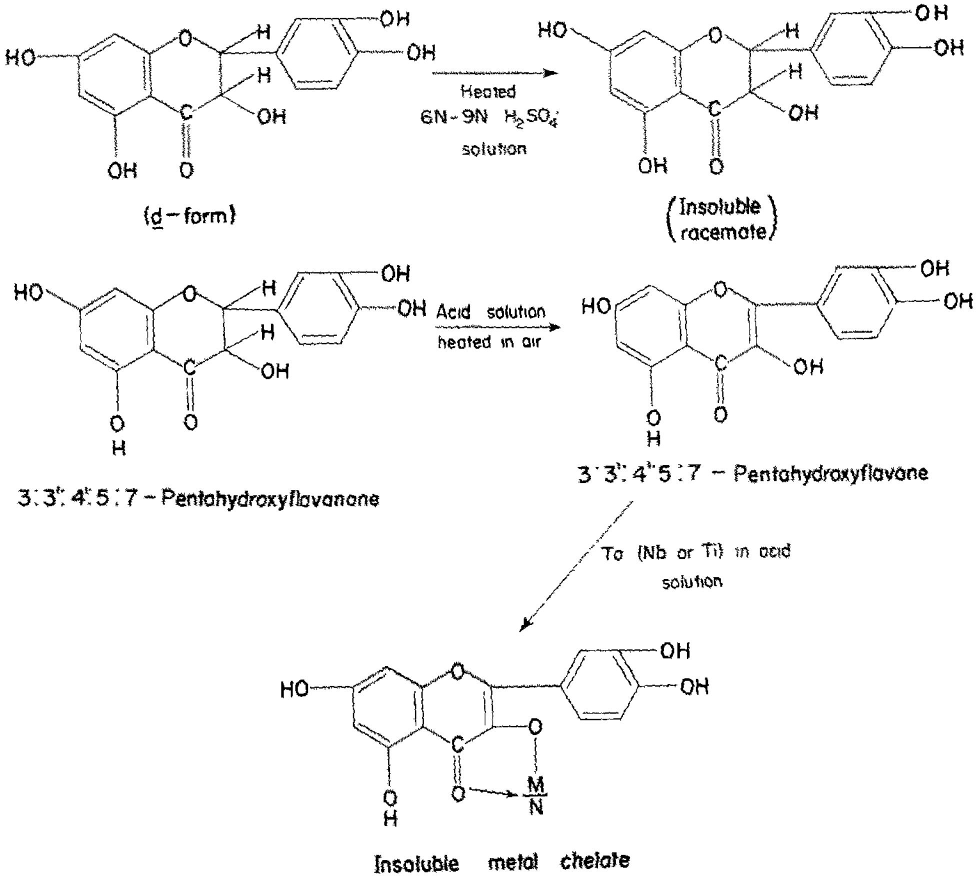

FIG. 1.—Transformation of flavanone to flavone and the formation of insoluble chelates.

EXPERIMENTAL

Reagents

DHQ: Prepared as described by Kurth and Chan.[12]

Molybdenum stock solution: To 4·9042 g of $(NH_4)_6MO_7O_{24}\cdot 4H_2O$ (analytical reagent, Merck & Co., Inc.) was added a small amount of water. The clear solution was diluted to 1000 ml (1 ml = 4 mg of molybdenum oxide).

Tungsten stock solution: To 5·69 g of $Na_2WO_4\cdot 2H_2O$ (analytical reagent, J. T. Baker Chem. Co.) sufficient water was added to dissolve the solid, then the solution was diluted to 1000 ml (1 ml = 4 mg of tungsten oxide).

Titanium stock solution: A mixture of 0·5000 g of titanium oxide (analytical reagent, J. T. Baker Chem. Co.) and 5 g of potassium bisulphate was fused until a clear mass resulted. The melt was cooled, then dissolved in concentrated sulphuric acid. More concentrated sulphuric acid was added until the final volume was 100 ml (1 ml ≡ 5 mg of titanium oxide).

Zirconium stock solution: To 3·2692 g of $ZrOCl_2 \cdot 8H_2O$ (analytical reagent, Fisher Scientific Co.) was added 10 ml of $18N$ sulphuric acid. The mixture was heated until fumes of sulphur trioxide appeared. Concentrated sulphuric acid (22 ml) was added. The mixture was cooled and carefully diluted to 250 ml (1 ml ≡ 5 mg of zirconium oxide).

Tantalum and niobium stock solutions: Tantalum pentoxide, reagent grade, was from Fisher Scientific Co. and niobium pentoxide, reagent grade, from A. D. Mackay Inc. Spectrographic determination indicated that only a trace of impurities such as Si, Fe, Mg, and Sn were present in these oxides. Fusion of niobium pentoxide with potassium bisulphate and solution of the melt in concentrated sulphuric acid and saturated ammonium oxalate solution was accomplished without difficulty. However, in the early stage of this study, fusion of tantalum pentoxide and potassium bisulphate always gave a cloudy sulphuric acid-saturated oxalate solution. After many trials, the following procedure worked well and a clear solution was obtained with a single fusion.

In a 20-ml silica crucible was placed 3 g of reagent-grade potassium bisulphate. A sample of 400 mg of tantalum (or niobium) pentoxide was weighed, placed in a 30-ml beaker (tall-form) and, with a stirring rod, mixed thoroughly with 13 g of potassium bisulphate. The mixture was transferred to the fusion crucible. The beaker and the stirring rod were cleaned twice with 2 g of potassium bisulphate and placed on top of the mixture in the crucible. Fusion was watched with great care so that no spattering took place. In this way, it was found that a single fusion will effect complete solution of the tantalum (or niobium) pentoxide. The melt was extracted with hot concentrated sulphuric acid, followed by cooling, then by the addition of saturated ammonium oxalate solution. The solution was made up to 500 ml, having a ratio of concentrated sulphuric acid to saturated ammonium oxalate of 0·825.

H_2SO_4-*DHQ-quercetin wash solution 1N:* Five g of DHQ were dissolved in 500 ml of $1N$ sulphuric acid and refluxed for 24 hr. The yellow wash solution was filtered after cooling to room temperature.

Saturated aqueous quercetin wash solution: Prepared by suspending 5 g of quercetin in 500 ml of distilled water. Any undissolved quercetin was filtered off. Quercetin can best be prepared by the method of Kurth and Chan,[13] using DHQ as the starting material. This is conveniently carried out by refluxing 200 ml of a solution containing 10 g of DHQ with 20 g of sodium bisulphite and filtering off any quercetin at intervals of 20 to 25 min. The yellow quercetin melts with sublimation at 316–317°.

Apparatus

Beckman DU Spectrophotometer

Procedure

1. *Precipitation and determination of tantalum and of niobium with DHQ*

A sample containing not more than 20 mg of tantalum oxide (or not more than 20 mg of niobium oxide) is fused in a 20-ml silica crucible with 1 g of potassium bisulphate until completely dissolved. The melt, after cooling to room temperature, is extracted with 25·0 ml of hot concentrated sulphuric acid in four to five portions. Each extract is cooled to room temperature and poured into a 250-ml beaker containing 30 ml of saturated ammonium oxalate. (If properly carried out the resulting solution is colourless and clear). To a 100-ml beaker containing 45 ml of hot water is added 0·5 g of DHQ (1·5 g in the case of the niobium determination) and heated to dissolve. Add, with stirring, the DHQ solution to the covered beaker containing the hot solution of tantalum and boil* for 1 hr (in the case of the niobium determination 15 hr†). To avoid excessive reduction of the volume of solution during boiling, cold distilled water is placed on the concave side of the watch-glass cover.

Add to the reacting solution, after removal from the hot-plate, 50 ml of cold water. Let stand 1 hr.

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* To avoid bumping due to superheating, it is advisable to heat only part of the bottom of the beaker so that boiling takes place on one side of the beaker.

† The duration of boiling depends on the amount of tantalum and of niobium present, and on the manner in which the DHQ is prepared.

Filter through a Whatman No. 40 filter paper and wash four times with 5-ml portions of $1N$ sulphuric acid-DHQ-quercetin solution and 6 times with 5-ml portions of saturated quercetin solution. Place the filter with its contents in a weighed platinum crucible, dry in an oven at 105°, then ignite to constant weight in an electric muffle furnace heated to 950° (or in a Meker burner having the same temperature, as determined by an optical pyrometer).

Evaporate the filtrate and washings to 140 ml. If precipitation is complete, no more insoluble chelate will appear.

2. *Separation of tantalum from niobium*

A. *Determination of tantalum:* The oxide sample (containing not more than 20 mg of tantalum oxide and not more than 20 mg of niobium oxide) is fused with potassium bisulphate as in 1. The melt, cooled to room temperature, is extracted with 16·8 ml of hot concentrated sulphuric acid in four to five portions. Each extract is cooled to room temperature and poured into a 250-ml beaker containing 30 ml of saturated ammonium oxalate. Heat the clear liquid to 70° and add 1·0 g of DHQ dissolved in 53 ml of hot water. Boil the solution until it turns to brown. Add 20 ml of water and decant through a Whatman No. 40 filter paper. Wash and ignite the precipitate as in 1. Reserve the last 20 ml of the washings for dissolving the DHQ to be used in the niobium determination under B. Evaporate the filtrate to 100 ml for the determination of niobium. A yellow precipitate which appears during the course of the evaporation is filtered through a Whatman No. 40 filter paper and ignited together with the main precipitate.

Determine the amount of niobium in the tantalum precipitate by fusing the entire or a part of the ignited oxide with 0·3–1·0 g of potassium bisulphate. Dissolve the melt with concentrated sulphuric acid. Add 0·1 ml of 30% hydrogen peroxide and make up to 10 ml in a volumetric flask. Compare the solution with standards similarly prepared in a Beckman spectrophotometer at 365 $m\mu$.[21] Reprecipitate tantalum if necessary by adding sufficient concentrated sulphuric acid and saturated ammonium oxalate and by following the procedure given above.

B. *Determination of niobium.* Evaporate the filtrate and the first 30 ml of the washings from the tantalum precipitation until the volume is about 75 ml. Cool the solution and add 7·6 ml of concentrated sulphuric acid. Dissolve 1–1·5 g of DHQ in the 20 ml of filtrate reserved from A and add it to the hot solution. Boil from 1–1·5 hr. Remove from the hot-plate and add 50 ml of water. Let stand for 1 hr. Decant the liquid through a Whatman No. 40 filter paper. Wash and ignite the precipitate as in 1. Evaporate the filtrate and washings to the same volume before filtration to ensure complete precipitation.

RESULTS AND DISCUSSION

The knowledge gained from the many experiments performed elsewhere[11,12] on the air oxidation of DHQ reduced the effort and time on this phase of the present experimental work. Nevertheless, a series of experiments has been conducted here to determine the optimum conditions consistent with good analytical procedures. Only a limited number of the experiments are given in this paper. A number of variables may be cited as follows:

1. Concentration of DHQ in solution.
2. Source and method of extraction of DHQ and its effects on the precipitation.
3. Concentration of sulphuric acid for the reaction between DHQ and tantalum or niobium.
4. Quantity of saturated ammonium oxalate solution added to prevent hydrolysis of the earth acids.
5. Time of boiling the reacting solution.
6. Time of standing after boiling for complete precipitation.
7. Nature of wash solutions.
8. Titanium, molybdenum, and zirconium contamination of the tantalum and niobium precipitate.

Some of the experiments on the precipitation of tantalum and niobium with DHQ are shown in Table I. These results firmly establish that, although tantalum and niobium solutions containing DHQ, sulphuric acid, and ammonium oxalate will remain clear at room temperature for many days, DHQ, under optimum conditions, can be made to react to form the corresponding flavone and thus quantitatively precipitate tantalum or niobium. A detailed study of these results has revealed that for complete precipitation under identical experimental conditions, a greater excess of DHQ is needed to precipitate niobium than to precipitate tantalum. Because tantalum is the first to precipitate from solutions of tantalum and niobium and its precipitation is accomplished with relative ease, attempts have been made to effect a quantitative separation of these two elements, with some success as shown in Table IV. This indicates an improvement over previous results obtained by other investigators, who used an acetone solution of quercetin, added by the dropwise technique.[24]

TABLE I.—STUDY OF VARIABLES ON THE DETERMINATION OF TANTALUM AND NIOBIUM WITH DHQ

Experimental conditions: Sat. $(NH_4)_2C_2O_4$, 30 ml; total volume, 100 ml.

Normality of H_2SO_4	Boiling		Water added after cooling, *ml*	Time of standing, *hr*	DHQ		Ta_2O_5		Nb_2O_5	
	Time, *hr*	Temp, °*C*			Lot no.	Amount used, *g*	Added, *mg*	Found, *mg*	Added, *mg*	Found, *mg*
7	3	100	None	None	1	1	21·4	21·7	—	—
1st–10 2nd–6	1	100	67	1	1	1	21·4	21·3	—	—
1st–10 2nd–6	0·75	100	67	1	1	0·5	21·4	20·2	—	—
6	1·5	94	—	0·5	1	0·5	20·0	18·7	—	—
9	0·25	100	50	None	1	0·5	20·0	15·1	—	—
9	1	100	50	1	6	0·5	20·0	19·8	—	—
9	1	100	50	1	1	0·30	20·0	19·7	—	—
6	None	Room	50	72 (after mixing hot. soln.)	1	0·10	20·0	1·6*	—	—
15	1	100	50	1	1	0·5	20·0	20·0	—	—
18	1	100	50	1	1	0·5	20·2	20·2	—	—
7	6	100	None	None	1	1	—	—	20·0	17·3
7	1	100	None	None	1	0·5	—	—	20·0	3·8
1st–9 2nd–6	0·75	100	50	1	1	0·5	—	—	20·0	11·2
9	0·75	100	50	1	1	0·5	—	—	20·0	15·4

* This amount was due probably to mixing the two solutions at an elevated temperature.

Acid concentration plays an important role in the quantitative precipitation of tantalum and of niobium. Present experiments have shown that precipitation is less complete at lower acidity than at higher acidity. This is a phenomenon which may be considered noteworthy for the separation of elements in general. It is an established fact that if precipitation is attempted in highly acidic solution, a separation from impurities is more likely. With 4*N* sulphuric acid solution, almost no niobium precipitated even after prolonged boiling. However, with 9*N* or higher acidities, both tantalum and niobium were found to precipitate quantitatively. The optimum acid concentration for the separation of tantalum from niobium is between 4·5 and 6·5*N*. In the present study 6*N* sulphuric concentration is used for this separation.

Tantalum and niobium oxides shown in Table I were determined semi-quantitatively for the presence of any potassium adsorbed or co-precipitated with the chelates by using an emission spectrographic method. For a 20-mg sample, the amount of potassium in the oxides varies from 0·01 to 0·2 mg and is 0·1 mg on average. A number of oxides also were used for the determination of sulphate adsorbed or co-precipitated during the precipitation procedure. The amount of sulphate found in the precipitate is of the same order of magnitude as that of potassium present in these oxides.

In Table II, methods of extraction and preparation of the different lots of DHQ are shown. Lot 1 in Table II was prepared by aqueous extraction of the cork portion of Douglas fir bark, converted to alkali salt of DHQ, filtered, then acidified with hydrochloric acid. The material was crystallised once from water. For the method of preparation, see the work of Kurth, Hergert and Ross[14]. The cork portion of the bark was purchased from Weyerhaueser Timber Company, Longview, Washington. Lot 2 was prepared in the same way as Lot 1 with the exception that it was crystallised twice. Lot 3 is a mixture of both the *d*-form and the *l*-form of DHQ. Lot 4 was prepared in the same as was Lot 1 but the material showed a slight yellow discoloration. Lot 5 was prepared by aqueous extraction of Douglas fir cork followed by separation from tannin with ether and crystallised from water twice using activated charcoal. Lot 6 was prepared by ether extraction of Douglas fir cork after wax had been removed, then crystallised from water. For methods of extraction and purification of DHQ, see Kurth and Chan.[12] All of the DHQ in these lots with the exception of Lot 4 is colourless. Regardless of methods and procedures of extraction and preparation, DHQ precipitates tantalum and niobium quantitatively. It was noted that the colour and the rate of precipitation are, however, different with the different lots. For instance, in Lot 4, precipitation of tantalum commenced immediately when a hot solution of DHQ was added to a hot solution consisting of tantalum, 6*N* or 9*N* sulphuric acid, and ammonium oxalate. On the other hand, precipitation of tantalum by DHQ from Lot 5 and Lot 6 will not take place in a solution of 9*N* sulphuric acid and saturated oxalate until 15 min of boiling has elapsed. Quantitative results are shown in Table II. The precipitate of tantalum chelate from DHQ is yellowish or

TABLE II.—METHOD OF EXTRACTION OF DHQ AND ITS EFFECTS ON THE PRECIPITATION OF TANTALUM AND NIOBIUM

Experimental conditions: H_2SO_4, 9*N*; sat. $(NH_4)_2C_2O_4$, 30 ml; total volume 100 ml; water added after boiling, 50 ml; standing time 1 hr.

DHQ		First appearance of precipitate after boiling, *min*	Boiling time, *hr*	Ta_2O_5		Nb_2O_5	
Lot no.	Used, *g*			Added, *mg*	Found, *mg*	Added, *mg*	Found, *mg*
1	0·5	5	1	20·0	20·0	—	—
2	0·5	5	1	20·0	20·3	—	—
3	0·5	5	1	20·0	19·9	—	—
4	0·5	0	1	20·0	20·0	—	—
5	0·5	15	1	20·0	20·2	—	—
6	0·5	15	1	20·0	19·8	—	—
2	1·0	5	1	—	—	20·0	20·4
3	1·0	5	1	—	—	20·0	20·0
5	1·0	20	2·5	—	—	20·0	20·3
6	1·0	20	2·5	—	—	20·0	19·9
6	1·5	25	1·5	—	—	20·0	20·0

light orange in colour. The precipitate of niobium, on the other hand, is deep red or maroon. These precipitates settle readily; they can be filtered without difficulty. Normally the precipitate is fairly yellow at the start and as the reaction progresses, the colour changes slightly to yellowish-orange and sometimes a brownish tint appears when the acid concentration is high. This discoloration is probably due to the presence of niobium or unreacted quercetin.

In spite of the fact that the precipitation of tantalum or of niobium is quantitative under the conditions tried, it is essential that the DHQ used be specified. For the purpose of reproducibility the DHQ must have the following characteristics: crystallised DHQ has 2·5 moles of water, m.p. 241–242° and optical rotation $[\alpha]_D^{25}$ +39 (4 g in 100 ml of equal volumes of acetone and water). The DHQ meeting these specifications was prepared by the method described by Kurth and Chan.[12]

Methods of X-ray diffraction and photomicrography are used to identify the transformation of DHQ to quercetin under the conditions used for the precipitation of tantalum and niobium. Figs. 2 and 3 show the different diffraction patterns which serve to distinguish these compounds.

Table III shows that zirconium and molybdenum can be separated from tantalum and from niobium. On the other hand, as much as 3·6 mg of titanium oxide was found in a 20-mg sample of tantalum oxide when 5·0 mg of it was added to the solution before precipitating tantalum with DHQ. The results indicate that the greater the amount of titanium in the mixture, the greater will be the contamination. In 9*N* sulphuric acid, the presence of tungsten to the extent of 24 mg of tungsten oxide gave a cloudy solution even though 3 g of tartaric acid is present.

TABLE III.—DETERMINATION OF TANTALUM AND OF NIOBIUM IN THE PRESENCE OF ZIRCONIUM, MOLYBDENUM, AND TITANIUM

Experimental conditions: H_2SO_4, 9*N*; sat. $(NH_4)_2C_2O_4$, 30 ml; DHQ (Lot 1) for Ta determination 0·5 g, for Nb determination 1 g; total volume, 100 ml; boiling time for Ta determination, 1 hr for Nb determination, 1·5 hr; water added after boiling, 50 ml; standing time, 1 hr.

Zirconium oxide added, *mg*	Molybdenum oxide added, *mg*	Titanium oxide added, *mg*	Ta_2O_5		Nb_2O_5	
			Added, *mg*	Found, *mg*	Added, *mg*	Found, *mg*
30·0	—	—	20·0	20·0	—	—
60·0	—	—	20·0	20·0	—	—
120·0	—	—	20·0	30·0	—	—
15·0	—	—	—	—	20·0	19·7
30·0	—	—	—	—	20·0	20·0
60·0	—	—	—	—	20·0	20·3
—	24·0	—	20·0	20·4	—	—
—	48·0	—	20·0	21·2	—	—
—	—	5·0	20·0	23·6	—	—
—	—	10·0	20·0	25·5	—	—
—	—	20·0	20·0	28·7	—	—

By the dropwise addition of quercetin reagent to a 50:50 mixture of tantalum and

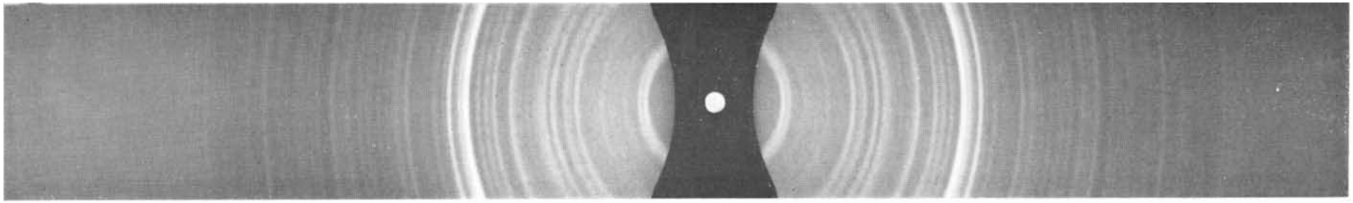

Fig. 2.—X-ray diffraction pattern of DHQ extracted from Douglas fir bark by the method of Kurth and Chan.[12]

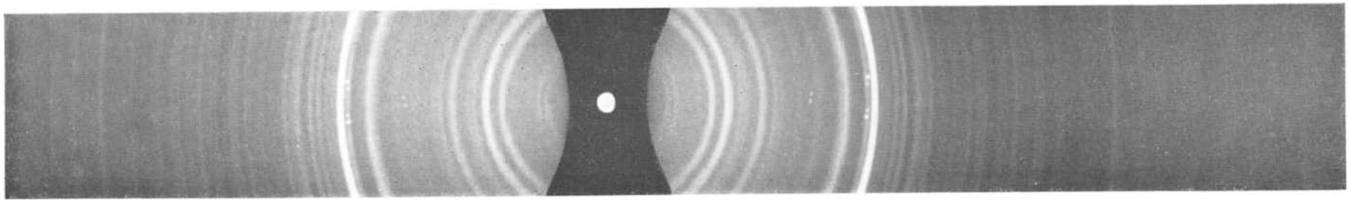

Fig. 3.—X-ray diffraction pattern of quercetin prepared by the method of Kurth and Chan.[13]

niobium, earlier investigators[24] have found that 22–35% of niobium oxide is present in the tantalum precipitate. Thus these investigators concluded that no separation of tantalum from niobium can be achieved by the use of quercetin or morin.

Attempts have been made to separate tantalum from niobium by regulating the acidity and the amount of DHQ in the boiling mixture. It was found that, in 4–6*N* sulphuric acid solution, the precipitation of tantalum will take place first in the homogeneous solution. As long as tantalum is present in the mixture, the flavone, slowly generated from DHQ, will precipitate it and practically no niobium will be precipitated. After all of the tantalum has been precipitated, the flavone from DHQ will then precipitate the niobium. The two stages of precipitation can be observed by the change in colour of the precipitate.

In the present study many attempts were made to effect a sharp separation, but with only partial success. It was finally discovered that in order to precipitate all of the tantalum from a solution, a small amount of niobium accompanied the tantalum. A correction was then made on the niobium precipitated. The small amount of niobium oxide in the tantalum oxide can be quickly and reliably determined spectrophotometrically using concentrated sulphuric acid and hydrogen peroxide. The results are shown in Table IV.

TABLE IV.—SEPARATION OF TANTALUM FROM NIOBIUM USING THE METHOD OF PRECIPITATION FROM HOMOGENEOUS SOLUTION WITH DHQ

Experimental conditions: H_2SO_4, 6*N*; sat. $(NH_4)_2C_2O_4$, 30 ml; total volume, 100 ml; DHQ for Ta determination, 1·0 g, for Nb determination, 1·5 g (1–5), 1·0 g (6); boiling time for Ta determination, 70 min (5), 100 min (4), 130 min (3), 160 min (1, 2, 6), for Nb determination, 150 min; standing time for Nb determination, 60 min, for Ta determination, none; water added after boiling for Nb determination, 50 ml, for Ta determination, none.

	$Ta_2O_5 + Nb_2O_5$ found, *mg*	Nb_2O_5 found spectrophotometrically, *mg*	Ta_2O_5			Nb_2O_5			$Ta_2O_5 + Nb_2O_5$		Diff,
			Present, *mg*	Found, *mg*	Diff, *mg*	Present, *mg*	Found, *mg*	Diff, *mg*	Present, *mg*	Found gravimetrically + spectrophotometrically, *mg*	*mg*
1.	21·1	1·26	20·0	19·8	−0·2	20·0	20·5	+0·5	40·0	40·3	+0·3
2.	21·2	1·08	20·0	20·1	+0·1	13·3	13·8	+0·5	33·3	33·9	+0·1
3.	17·0	1·66	16·0	15·3	—0·7	20·0	20·5	+0·4	36·0	35·8	−0·2
4.	12·9	1·98	11·2	10·9	−0·3	20·0	20·2	+0·2	31·2	31·1	−0·1
5.	5·8	1·04	5·6	4·8	−0·8	20·0	20·6	+0·6	25·6	25·4	−0·2
6.	20·7	0·72	20·0	20·0	0·0	4·0	3·9	−0·1	24·0	23·9	−0·1

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Zusammenfassung—3:3′:4′:5:7-Pentaoxyflavanon in stark saurer Lösung (6–9*N*) gibt keine Fällung mit Niob und Tantal. Wird die Lösung jedoch in Gegenwart von Luft gekocht, so oxydiert das Flavanon zu 3:3′:4′:5:7-Pentaoxyflavon, welches die genannten Metall fällt. Unter den Fällungsbedingungen racemisiert das Flavanon. Das Racemat ist schwer löslich, sodass es im Metallniederschlag gefunden werden kann, was jedoch die quantitative Fällung nicht beeinflusst.

Die Fällung kann durch Regulieren der Acidität, Dauer des Kochens und Konzentration des Flavanons kontrolliert werden. Experimentelle Ergebnisse werden mitgeteilt. Zirkon und Molybdän stören nicht, Titan jedoch muss abwesend sein.

Da die Bildung des Flavons langsam ist, findet eine gleichmässige Fällung durch die gesamte Lösung statt. Daher ist die Absorption von Kalium und Sulfat äuasserst gering und praktisch vernachlässigbar. Das steht in vorteilhaftem Gegensatz zu der tropfenweisen Zugabe von Flavone in früher beschriebenen Methoden, die stark nuter Mitfällungserscheinungen leiden.

Tantal- und Nioboxyd werden mit Kaliumbisulfat aufgeschlossen. Flussäure wird nicht verwendet, weshalb sich der Gebrauch von Polyäthylenapparaturen erübrigt.

Résumé—La 3:3′:4′:5:7-pentahydroxyflavanone en solution acide moyennement concentrée (6*N*–9*N*) ne précipite pas le tantale et le niobium; cependant, en chauffant ou en portant à l'ébullition, en présence d'air, cette flavanone est transformée en 3:3′:4′:5:7-pentahydroxyflavone, qui précipite le tantale et le niobium en solution. Dans les conditions de précipitation utilisées, il se produit une racémisation de la flavanone. La flavanone racémisée, qui est moins soluble que la forme D originale, peut accompagner les précipités de tantale et de niobium sans gêner le dosage quantitatif de ces éléments.

La précipitation des complexes du tantale et du niobium peut être controlée par le réglage de l'acidité, la durée de l'ébullition, ainsi que la concentration de la flavanone. L'auteur donne les résultats expérimentaux et les processus de précipitation et de dosage en solution homogène des complexes du tantale et du niobium. Le zirconium et le molybdène ne gênent pas le dosage. Le titane doit être absent ou présent seulement en très faible quantité.

Comme le formation du réactif précipitant, la flavone, à partir de la flavanone est comparativement lente, la précipitation du tantale et du niobium est uniforme dans toute la solution. Par cette technique, l'auteur montre que l'adsorption et la coprécipitation des ions potassium et sulfate dans la solution sont négligeables. Cela est à l'opposé de l'addition goutte à goutte, moins efficace, de flavone, mentionnée par des chercheurs plus anciens; dans cette méthode, l'adsorption et la coprécipitation sont marquées.

Dans cette étude, les oxydes de tantale et de niobium ont été fondus avec du bisulfate de potassium. Il n'est pas nécessaire d'utiliser d'acide fluorhydrique pour dissoudre ces oxydes, et c'est pourquoi un appareillage en polyéthylène n'est pas exigé.

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SOME PHYSICAL AND CHEMICAL PROPERTIES OF VANADIUM DI- AND TRI-CHLORIDES

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Summary—New physical property data are reported for the compounds VCl_2 and VCl_3. Both compounds hydrolyse and oxidise in acidic aqueous solution, the former rapidly and the latter slowly. They are slightly soluble in organic solvents and the solutions are stable when protected from moisture and oxygen of the air. Heated in air, VCl_2 begins to oxidise to V_2O_5 around 300°, but some formation and volatilisation of $VOCl_3$ occurs; under similar conditions VCl_3 is converted to volatile $VOCl_3$ around 250°. Heated in argon, VCl_2 volatilises at 1000°, whereas VCl_3 first disproportionates at 600° to volatile VCl_4 and solid VCl_2, and the latter volatilises as the temperature is raised to 1000°. X-ray diffraction data are given for VCl_2.

THE lower chlorides of vanadium, VCl_2 and VCl_3, have been known since the time of Berzelius. They have never been commercially available and as a result their properties are, even today, not too well known. About the only use to which they have been put is as titrimetric agents in analytical chemistry.[1] Recently, these compounds have been offered for sale, particularly as catalysts for olefin polymerisations. Because of their impending industrial utility, it is timely to study the physical and chemical properties of the commercial materials in greater detail. In this paper the results of recent studies on their solubilities and their hydrolytic and thermal stabilities are given. Powder X-ray diffraction analysis is also given for vanadium dichloride; corresponding data for vanadium trichloride have already been published.[2]

EXPERIMENTAL

Preparation of materials

Fifty-one lb of vanadium tetrachloride, made by direct chlorination of scrap vanadium or vanadium carbide, were refluxed in a 5-gal, glass-lined vessel and the liberated chlorine allowed to escape:

$$2VCl_4 \rightarrow 2VCl_3 + Cl_2\uparrow .$$

Thirty-three lb of vanadium trichloride were obtained, *i.e.* a 70% yield based on vanadium. Analysis of the product showed 94·6% VCl_3 and 5·4% VCl_4 for a gross composition of approximately $VCl_{3\cdot04}$.

Vanadium dichloride was prepared by reducing this vanadium trichloride with hydrogen at 750°. Ninety-two per cent conversions to material consisting of 99·57% VCl_2 and 0·25% VCl_3 were obtained. The iron content of the product was less than 0·10%.

These products are, therefore, technical-grade compounds rather than ultrapure chemicals. Some of their known properties, as reported in the literature, are as shown in Table I.

Solubilities

The organic solvents used were reagent quality in all cases. The benzene, ethyl ether, and carbon tetrachloride were dried by storing in contact with sodium, then distilled. The tetrahydrofuran was refluxed over and distilled from caustic soda to remove peroxide contamination, then dried over Linde Molecular Sieves. The ethanol was slurried with Molecular Sieves, refluxed over freshly prepared calcium oxide and finally distilled from additional lime. The acetone was dried over Molecular Sieves and distilled from anhydrous potassium carbonate

The water remaining in the solvents was determined with Karl Fischer reagent. Values obtained are given in Table II.

TABLE I

	VCl_2	VCl_3
Melting point	Sublimes at dull red heat, in H_2 or CO_2	Non-volatile; forms red $VOCl_3$ when heated in air[3]
Colour and form	Hygroscopic, apple-green hexagonal plates	Hygroscopic, peach to purple coloured plates
Sp. gr.	3·09[4,5]	2·82[5]

TABLE II

Solvent	Water, %
Carbon tetrachloride	0·004
Benzene	0·004
Ethyl ether	0·017
Tetrahydrofuran	0·001
Ethanol	0·040

The solubilities of the vanadium chlorides were determined by adding excess solids to the solvents in an argon atmosphere, agitating the mixtures in a constant temperature bath at 25° for 18 hr, and analysing filtered aliquots of the solutions for the total metal contents. These values were then calculated to the weights of metal chlorides in the solutions. Values obtained are shown in Table III, with the colours of the solutions indicated parenthetically.

TABLE III. SOLUBILITIES IN g/100 ML AT 25°

	VCl_2	VCl_3
Acetone	0·07 (blue)	2·47 (red)
Benzene	insoluble	insoluble
Carbon tetrachloride	insoluble	insoluble
Ethanol	0·06 (blue)	3·20 (green)
Ethyl ether	0·04 (blue)	0·09 (blue)
Tetrahydrofuran	0·04 (blue)	0·04 (colourless)

Stability in aqueous solutions

The literature contains conflicting statements as to the stability of vanadium di- and tri-chlorides in water. Vanadium dichloride, in particular, has been variously reported as stable in 0·5*N* hydrochloric acid solution[6] and as soluble with decomposition.[7] Both of these phenomena have been observed in our work. One sample of crystals was found to be very slowly wetted by water, but eventually to dissolve giving solutions which were fairly stable at room temperatures; another batch dissolved immediately in water or dilute hydrochloric acid giving solutions which decomposed rapidly. The difference undoubtedly lay in the way the compound was prepared and perhaps in the presence of traces of catalytic materials. The vanadium dichloride product studied in this investigation was the form that is reactive to water; it decomposes rapidly in hydrochloric acid solutions and much more slowly in dilute sulphuric acid solutions.

In order to study this behaviour in greater detail, solutions containing 0·2% of metal chloride were prepared in de-aerated water containing 5% sulphuric acid. Some of the solutions were exposed to air and some were kept under argon for the duration of the test. The solutions were not shaken. Fig. 1 shows the rate of oxidation of the vanadium di- and tri-chlorides in the solutions under these conditions. Clearly vanadium dichloride begins to decompose rapidly and immediately, and vanadium trichloride much more slowly. Over a period of 12 hr less than 5% of the vanadium trichloride, and 50 to 60% of the vanadium dichloride, is oxidised.

Thermal stability

Little information is contained in the literature concerning the stability[3,8] of vanadium di- and tri-chlorides. The thermal results reported here were measured on an automatic recording Stanton Thermobalance. This apparatus permits continuous weighing on an analytical balance while the sample is being heated in a controlled atmosphere. Furnace temperature and sample weight are followed simultaneously and automatically recorded on a twin-pen electronic recorder. The results here presented were obtained using a heating programme of 4 hr from room temperature to 1400°, *i.e.* a temperature rise of approximately 6° per min. Some tests were made in a flowing argon atmosphere (3 litres of argon per min through the furnace tube) and some in an ordinary air stream. Since the chlorides are hygroscopic all transfers were made in a dry box containing argon and all weighings were made using argon-filled weighing bottles. The weighed test samples were heated in a platinum crucible. The sample weight taken was approximately 500 mg and for convenience all changes in weight were recalculated to a 1-g sample basis before plotting as a function of the change in temperature.

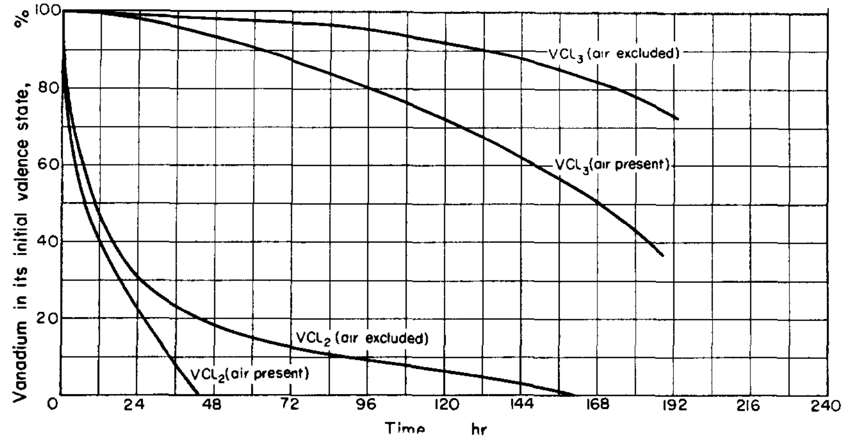

FIG. 1.—Stability of VCl_2 and VCl_3 in 5% sulphuric acid.

The results obtained are shown in Fig. 2. It must be remembered that these curves are the results of heating the samples to 1400° in 4 hr. Somewhat differently shaped curves would be obtained by holding the furnace temperature constant for a period of time at any temperature where a weight change is in progress. A descending slope indicates a weight loss. A horizontal line indicates a stable composition to be present.

The upper curves show that vanadium di- and tri-chloride both decompose in the temperature range between 250 and 350° when heated in air, vanadium dichloride being slightly more stable. From the measured weight losses it can be shown by calculation that vanadium dichloride does not convert quantitatively to vanadium pentoxide. The recorded loss in weight is greater than that necessary for conversion to the oxide, indicating that some of the vanadium volatilised. Thus, it is very probable that some volatile oxychloride is formed simultaneously with the oxidation to vanadium pentoxide. The small increase in weight occurring above 350° corresponds to oxidation of lower oxide states to pentoxide.

When vanadium trichloride is heated in air it forms mainly vanadium oxytrichloride,[3] which immediately boils off. The reaction proceeds rapidly above 250°, as shown by the curve in the figure:

$$VCl_3 + O_2 \rightarrow VOCl_3 \uparrow .$$

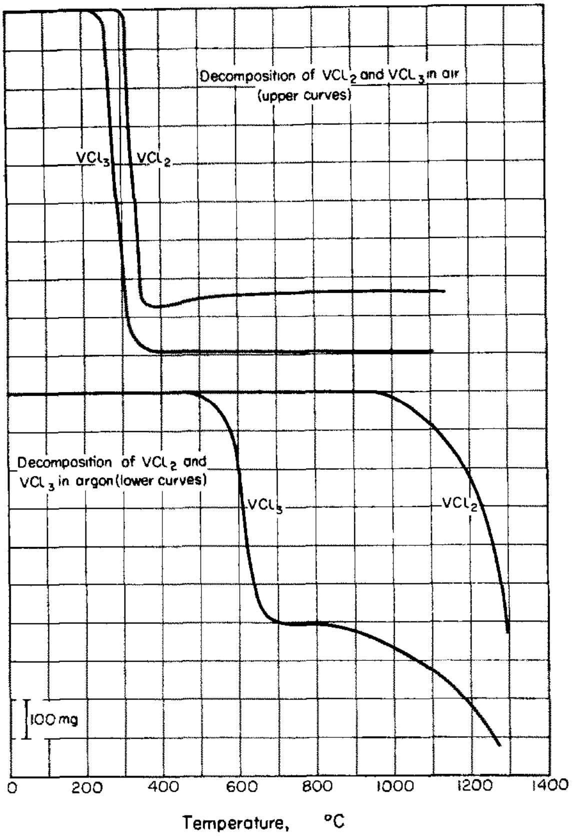

FIG. 2.—Thermal decomposition of vanadium chlorides.

TABLE IV

d (observed)	I (relative)	d (observed)	I (relative)
6·311	1	1·645	6
4·042	10	1·529	2
2·906	5	1·503	3
2·750	6	1·454	7
2·122	7	1·372	2
2·016	3	1·341	2
1·978	0·5	1·319	0·5
1·938	0·5	1·243	3
1·797	5	1·215	5
1·699	1		

In an inert atmosphere (lower curves) vanadium dichloride is seen to sublime at temperatures above 1000°. Vanadium trichloride first disproportionates at 600° to give vanadium tetrachloride, which boils off, and vanadium dichloride, which remains behind. At 1000° this vanadium dichloride then volatilises away.

X-ray diffraction

Powder X-ray diffraction analysis of vanadium dichloride was carried out. Table IV gives the "d" lines and relative intensities on a scale of ten units from unfiltered chromium radiation.

Zusammenfassung—Neue physikalische Daten für die Verbindungen VCl_2 und VCl_3 werden mitgeteilt. Beide Verbindungen hydrolysieren und oxydieren in Wàssriger Lösung, die erstere viel schneller als die letztere. Beide Verbindungen sind sehr wenig löslich in organischen Solventien. Die Lösungen sind stabil, wenn Zutritt von Feuchtigkeit und Luftsauerstoff ausgeschlossen wird. Wenn in Luft erhitzt, beginnt bei etwa 300°C das VCl_2 zu V_2O_5 zu oxydieren, wobei jedoch zu einem kleinen Teil Vanadin-oxychlorid gebildet wird, welches sich verflüchtigt. Unter den gleichen Bedingungen geht VCl_3 bei 250° in fluchtiges $VOCl_3$ über. Wenn unter Argon erhitzt verflüchtigt sich VCl_2 bei 1000°. VCl_3 disproportioniert bei 600° zu flüchtigem VCl_4 und festem VCl_2 welch letzteres bei höherer Temperatur verflüchtigt. Röntgenstrahlungsdaten werden für VCl_2 mitgeteilt.

Résumé—Les auteurs donnent de nouveaux résultats sur les propriétés physiques des composés VCl_2 et VCl_3. Ces deux composés s'hydrolysent et s'oxydent en solution aqueuse, le premier rapidement et le dernier lentement. Ils sont faiblement solubles dans les solvants organiques, et les solutions sont stables quand elles sont protégées de l'humidité et de l'oxygène atmosphérique. Chauffé à l'air, VCl_2 commence à s'oxyder en V_2O_5 vers 300°, mais il y a formation et volatilisation d'oxychlorure de vanadium; dans des conditions semblables VCl_3 se transforme en $VOCl_3$ volatile vers 250°. Chauffé sous argon, VCl_2 se volatilise à 1000°, alors que VCl_3 se dismute à 600° en VCl_4 volatile et VCl_2 solide, et ce dernier se volatilise quand la température atteint 1000°. Des résultats de diffraction des rayons X sont donnés pour VCl_2.

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SPECTROPHOTOMETRIC DETERMINATION OF RHENIUM WITH 4-METHYLNIOXIME*†

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Summary—A simple method applicable to the spectrophotometric determination of less than 0·001% to more than 1·0% of rhenium in molybdenite concentrate and in "molybdenite roaster flue dust" has been developed. Interfering elements commonly found in these materials are removed in three operations: evaporation with hydrochloric acid, precipitation of hydrous oxides with ammonia, and formation of organometallic compounds with ethyl xanthate and chloroform extraction. The method is based on the formation of a soluble, stable, yellow-green rhenium-4-methylnioxime chelate where rhenium^{VII} is reduced by tin^{II} chloride in a dilute hydrochloric acid solution in the presence of 4-methylnioxime (4-methyl-1:2-cyclohexanedionedioxime). The colour develops in less than 5 min and the chloroform extract shows a maximum absorption at 436 mμ. The calibration curve conforms to Beer's law. The molar extinction coefficient for rhenium-4-methylnioxime is about $6{\cdot}89 \times 10^4$ as compared to less than $4{\cdot}5 \times 10^4$ reported for other methods for rhenium.

VOTER and Banks[15] pointed out that six- or seven-membered alicyclic *vic*-dioximes with oxime groups attached to adjacent carbon atoms have a much higher molar solubility in water than straight chain aliphatic *vic*-dioximes and that they are more sensitive reagents for the detection of submicrogram amounts of nickel and palladium. Banks and Hooker[2] reported the use of 4-methylnioxime as an excellent gravimetric reagent for both nickel and palladium. Banks and Smith[3] used palladium 4-methylnioxime chelate to develop a spectrophotometric method that had several advantages over other methods.

A similarity of the chemical reactions of nickel, palladium and rhenium with straight-chain aliphatic *vic*-dioximes suggested the possibility of using 4-methylnioxime as a chelating reagent for rhenium.

The method described in this paper is based on the formation of a soluble, stable, yellow-green rhenium-4-methylnioxime chelate, where rhenium^{VII} is reduced by tin^{II} chloride in a dilute hydrochloric acid solution in the presence of 4-methylnioxime.

The colour develops almost immediately and the absorbancy of the chloroform extract of the chelate and the blank remain almost constant for 24 hr or more when room temperature is about 25° and the complex is formed and extracted under optimum conditions.

The calculated molar extinction coefficient for rhenium-4-methylnioxime is about $6{\cdot}89 \times 10^4$, compared to less than $4{\cdot}5 \times 10^4$ reported for other methods for rhenium.

This method is applicable to the spectrophotometric determination of less than 0·001% to more than 1·0% of rhenium in molybdenite concentrate and in "molybdenite roaster flue dust". Interfering elements[11]—molybdenum, iron, copper, selenium,

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nickel, gold, and silica—commonly found in these materials are removed in three operations: evaporation with hydrochloric acid, hydrous oxide precipitation with ammonia and organometallic compound formation with ethyl xanthate[6,7,8,10,12] and extraction from a dilute hydrochloric acid solution with chloroform.

EXPERIMENTAL

Apparatus

Beckman Model D.U. Spectrophotometer equipped with ultraviolet attachment, matched 1·000-cm silica cells and matched 1·000-cm stoppered Corex cells.

Leeds and Northrup Model 7664 pH Meter (line operated).

Reagents

Standard rhenium stock solution: Prepared from potassium perrhenate with a 99·5% assay obtained from A. D. Mackay, Inc. A solution containing 1·0 mg of rhenium per ml was prepared by dissolving 0·3883 g of the potassium perrhenate in de-ionised water and diluting to 250 ml in a volumetric flask.

Standard rhenium working solutions: Prepared by diluting appropriate aliquots of the stock solution.

4-*Methylnioxime solution:* A 0·34% aqueous solution was used. This approximately saturated solution is stable indefinitely.[1]

Tin^{II} chloride stock solution: Dissolve 3 g of Mallinckrodt analytical reagent tin^{II} chloride dihydrate in 40 ml of concentrated hydrochloric acid and dilute to 100 ml in a volumetric flask with water. This gives a solution approximately 2·5% in tin^{II} chloride.

Ammonium molybdate: Mallinckrodt analytical reagent.

Liquid bromine: Baker & Adamson reagent-grade.

Potassium ethyl xanthate solution: Dissolve 27 g of the salt in water, filter and dilute to 50 ml. Highest purity potassium ethyl xanthate obtained from Eastman Kodak Company was used without purification. Prepare this solution fresh daily.

Chloroform: Baker and Adamson reagent-grade.

All other chemicals used were of analytical reagent quality.

Procedure

Standardisation curve. A calibration curve was prepared by running 6 or more samples ranging from 20 to 160 μg of rhenium, and by plotting micrograms of rhenium versus absorbance at 436 mμ. The straight-line relationship extrapolates through the origin when the extractions are made under optimum conditions.

No interfering elements present. Transfer a nearly neutral solution, containing not more than 160 μg of rhenium as perrhenate, to a 50-ml glass-stoppered volumetric flask. Add 25 ml of 4-methylnioxime solution, 5 ml of tin^{II} chloride solution, dilute to the mark with water and mix. Let stand 5 min, then transfer the solution quantitatively to a 125-ml glass-stoppered separatory funnel. Extract the aqueous phase at room temperature (20–30°) with three portions (4, 3 and 3 ml) of chloroform.[5] Drain the chloroform layers into a 10-ml volumetric flask, and dilute to volume with chloroform. Measure the absorbance of the chloroform phase of the chelate at 436 mμ in a 1-cm stoppered Corex cell versus the chloroform extract of a blank solution prepared in the same manner except for the exclusion of the perrhenate. Convert the absorbance to micrograms of rhenium with the aid of a calibration curve. The range of application can be controlled by varying the size of sample or by diluting to volume and taking an aliquot.

Interfering elements present. Cautiously decompose a sample, containing 160 to 50 μg of rhenium and less than 200 mg of molybdenum, with dilute nitric acid on a steam bath until red fumes have cleared from the beaker. Add concentrated hydrochloric acid and digest the mixture below 100° to a volume of not less than 3 ml to remove nitrate ions. Add hydrochloric acid repeatedly in 5- to 25-ml increments depending on the amount of nitric acid used until all of the nitrate is removed. Usually five or six additions of the hydrochloric acid are required.

After all of the nitrate has been removed from the sample, add 20 ml of water and filter to remove the silica.

Removal of interfering ions. Adjust the silica-free filtrate to a pH of about 9 to 10 with concentrated ammonia. Heat the solution to near boiling for 1–2 min, add filter paper pulp and let stand until the hydrous oxide colloidal particles agglomerate and settle out. Filter and wash the precipitate with 1% ammonium chloride solution. Neutralise the filtrate with sulphuric acid, then add 2 drops of sulphuric acid (sp. gr. 1·84) in excess. Add 10 drops of liquid bromine to ensure that all of the molybdenum in the sample is in the highest valency state. Heat the sample on a low-temperature hot plate, without boiling, to remove the excess bromine. Dilute to volume samples containing more than 160 μg of rhenium and/or about 200 mg of molybdenum and take a suitable aliquot.

Adjust the pH of the solution within the range of 9 to 11 with approximately 5*N* sodium hydroxide solution. Concentrate the solution on a low-temperature hot plate to a volume of 20 to 25 ml, cool to room temperature and transfer to a glass-stoppered 250-ml separatory funnel, add 10 ml of xanthate solution and mix. Add 6 ml of hydrochloric acid (sp. gr. about 1·36), shake for 5 sec and finally add 50 ml of chloroform. Shake vigorously for 1 min and let stand until separation of the two layers is complete. The aqueous layer should be colourless or very pale pink. The chloroform layer should have an intense red-violet colour. Draw off the chloroform layer and discard it. Continue the extraction with three more 25-ml portions of chloroform to complete the removal of the xanthate complexes. Transfer the sample quantitatively to a 250-ml beaker, add approximately 0·3*N* potassium permanganate solution dropwise until the permanganate colour persists, then add a drop or two in excess. Destroy the permanganate colour in the sample with a drop of tin^{II} chloride colution. Add about 3 ml of concentrated ammonia and adjust the pH within the range of 8 to 9. Evaporate the sample on a hot plate to a volume of less than 100 ml. Add filter paper pulp, filter the manganese hydrous oxide precipitate and wash with hot 1% ammonium chloride solution.

Adjust the filtrate to a pH of 7 to 6 with dilute hydrochloric acid solution and evaporate on a low-temperature hot plate, without boiling, to a volume of about 20 ml. Continue the evaporation on a steam bath to a volume of about 5 ml. The salts which crystallise out during the evaporation dissolve when 25 ml of 4-methylnioxime solution is added. Quantitatively transfer the sample to a 50-ml glass-stoppered volumetric flask. Add 5 ml of tin^{II} chloride solution, dilute to the mark with water, mix and extract with chloroform.

DEVELOPMENT OF THE METHOD

Preparation of sample

Two methods have been used for the decomposition of molybdenite concentrate and "molybdenite roaster flue dust" samples—fusion with sodium peroxide[10] and treatment with nitric acid.[10]

Investigation in this laboratory showed that nitric acid treatment offered two advantages over sodium peroxide fusion: (1) the operation is simpler, and (2) later evaporation with hydrochloric acid to remove nitrate ions volatilises selenium[16] and dehydrates the silica, which can be removed by filtration. Hydrochloric acid should be added as soon as the initial reaction with nitric acid is complete, to avoid the separation of molybdenum^{VI} oxide.

Care should be taken during this and subsequent evaporations to avoid losing rhenium by volatilisation.[9,14] Rhenium is not volatilised by boiling alkaline solutions.[13]

Effect of foreign ions.

The effect of a number of ions on the 4-methylnioxime method for rhenium is illustrated in Table 1.

Ethyl xanthate extraction of interfering elements

The ethyl xanthate extraction technique for removing molybdenum[7] and selenium[10]

Table I. Effect of foreign ions
(100 μg of rhenium present)

Ion	Added as	Amount of ion added, *mg*	Rhenium found, *μg*
Strontium^{II}	$SrCl_2$	100	95·0
Magnesium^{II}	$MgCl_2$	100	101·0
Barium^{II}	$BaCl_2$	100	97·0
Zinc^{II}	$ZnCl_2$	100	95·0
Cadmium^{II}	$CdCl_2$	100	97·0
Aluminium^{III}	$AlCl_3$	100	98·0
Manganese^{II}	$MnCl_2$	100	90·0
Nickel^{II}	$NiCl_2$	1	113·0
Cobalt^{II}	$CoCl_2$	1	143·0
Iron^{II}	$Fe(NH_4)_2(SO_4)_2$	1	165·0
Iron^{III}	$FeCl_3$	1	275·0
Copper^{I}	Cu_2Cl_2	1	122·0
Copper^{II}	$CuCl_2 2NH_4Cl$	1	132·0
Chromium^{III}	$CrCl_3$	1	82·5
Zirconium^{IV}	$ZrOCl_2$	1	87·0
Nitrate	NH_4NO_3	100	100·0
Nitrate	NH_4NO_3	200	92·0
Nitrate	NH_4NO_3	300	81·0
Bromide	KBr	100	104·5
Iodide	KI	100	111·5
Sulphate	Na_2SO_4	100	100·0
Perchlorate	$HClO_4$	100	105·0
Vanadate	$NaVO_3$	100	103·5
Thiocyanate	KCNS	100	100·0
Acetate	$NaC_2H_3O_2$	100	105·0
Citrate	$(NH_4)_2HC_6H_5O_7$	100	101·5
Tartrate	$(NH_4)_2C_4H_4O_6$	100	104·5
Oxalate	$(NH_4)_2C_2O_4$	100	104·0
Phosphate	H_3PO_4	100	Interference
Phosphate	K_2HPO_4	100	Interference

as modified by Meloche, Martin and Webb[12] was extended to the separation of iron,[6] gold, copper, nickel,[6] arsenic[8] and molybdenum from small amounts of rhenium. The following amounts of these elements were separated by ethyl xanthate extraction from 100 μg of rhenium—4·658 g of gold as chlorauric acid, 100 mg of molybdenum as ammonium molybdate, 5 mg of iron as iron^{III} chloride, 1 mg of arsenic as sodium arsenate, 500 μg of copper as copper^{II} ammonium chloride—and the rhenium determined with a maximum absolute error of $+0·004$ μg of rhenium. This corresponds to an error of 0·004% rhenium when calculated on the basis of a 0·1-g sample.

Erratic results were sometimes obtained on synthetic samples when bromine oxidation of molybdenum[10] was omitted and also when oxidation with potassium permanganate[12] after xanthate extraction was omitted.

Absorption spectra of reagents

To determine the effect the reagents used in the procedure might have on the absorption spectra of rhenium 4-methylnioxime complex, the saturated aqueous solution of 4-methylnioxime, the chloroform extract of 4-methylnioxime, and the chloroform extract of tin-4-methylnioxime were prepared and their absorbancies were measured. Neither the aqueous solution nor the chloroform extract of 4-methylnioxime absorbs throughout the entire visible region. The chloroform extract of tin-4-methylnioxime absorbs at 436 mμ. However, this interference is cancelled in the determination of rhenium because the chloroform extract of a blank containing all of the reagents except rhenium is used in "zero-setting" the instrument.

Rhenium-4-methylnioxime complex

The yellow-green colour of the rhenium-4-methylnioxime compound used for the spectrophotometric determination of rhenium reached a maximum intensity in less than 5 min. The distribution ratio of the complex between chloroform and water is about 85. Thus it is necessary to extract with three portions of chloroform for quantitative extraction of the complex.[5] However, good results can be obtained by extracting with one 10-ml portion of chloroform provided the same technique is used to prepare the calibration curve (Table II). The change in absorbancy of the chloroform phase of the complex and blank was negligible for 24 hr or more when room temperature was about 25° and the complex was formed and extracted under optimum conditions.

Effect of reagent concentrations

The hydrochloric acid concentration at which the complex is formed and extracted is rather critical. The maximum colour intensity is developed with a hydrochloric acid concentration of $0{\cdot}43 \pm 0{\cdot}05N$. The absorbancy decreases and the rate of fading increases somewhat for higher and lower concentrations of acid. The optimum tin$^{\mathrm{II}}$ chloride concentration for maximum development and stability of colour was found to be 0·25%. A 20% increase or decrease in concentration of tin$^{\mathrm{II}}$ chloride only produced a 1 to 1·5% deviation respectively in the absorbancy. The optimum con-

TABLE II. RESULTS OBTAINED WITH U.S. BUREAU OF MINES SAMPLES

Sample	Certified value,* %	Experimental value, %	Difference	Other materials present as determined by U.S. Bureau of Mines, %						Other elements known
				Mo	Se	S	Cu	Fe	Au	
Molybdenite concentrate	0·12	0·130‡ 0·128‡ 0·132§ 0·131§	0·010 0·008 0·012 0·011	56·4	—	—	0·7	—	5·3†	
Low grade "molybdenite roaster flue dust"	0·48	0·488‡ 0·487‡ 0·477§ 0·486§	0·008 0·007 0·004 0·006	35·0	1·0	2·36	0·5	3·6	—	
High grade "molybdenite roaster flue dust"	0·96	1·010‡ 1·000‡ 0·956§ 0·959§	0·050 0·040 0·004 0·001	28·4	10·0	—	—	—	—	
Rhenium bearing synthetic samples	0·0050	0·0051‡ 0·0054‡	0·0001 0·0004	2·5						Si, Al, Mg, Ca, Na, K, Fe, Cl, As, Ba, & Cu.
	0·0012	0·0014§ 0·0012§ 0·0011§	0·0002 0·0000 0·0001	0·6						

* Figure given by the Salt Lake City Metallurgy Research Center, U.S. Bureau of Mines, Salt Lake City, Utah, U.S.A

† Ounces per ton.

‡ Single extraction.

§ Triple extraction.

concentration of hydrochloric acid and tin$^{\text{II}}$ chloride is readily obtained by preparing the tin$^{\text{II}}$ chloride reagent with the desired amount of each present, then measuring the reagent with a pipette.

Eighty-five mg of 4-methylnioxime (25 ml of the stock solution) are capable of converting 160 μg of rhenium in 50 ml of solution quantitatively to the rhenium-4-methylnioxime complex. Less than 1% deviation in the absorbancy is produced by varying the concentration of the 4-methylnioxime by ±20% from the optimum—85 mg per 50 ml of solution.

APPLICATION OF METHOD

This procedure has been successfully applied to the analyses of synthetic samples prepared in this laboratory containing arsenic, copper, gold, iron, and molybdenum and to three rhenium-containing materials and two synthetic samples[4] obtained from the Salt Lake City Metallurgy Research Center, U.S. Bureau of Mines, Salt Lake City, Utah, U.S.A. (Table II).

The proposed method makes possible the determination of rhenium in all rhenium-bearing materials found in U.S.A.

Zusammenfassung—Eine methode zur photometrischen Bestimmung von weniger als 0·001% bis über mehr als 1% Rhenium in Molybdenit und Flugstaub nach der Röstung von Molybdenit wurde entwickelt. Störelemente, die normalerwiese vorhanden sind, werden durch drei Operationen entwernt: Abrauchen mit Salzsäure, Hydroxydfällung mit wässrigem Ammoniak und Chloroformextraktion der Metalläthylxanthate. Die Bestimmung basiert auf der Bildung einer löslichen, stabilen, gelb-grünen Chelatverbindung mit 4-Methylnioxim. Rhenium(VII) wird in Gegenwart des Reagenses durch Zinn(II) in salzsaurer Lösung reduziert. Die Farbentwicklung findet in weniger als 5 Minuten statt. Das Absorptionsmaximum liegt bei 436 mμ; Beer's Gesetz wird befolgt. Der molare Extinktionskoeffizient beträgt 6·89 × 10^4 im Vergleich zu unter 4·5 × 10^4 fur andere Methoden zur Bestimmung von Rhenium.

Résumé—Les auteurs ont développé une méthode simple applicable au dosage spectrophotométrique de moins de 0,001 pour cent à plus de 1,0 pour cent de rhénium dans un concentré de molybdénite et dans "molybdenite roaster flue dust". Les éléments gênants couramment rencontrés dans ces produits sont éliminés en trois opérations, à savoir, évaporation avec de l'acide chlorhydrique, précipitation des hydroxydes par l'ammoniaque et formation de composés organométalliques avec le xanthate d'éthyle, et extraction par le chloroforme. La méthode est basée sur la formation d'un chelate rhénium-4-méthylnioxime jaune-vert, stable, soluble où le rhénium (VII) est réduit par le chlorure stanneux en solution acide chlorhydrique dilué en présence de 4-méthylnioxime. La couleur se développe en moins de cinq minutes, et le corps extrait par le chloroforme montre un maximum d'absorption à 436 mμ. La courbe de calibrage est conforme à la loi de Beer. Le coefficient d'extinction molaire du rhénium-4-méthylnioxime est environ 6,89 . 10^4, alors qu'il est inférieur à 4,5 . 10^4 pour les autres méthodes de dosage du rhénium.

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A STUDY OF THE SEPARATION OF PHOSPHATE ION FROM ARSENATE ION BY SOLVENT EXTRACTION

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Summary—The results presented confirm the postulate of Keggin that oxygen-containing materials are good solvents for heteropoly acids. The results also show that none of the solvents examined will completely separate phosphate ion from arsenate ion with a single extraction.

The butanol-chloroform system is studied extensively. The results show that as the percentage of butanol is increased in the mixed solvent, the percentage of phosphate and arsenate extracted also increases. Of the various concentrations of butanol studied, the 10% concentration shows the most promise as a selective extractant for phosphate consistant with a high yield. The results also show that the amount of arsenate ion extracted with any given concentration of butanol is relatively independent of the concentration of phosphate ion in the system.

INTRODUCTION

THE separation of phosphate ion from arsenate ion is an important problem in analytical chemistry. The separation is especially difficult when the amount of arsenate ion is large as compared to that of phosphate. Precipitation methods do not serve to separate phosphate from arsenate, as similar insoluble arsenate compounds are formed. The gathering of phosphate ion on a precipitate of aluminum or iron^{III} hydroxide has been used to separate phosphorus from other elements but, here again, arsenate interferes. Arsenate can be separated from phosphate by reducing the arsenic to the tervalent state, then boiling with either hydrochloric acid or hydrofluoric acid. In this process the arsenic is volatilised from solution but this method is quite long and is not suitable for removing microgram amounts of arsenate from solution. Of all the various methods solvent extraction procedures have shown the most promise. For this reason, this study has been limited to solvent extraction techniques.

There are many methods in which phosphate ion is separated from other elements by extracting phosphomolybdic acid with an organic solvent. Wu[19] and Copaux[4] used diethyl ether as the solvent for the heteropoly acid. Scroggie[14] found that esters, ketones, aldehydes, and ethers are good extractants but carbon disulphide, carbon tetrachloride, chloroform, benzene, and toluene are not. Keggin[8] postulated that oxygen-containing materials are good solvents for heteropoly acids. Other solvents that have been used to extract heteropoly acids include ethyl acetoacetate,[16] ethyl acetate,[7] butyl acetate,[9] 2-methyl-1-propanol,[2,3,15] 3-methyl-1-butanol,[11] 1-octanol,[13] and 1-butanol.[17] Mixtures of 1-butanol in chloroform have also been used to extract phosphomolybdic acid from arsenomolybdic acid.[1,5,6,10] In all of the above mentioned solvents, arsenic was extracted to some extent also and only a limited amount could be tolerated without interference. An article by Wadelin and Mellon[18] compares various solvents.

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Rosenheim[12] gives a general equation for the formation of heteropolymolybdic acids:

$$X^{n}O_{a}^{(2a-n)-} + 12MoO_{4}^{-2} + (24 + 2a - n)H^{+} \rightarrow H_{(12-n)}X(Mo_{2}O_{7})_{6} + (6 + a)H_{2}O \qquad (I)$$

where X is P^{V}, As^{V}, Si^{IV}, or Ge^{IV}. Inspection of equation (I) shows that a large excess of molybdate ions or hydrogen ions will force the reaction to the right. Wadelin and Mellon, however, were unable to utilise a high concentration of molybdate ion to enhance the formation of the heteropoly acid because it exhibits strong absorption in the same region as the complexes they measured.

In the present work, various solvents were studied using radiochemical methods. The chloroform-butanol system was examined extensively. Unlike the spectrophotometric method, none of the solution variables affect the accuracy of the measurements made on the system.

EXPERIMENTAL

Reagents

In addition to standard laboratory reagents, the following solutions were used:

Phosphorus-32 and Arsenic-76 tracer solutions: Solutions of these isotopes, in the form of phosphate and arsenate, were diluted to the desired activity with 0·01*N* hydrochloric acid.

Phosphorus carrier: Dissolve 2·8657 g of pure potassium dihydrogen phosphate (KH_2PO_4) in 100 ml of water and dilute to 1 litre. The resulting solution contains 2·00 mg of phosphate ion per ml.

Arsenic carrier: Dissolve about 4·5 g of disodium hydrogen arsenate ($Na_2HAsO_4 \cdot 7H_2O$) in 100 ml of water and dilute to 1 litre. The resulting solution contains about 2 mg of arsenate ion per ml.

Magnesia mixture: Dissolve 55 g of magnesium chloride ($MgCl_2 \cdot 6H_2O$) and 140 g of ammonium chloride in 500 ml of water. Add 130 ml of concentrated ammonium hydroxide and dilute to 1 litre.

Organic solvents: All organic solvents were chemically pure or reagent-grade. Mixed solvents were prepared on a volume percentage basis by adding the required volumes of each component using a pipette.

Apparatus

Various methods were used to detect and count the activities of the isotopes used in this work. Beta activity was measured with end-window Geiger tubes of both the halogen and organic quenched types. Gamma radiation was measured with a thallium-activated sodium iodide crystal in the form of a well-type scintillation detector. The counts were recorded with a variety of commercial scalers.

General procedure

Various concentrations of reagents are recommended in the literature for the extraction of heteropolymolybdic acids. The following concentrations were decided upon as being representative and consistent with a large molybdate and hydrogen ion concentration. The hydrochloric acid concentration was 50% (V/V) and the sodium molybdate was 0·31*M* (15 ml of 20% sodium molybdate solution in 40 ml of final solution). All extractions were performed with 40 ml of solution in each phase. After preliminary experimentation, the following general procedure was developed to determine the amount of phosphate extracted.

Procedure

(1) Pipette exactly 5 ml of phosphate carrier into a 250-ml separatory funnel.

(2) Add an amount of ^{32}P tracer solution (10–50 μl) to give an activity of 10,000-15,000 cpm.

(3) Add 15 ml of 20% sodium molybdate solution.

(4) Add 50 ml of the solvent being examined.

(5) Add 20 ml of concentrated hydrochloric acid, stopper the funnel, shake for 2 min, and allow the phases to separate.

(6) Separate the layers, discard the aqueous phase, and add 50 ml of $3M$ ammonium hydroxide-$1M$ ammonium chloride buffer solution to the organic phase, shake 2 min, and allow the phases to separate.

(7) Drain the aqueous layer into a 150-ml beaker and heat to boiling.

(8) Add 10 ml of magnesia mixture and allow to stand until cool.

(9) Collect the precipitate of magnesium ammonium phosphate on a filter disc in a Hirsch funnel. Wash the precipitate with three 10-ml portions of buffer solution and three 5-ml portions of acetone.

(10) Air dry the precipitate and beta count.

(11) The percentage of phosphate extracted is found using the equation:

$$\%\ \text{extracted} = \frac{A_1 \times 100}{A_2}$$

where A_1 = the activity of the precipitate (cpm),
and A_2 = the activity of the original tracer solution (cpm).

A procedure similar to the above was used to determine the percentage of arsenate extracted with the same solvents. The numbered steps in the general procedure were replaced by the following:

(1a) Pipette exactly 5 ml of arsenate carrier into a 250-ml separatory funnel.

(2a) Add an amount of ^{76}As tracer solution (10–50 μl) having a total activity of 70,000–80,000 CPM.

Steps 3, 4, and 5 are the same as above.

(6a) Pippette a 5-ml portion of each layer into different test tubes suitable for use in a well-type scintillation counter.

(7a) Count each layer. The percentage of arsenate extracted is calculated by means of the following equation:

$$\%\ \text{extracted} = \frac{A_0 \times 100}{A_0 + A_a}$$

where A_0 = the activity of the organic phase (cpm),
and A_a = the activity of aqueous phase (cpm).

RESULTS

Using the above procedures, several solvents were examined to determine how much phosphate and arsenate was extracted by each. The results of these experiments are shown in Tables I and II.

The results obtained in the first two sets of experiments indicated that 20% butanol in chloroform was a promising solvent, in that a large percentage of phosphorus was extracted while only a small amount of arsenic was carried through. It was thought

TABLE I.—PERCENTAGE OF PHOSPHATE EXTRACTED USING VARIOUS ORGANIC SOLVENTS

Solvent	% Phosphate extracted ±5%*
Ethyl acetoacetate	100·00
20% Butanol in chloroform	94·97
Ethyl acetate	79·92
Butyl acetate	73·58
50% *Iso*butanol in benzene	72·63
*Iso*butanol	67·21
1-Butanol	60·63
1-Octanol	29·86
Chloroform	00·00
Benzene	00·00

* Average of two determinations

TABLE II.—PERCENTAGE OF ARSENATE EXTRACTED USING VARIOUS ORGANIC SOLVENTS

Solvent	% Arsenic extracted ±5%*
20% Butanol in chloroform	4·74
Butyl acetate	8·49
1-Octanol	14·39
Ethyl acetate	29·46
50% *Iso*butanol in benzene	36·76
*Iso*butanol	87·05
1-Butanol	87·91
Ethyl acetoacetate	96·67
Chloroform	00·00
Benzene	00·00

* Average of two determinations

that a more favourable mixture of 1-butanol might exist for this extraction. To this end, the same procedures were used to determine the percentage of phosphate and arsenate extracted with various concentrations of 1-butanol. The extractions of arsenate were made with three concentrations of this ion. Extractions were performed both in the presence and absence of phosphate ion to determine the effect of this variable. The experimental conditions and results are shown in Tables III, IV, and V.

TABLE III.—PERCENTAGE OF PHOSPHATE EXTRACTED USING VARIOUS CONCENTRATIONS OF 1-BUTANOL IN CHLOROFORM

% Butanol	% Phosphate extracted ±5%*
20	94·97
19	95·04
18	97·23
17	93·26
16	92·99
15	96·31
10	85·60
7·5	55·01
5·0	18·30

* Average of two determinations

TABLE IV.—PERCENTAGE OF ARSENATE EXTRACTED USING VARIOUS CONCENTRATIONS OF 1-BUTANOL IN CHLOROFORM

% Butanol	% Arsenic extracted at indicated level*		
	10-mg	100-μg	Tracer
5	0·20	0·27	0·076
10	0·36	1·42	0·78
15	1·56	2·45	1·99
20	5·16	4·58	4·17
30	13·57	13·15	13·06

* Average of two determinations

TABLE V.—PERCENTAGE OF ARSENATE EXTRACTED USING VARIOUS CONCENTRATIONS OF 1-BUTANOL IN CHLOROFORM WITH 10 mg OF ADDED PHOSPHATE

% Butanol	% Arsenic extracted at indicated level*		
	10-mg	100-μg	Tracer
5	0·073	0·14	0·12
10	0·69	0·88	0·80
15	2·30	1·61	1·77
20	4·32	3·62	4·50
30	12·12	12·38	12·38

* Average of two determinations

Zusammenfassung—Das Postulat von Keggin, wonach sauerstoffhaltige verbindungen gute Lösemittel für Heteropolysäuren sind, wird bestätigt. Keines der untersuchten Lösemittel kann eine völlige Trennung von Phosphat und Arsenat in einem Extraktionschritt bewirken. Das System Butanol-Chloroform wurde eingehend studiert. Mit ansteigender Butanolkonzentration steigen die extrahierten Phosphat und Arsenatmengen an. Eine Butanolkonzentration von 10% scheint meistversprechend für eine selektive Phosphatextraktion zu sein. Die extrahierte Arsenatmenge ist weitgehend unabhängig von der vorherrschenden Phosphatkonzentration.

Résumé—Le postulat de Keggin, à savoir que les substances contenant de l'oxygène sont de bons solvants des hétéropolyacides, est confirmé. Aucun des solvants étudiés ne sépare complètement l'ion phosphate de l'ion arséniate en une seule extraction. Le système butanol-chloroforme a été très étudié. Quand le pourcentage de butanol augmente dans le mélange de solvants, le pourcentage de phosphate et d'arséniate extraits augmente aussi. Parmi les concentrations variées de butanol étudiées, 10 pour cent offrent le plus de promesses comme produit extrayant sélectivement le phosphate, avec un rendement important. La quantité d'arséniate extraite par toute concentration de butanol est relativement indépendante de la concentration d'ion phosphate dans le système.

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THE PRECIPITATION OF HYDRATED COBALT 1-NITROSO-2-NAPHTHOLATE FROM HOMOGENEOUS SOLUTION[*][†]

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Summary—A method has been developed for determining cobalt by precipitating cobalt^{III} 1-nitroso-2-naphtholate from homogeneous solution. The reagent is synthesised within the reaction mixture by treating 2-naphthol with nitrous acid in the presence of cobalt^{II} ion. Thus nitrous acid serves the dual role as oxidant for the cobalt^{II} ion and also as a reactant in the synthesis of the reagent. Excess reagent precipitates after the cobalt nitroso-naphtholate has settled. A washing procedure has been developed to eliminate the excess reagent without affecting the cobalt nitroso-naphtholate. After washing to remove excess reagent and filtration, the precipitate is dried at 115° and weighed as $Co(C_{10}H_6O_2N)_3 \cdot H_2O$.

The presence of fluoride prevents the interference of iron, tungsten and other elements which form strong fluoride complexes.

The precision and accuracy is within 0·1 mg of cobalt at a 10-mg level and within 0·2 mg of cobalt at a 50-mg level.

INTRODUCTION

Although many precipitants have been used for the gravimetric determination of cobalt,[1–3] the one most often selected because of the extreme insolubility of its cobalt complex and its alleged ability to separate cobalt from nickel is 1-nitroso-2-naphthol.[4] The resulting 1-nitroso-2-naphtholate is bulky and, therefore, is filtered and washed with difficulty. The cobalt naphtholate is generally believed to be in the tervalent state and thus the cobalt^{II} ion in aqueous solution has been oxidised at the expense of the reagent. The reduction product of the reagent co-precipitates with the cobalt naphtholate. The precipitate is, therefore, not pure and cannot be weighed directly but must be converted into a suitable weighing form such as Co_3O_4, an oxide of variable composition, reduction of the oxide to the metal in a stream of hydrogen, or conversion to the sulphate.

The present investigation was initiated to develop a better gravimetric method for the separation and determination of cobalt. The problem was two-fold in nature: it was hoped to produce a precipitate with superior physical properties using 1-nitroso-2-naphthol on the one hand, and one which could be weighed directly without conversion into another form, on the other hand.

The method of precipitation from homogenous solution, by decreasing supersaturation, frequently has the effect of increasing particle size and decreasing contamination and coprecipitation.[5,6]

A pure precipitate of cobalt 1-nitroso-2-naphtholate can be weighed directly. This

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not only eliminates the conversion to another weighing form, but also has the advantage of a favourable gravimetric factor.[7] As mentioned above, the cobalt 1-nitroso-2-naphtholate formed from cobalt^{II} solutions is usually contaminated with the reduction products of the 1-nitroso-2-naphthol. Other investigators have attempted to pre-oxidise the cobalt^{II} ion before the precipitant was added by the formation of cobalt^{III} hydroxide which was subsequently dissolved in acetic acid.[8] Such a method suffered from the difficulty of redissolving the hydrous oxide. In fact, as a recent paper by Kolthoff and Jacobsen[9] points out, the precipitation probably took place from a cobalt^{II} solution rather than a cobalt^{III} solution, as claimed originally. Synthesis of the 1-nitroso-2-naphthol within the solution was found to be a workable approach to the cobalt precipitation.

EXPERIMENTAL

Reagents

2-naphthol solution: Prepared by dissolving 0·5 g of technical grade 2-naphthol in 100 ml of a warm 25% glacial acetic acid solution.

Hydrochloric acid, acetic acid and ammonia, 1:10 *solutions:* Prepared by diluting 10 ml of the respective concentrated reagent-grade solutions to 100 ml.

Hydrochloric acid, 1:20 *solution:* Prepared by diluting 5 ml of concentrated reagent-grade hydrochloric acid to 100 ml.

Ammonium fluoride solution, 25%: Prepared by dissolving 25 g of reagent-grade ammonium fluoride and diluting to 100 ml.

Apparatus

Crucibles: Selas porcelain filtering crucibles No. 3010 were used (medium porosity).

Radioactive tracer studies were made with a well-type γ-scintillation counter using the appropriate isotopes.

Procedure

To 10 ml of a neutral or slightly acid solution* containing from 1 to 90 mg of cobalt in a 600-ml beaker, add 10–15 drops of glacial acetic acid, 4 or 5 ice cubes (made from distilled water) and 1 g of sodium nitrite.† Stir and allow to stand for 10 min with occasional stirring, preferably by clean air or oxygen.

Add 100 ml of 25% ammonium fluoride solution, stir, then add the appropriate quantity of 2-naphthol solution‡ rapidly and with vigorous stirring. Continue to stir for 1 min, add sufficient ice (2 or 3 more cubes) to keep the solution cold for the next 0·5 hr. Allow to stand for 0·5 hr or until the supernatant liquid is *clear yellow.*

Decant the clear liquid through an unweighed§ porcelain filtering crucible, leaving as little of the filtrate as possible in the beaker. Wash any solid adhering to the crucible back into the beaker using water. Heat the contents of the beaker on a hot plate (temperature between 50° and 60°) for approximately 0·5 hr with occasional stirring at the beginning. Remove from the hot plate, allow to settle and decant through the crucible, again washing any adhering precipitate back into the beaker with water.

Add 100 ml of 1:20 hydrochloric acid and heat nearly to boiling, but do not boil. Allow to settle. Decant.

Add 1:10 ammonia solution, heat to boiling. Allow to settle. Decant.

Add 1:10 acetic acid, heat to boiling. Allow to settle. Decant.

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* In the case of solutions containing vanadium, chromium, manganese, molybdenum, *etc.*, the solution should be treated with nitric acid or ammonium persulphate to be sure that these ions have been oxidised to vanadate, chromate, permanganate or molybdate, respectively.

† 90–150 mg of cobalt can be precipitated if 2 g of sodium nitrite are added.

‡ The amount of 2-naphthol to be added is determined by the amount of cobalt in the sample. To find the correct number of ml of stock solution which must be added multiply the approximate number of mg of cobalt to be precipitated by 2 and add 10. For example, if the sample is known to contain approximately 15 mg of Co^{2+}, add $30 + 10 = 40$ ml of the 2-naphthol solution. This is not critical; 20 ml (0·1 g) of 2-naphthol in excess only prolongs the washing of the precipitate from the reagent.

§ The crucible cannot be pre-weighed because of weight loss owing to the presence of fluoride.

Continue to wash with hot 1:10 hydrochloric acid until the wash water is colourless. Boiling in hydrochloric acid is not harmful after the first wash.

After the wash water is colourless, transfer quantitatively to the crucible. Dry the precipitate to constant weight at 115°.

Dissolve the precipitate by washing the crucible with chloroform until all of the red precipitate has been dissolved. Dry to constant weight at 115°.

The gravimetric factor for cobalt in the precipitate is

$$\frac{Co}{Co(C_{10}H_6O_2N)_3 \cdot H_2O} = 0{\cdot}0965.$$

DISCUSSION

Since iron which also forms an insoluble nitroso-naphtholate complex is often associated with cobalt, it is commonly removed by treatment with zinc oxide. Such a procedure, however, does not remove tungsten and certain other interfering ions. Tungsten and iron^{III} form stable fluoride complexes, and in consequence are prevented from precipitating. Cobalt, however, forms no such stable fluoride. The effect of the addition of ammonium fluoride to the reaction mixture was studied using radioactive iron-59 and cobalt-60 as tracers. This showed that the precipitation of cobalt 1-nitroso-2-naphtholate was as complete in the presence of fluoride ion as in the absence of this ion. In fact, in the presence of fluoride, the precipitate was more dense and settled more rapidly.

The presence of ammonium fluoride acts as an effective buffer, maintaining a pH of 3·8–4·0, a favourable range for two reasons: 1-nitroso-2-naphthol exists in two tautomeric forms, possibly only one of which precipitates the cobalt^{III} ion; some authors indicate that the precipitating tautomer exists only in mildly acidic solution.[10] The cobalt nitroso-naphtholate is not precipitated from strongly acidic solutions although it is insoluble in strong acids, once it is formed. Secondly, the oxidation of the cobalt^{II} ion must be carried out in weakly acidic solution because strong acids decompose the cobaltinitrite complex. Large quantities of acetic acid cause the precipitate to become bulky and colloidal, thus delaying the settling of the precipitate. The colloidal nature of the precipitate also causes low results. The correct acidity should be produced with as small a quantity of acetic acid as possible, thus the presence of ammonium fluoride is most beneficial.

TABLE I.—COMPLETENESS OF PRECIPITATION

Cobalt taken, *mg*	Cobalt found in filtrate, *mg*	
	Ammonium fluoride present	No ammonium fluoride present
10	0·005	0·03
15	0·003	
	0·008	
100	0·5	0·7
	0·1	

In an effort to avoid the use of low temperatures, several runs were made at an increased temperature of the precipitating mixture. In each case, however, some tarring occurred which gave rise to abnormally high results. This is probably due to the presence of excess nitrous acid in the precipitating mixture. In the recommended procedure, the filtrate containing nitrous acid is separated from the precipitate before the temperature is elevated.

The time needed for the settling of the precipitate varies somewhat. If the supernatant liquid is not a clear yellow the precipitate is probably colloidal. Vigorous stirring followed by settling of the precipitate a second time may clear the supernatant liquid. This difficulty is seldom encountered if sufficient 2-naphthol has been added.

TABLE II.—EFFECT OF VARIOUS WASH SOLUTIONS ON COBALT PRECIPITATE
(15 mg of cobalt present)

Wash solution	Amount of cobalt removed, *mg/100 mp*
1:20 HCl boiled 5 min at the beginning of washing	0·002
1:20 NH_4OH boiled 10 min	0·0026
1:3 acetic acid boiled	0·0089
1:10 acetic acid	0·0014
1:20 HCl boiled 5 min at end of washing	0·00075

TABLE III.—INTERFERENCE OF OTHER IONS (10-MG SAMPLES OF COBALT)

Ion present	Added as	Amount found in precipitate	Weight of cobalt
Mo	$Na_2MoO_4 \cdot H_2O$ (50 mg of Mo)	None	Theoretical
	Steel sample	Less than 0·1% (spectrographic)	
V	Na_3VO_4(50 mg of V)	None	Theoretical
	Steel sample	Less than 0·01% (spectrographic)	
As	Na_3AsO_4 (50 mg of As)	None	Theoretical
	Steel sample	Not present (spectrographic)	
Ag	Interferes		
Cu	Interferes		
W	Steel sample	Not present (spectrographic)	
Mn	Steel	Not present (spectrographic)	
Cr	Steel	Not present (spectrographic)	
Fe	10 mg of Fe/1 mg of Co $Fe(NH_4)SO_4 \cdot 12H_2O$	0·007 mg (radioactive tracer study)	

To ascertain the completeness of the precipitation of cobalt by the proposed method, a series of studies was made using radioactive cobalt-60. Tests were run with 10 mg and 100 mg of cobalt per run. The results are shown in Table I.

The precipitate must be washed carefully to remove excess reagent. For this reason the nature of the wash solution was very important. In order to test the efficacy of wash solutions without redissolving the precipitate, tracer studies with cobalt-60 were conducted. Following the reaction the precipitate was subjected to a series of appropriate wash solutions, and from the amount of radioactivity in the filtrate the amount of cobalt that had been redissolved was determined. The results are shown in Table II.

The initial wash with mineral acid, which is the most critical step in the analysis, removed small amounts of nickel or other metal naphtholates. If too much filtrate has been retained by the precipitate, or if the wash solution is too hot or added too rapidly without adequate stirring, tarry matter may be formed. The reagent itself is not very soluble in mineral acids but soluble in a base, thus one basic wash is included. A second wash with a base should be avoided since such a wash tends to cause the precipitate to peptise.

TABLE IV.—INTERFERENCE OF NICKEL

Nickel taken, *mg*	Cobalt		Cobalt error, *mg*
	Taken, *mg*	Found, *mg*	
Fluoride absent			
10	10·3	10·9	+0·6
50	10·3	11·8	+1·5
100	10·3	13·7	+3·4
200	10·3	17·3	+7·0
25	25·7	26·7	+1·0
Fluoride present			
10	10·3	10·35	0·05
	10·3	10·2	−0·1

Ions that commonly occur in association with cobalt were tested for interference. The results of this study are shown in Table III. Nickel was tested at several levels. The results are shown in Table IV. Amounts of nickel in excess of 10 mg caused the formation of a grey precipitate resulting in weights well above the theoretical value for the known amount of cobalt added. Copper and silver were found to interfere to a marked extent. The initial precipitate was black, indicating contamination.

TABLE V.—ANALYSIS OF N.B.S. STEEL NO. 153

Cobalt taken, %	Cobalt found, %	Devn. from av., %	Std. devn., %
8·45	8·42	−0·03	0·054
	8·38	−0·07	
	8·52	+0·07	
	8·48	+0·03	
	8·46	+0·01	

A U.S. National Bureau of Standards steel sample was analysed for cobalt. The results of this analysis appear in Table V.

The cobalt 1-nitroso-2-naphtholate precipitate forms in a dense layer on the bottom of the beaker. Although it does not appear to be either granular or crystalline, it is easy to handle if the directions are followed carefully. The precision is within 0·1 mg of cobalt at a 10-mg level and within 0·5 mg of cobalt at the 50-mg level (see Table VI). The most time-consuming step in the analysis is the washing of the precipitate. The method is more rapid and less time-consuming than many other gravimetric

TABLE VI.—DETERMINATION OF COBALT

Cobalt taken, *g*	Cobalt found, *g*	Cobalt found, *g* av.	Devn. from known val., *mg*	Devn. from av. val., *mg*	Std. devn., *mg*
0·0010	0·0011	0·0011	+0·1	0·0	0·07
	0·0010		0·0	−0·1	
	0·0011		+0·1	0·0	
0·0050	0·0050	0·0050	0·0	0·0	0·12
	0·0049		−0·1	−0·1	
	0·0049		−0·1	−0·1	
	0·0052		+0·2	+0·2	
0·0103	0·0102	0·0103	−0·1	−0·1	0·06
	0·0103		0·0	0·0	
	0·0103		0·0	0·0	
	0·0103		0·0	0·0	
	0·0104		+0·1	+0·1	
	0·0103		0·0	0·0	
0·0250	0·0250	0·0250	0·0	0·0	0·14
	0·0251		+0·1	+0·1	
	0·0248		−0·2	−0·2	
	0·0249		−0·1	−0·1	
0·0257	0·0257	0·0258	0·0	−0·1	0·23
	0·0261		+0·4	+0·3	
	0·0256		−0·1	−0·2	
	0·0257		0·0	−0·1	
0·0500	0·0495	0·0495	−0·5	0·0	0·41
	0·0499		−0·1	+0·4	
	0·0488		−1·2	−0·7	
	0·0498		−0·2	+0·3	
	0·0499		−0·1	+0·4	
	0·0491		−0·9	−0·4	
	0·0500		0·0	+0·5	
	0·0490		−1·0	−0·5	
	0·0496		−0·4	+0·1	
	0·0498		−0·2	+0·3	
	0·0498		−0·2	+0·3	
0·0515	0·0518		+0·3		0·1
	0·0519		+0·4		
0·1000	0·1009		+0·9		
0·1025	0·1025		0·0		

methods for the determination of cobalt. Digestion times, temperatures and pH's are not critical.

A modification is under investigation: To the basic solution potassium persulphate was added, thus acidifying the solution and destroying excess reagent. This appears to reduce the washing time appreciably.

Zusammenfassung—Eine Methode zur Bestimmung von Kobalt durch Fallung als Kobalti-1-nitroso-2-naphthol aus homogener Lösung wird beschrieben. Das Reagens wird in der Lösung synthetisiert durch Behandlung von 2-Naphthol mit salpetriger Säure in Gegenwart von Kobalt(II)-ion. Salpetrige Säure erfüllt zwei Funktionen, einmal oxydiert sie das Kobalt(II) zu Kobalt(III) und zweitens dient sie zur Synthese des Reagenses. Überschüssiges Reagens fällt nach Beendigung des Absetzens des Kobaltniederschlages aus. Eine spezielle Waschvorschrift wird mitgeteilt, welche erlaubt das überschüssige Reagens zu entfernen, ohne Kobaltnaphtholat anzugreifen. Nach waschen und trocknen (115°C) wird der Niederschlag bei als $Co(C_{10}H_6O_2N)_3 \cdot H_2O$ gewogen. Anwesenheit von Fluoridion verhindert Störungen durch Eisen, Wolfram und andere Elemente, die stabile Fluorokomplexe bilden. Genauigkeit und Reproduzierbarkeit ist innerhalb von 0·1 mg bei 10 mg Kobalt und 0·2 mg bei 50 mg Kobalt.

Résumé—Les auteurs ont mis au point une méthode de dosage du cobalt par précipitation du 1-nitroso-2-naphtol cobaltique en solution homogène. Le réactif est synthétisé au sein du mélange réactionnel en traitant du 2-naphtol par le l'acide nitreux en présence d'ions cobalteux. Cet acide nitreux joue le rôle d'oxydant pour les ions cobalteux, ainsi que de corps réagissant dans la synthèse du réactif. L'excès de réactif précipité après que le nitrosonaphtolate de cobalt se soit déposé. Une méthode de lavage a été mise au point pour éliminer l'excès de réactif sans agir sur le nitrosonaphtolate de cobalt. Après lavage pour enlever l'excès de réactif, et filtration, le précipité est séché à 115° et pesé à l'état de $Co(C_{10}H_6O_2N_3) \cdot H_2O$. La présence de fluorure empêche l'interférence du fer, du tungstène et d'autres élèments qui forment des complexes fluorure très stables. La précision est au moins 0,1 mg de Co pour une teneur de 10 mg et au moins 0,2 mg de Co pour 50 mg.

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PRECIPITATION OF PALLADIUM DIMETHYLGLYOXIMATE FROM HOMOGENEOUS SOLUTION

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Summary—Palladium can be quantitatively precipitated from homogeneous solution with dimethylglyoxime generated by the reaction between biacetyl and hydroxylamine. The chelate is precipitated as long yellow needles which are easy to filter and wash. The separation of palladium from platinum and nickel was investigated.

SALESIN and Gordon[1] have precipitated nickel with dimethylglyoxime generated *in situ* from biacetyl and hydroxylamine. This reaction for producing dimethylglyoxime can also be utilised for the precipitation of palladium. A general procedure is described herein which has been applied to the separation of palladium from platinum and from nickel. It should be adaptable, with suitable modifications where required, to systems containing other diverse ions.

EXPERIMENTAL

Reagents

Palladium: $PdCl_2 \cdot 2H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey) was dissolved in distilled water containing a small amount of hydrochloric acid and was standardised by precipitation with dimethylglyoxime.[2]

Platinum: Reagent-grade $H_2PtCl_6 \cdot 6H_2O$ (Mallinckrodt Chemical Works, New York, New York).

Nickel: Reagent-grade $NiSO_4 \cdot 6H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

Biacetyl: This reagent was prepared and used according to the directions of Salesin and Gordon.[1]

Hydroxylamine hydrochloride: Reagent-grade (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

All other chemicals were reagent-grade.

Procedure

Dilute the approximately neutral solution containing 1–25 mg of palladium as chloride or sulphate to about 250 ml, and add 9 ml of concentrated hydrochloric acid. Add, with stirring, 25 ml of a solution containing 120 mg of biacetyl, and then 25 ml of a freshly prepared solution containing 400 mg of hydroxylamine hydrochloride. Let the reaction mixture stand at room temperature for at least 16 hr. Before filtering, mechanically stir the solution for 1 hr. Filter through a weighing crucible of medium porosity, washing the precipitate first with dilute (1:99) hydrochloric acid and finally with water. Dry at 110° for 1–2 hr. The chelate, $Pd(C_4H_7N_2O_2)_2$, contains 31·67% of palladium.

RESULTS AND DISCUSSION

Preliminary studies of the precipitation of palladium from homogeneous solution indicated that crystals of palladium dimethylglyoximate with favourable characteristics could be produced in the same acidic medium, *i.e.* 3% by volume in hydrochloric acid, as is often recommended[2,3] for the conventional method using dimethylglyoxime. Nearly identical results could be obtained at pH 1 if 4 to 6 g of ammonium chloride, in a 300-ml volume, were present. Less well developed crystals were obtained in a sulphuric acid medium.

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The procedure given was developed for a maximum of 25 mg of palladium simply as a matter of convenience. In terms of this quantity of palladium, the amounts of biacetyl and hydroxylamine hydrochloride are, respectively, three and six times the stoichiometric values needed. With these amounts, in the absence of palladium, dimethylglyoxime will not precipitate by itself.

The precipitate of palladium dimethylglyoximate consists of long yellow needles, virtually identical to, though somewhat shorter in length than those shown in the photomicrographs of nickel dimethylglyoximate.[1] The precipitate filters well.

Because of a slight tendency toward supersaturation, it is necessary to terminate the precipitation process with stirring. As indicated in the procedure, a 1-hr stirring period is sufficient. However, the amount of palladium dimethylglyoximate which remains supersaturated is small and can also be separated if desired by the addition of a small quantity of an alcoholic solution of dimethylglyoxime at the end of the 16-hr reaction period.

Heating the reaction mixture at 50° was tried, both in order to reduce precipitation time and to improve further the physical characteristics of the precipitate. Although the reaction time can be shortened, there is no appreciable change in the precipitate, and in view of the greater possibility of reducing platinum at the higher temperature[4,5] room temperature conditions are prescribed.

In several instances (*cf.* Table I) the quantities of palladium in the filtrates and

TABLE I.—SEPARATION OF PALLADIUM DIMETHYLGLYOXIMATE BY PFHS
(Solutions were not mechanically stirred except where noted)

Palladium taken, *mg*	1.01	1.01	1.01	1.01	10.1	10.1	10.1	25.3	25.3	25.3	24.3[a]
Difference found, *mg*	−0.06	−0.09	±0.00	+0.04	±0.0	±0.0	−0.1	±0.0	±0.0	−0.1	±0.0
Palladium found in filtrate, *mg*		0.05	0.05	0.02	0.02	0.04	0.07	0.09		>0.1	0.08

[a] The reaction mixture was stirred mechanically for 6 hr after the reagents were added, then the solution was filtered.

TABLE II.—SEPARATION OF PALLADIUM DIMETHYLGLYOXIMATE FROM DIVERSE IONS BY PFHS AND CONVENTIONAL PRECIPITATION
(Solutions were mechanically stirred as described in the procedure except where noted)

Number	1	2	3	4	5	6	7	8	9
Method of precipitation	PFHS	Conv.	Conv.	Conv.	Conv.	PFHS	PFHS	PFHS	Conv.
Palladium taken, *mg*	10.1	9.7	9.7	9.7	24.3	24.3	24.3	24.3	24.3
Difference found, *mg*	−0.2	±0.0	+0.1	+0.1	+0.2	−0.3	−0.5	+0.2	+0.2
Diverse element taken, *mg*	Pt, 10	Pt, 10	Pt, 10	Pt, 25	Pt, 25	Pt, 50	Pt, 75	Pt, 75	Pt, 75
Modifications in procedure	a					a	a		

Number	10	11	12	13	14	15	16	17	18	19
Method of precipitation	PFHS	PFHS	Conv.	PFHS	PFHS	Conv.	PFHS	PFHS	Conv.	Conv.
Palladium taken, *mg*	24.3	24.3	24.3	97.3	97.3	97.3	24.3	24.3	24.3	24.3
Difference found, *mg*	+0.4	+0.1	+0.2	+0.6	+2.1	+0.7	+0.3	+0.3	+0.3	+0.1
Diverse element taken, *mg*	Pt, 100	Pt, 100	Pt, 100	Pt, 200	Pt, 200	Pt, 200	Ni, 1000	Ni, 1000	Ni, 1000	Ni, 1000
Modifications in procedure		b		c	c					

[a] No mechanical stirring at the end of the 16-hr reaction period.
[b] One ml of a 1% solution of dimethylglyoxime in ethanol was added before filtration.
[c] About 0.48 g of biacetyl and 1.6 g of hydroxylamine hydrochloride were used.

washings were determined by the addition of nitric and sulphuric acids, evaporation to fumes of the latter, and subsequent determination of the palladium with α-furildioxime.[6] The amount of unprecipitated palladium is negligible.

The results of Table II show that the method of precipitation of palladium dimethyglyoximate from homogeneous solution leads to separation results which are no better than those obtained by conventional precipitation. The only advantage offered by PFHS (precipitation from homogeneous solution) in the present case is an easily filtered and washed precipitate which does not clog a filter medium as is generally the case with the conventionally produced precipitate.

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Zusammenfassung—Palladium kann aus homogener Lösung quantitativ gefällt werden, wenn Dimethylglyoxim durch Reaktion zwischen Diacetyl und Hydroxylamin gebildet wird. Das Chelate wird in Form langer, gelber Nadeln erhalten, die leicht zu filtrieren und waschen sind. Die Trennung des Palladiums von Platin und Nickel wurde untersucht.

Résumé—Le palladium peut être précipité quantitativement en solution homogène par de la diméthylglyoxime formé par réaction entre du biacétyle et de l'hydoxylamine. Le chélate est précipité sous forme de longues aiguilles jaunes qui sont faciles à filtrer et à laver. La séparation du palladium d'une part, du platine et du nickel d'autre part, a été étudiée.

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DETERMINATION OF RADIOACTIVE COBALT IN MIXTURES OF RADIONUCLIDES

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Summary—A detailed procedure for the separation of radiocobalt from other active material is described. Precipitation as the mercurithiocyanate and as the anthranilate have been compared, and the latter has been shown to be somewhat preferable.

INTRODUCTION

Various radioactive isotopes of cobalt are known: ^{54}Co, ^{55}Co, ^{57}Co, ^{58}Co, ^{58}mCo, ^{60}Co, ^{60}mCo, ^{61}Co, and ^{62}Co.[4] Of these, ^{60}Co is the most important. This isotope is used widely in tracer studies and as a gamma radiation source. It is found frequently in coolant waters from nuclear reactors. Cobalt-60 has a half life of 5·3 years and emits a β-particle of 0·31 MeV energy and two γ-rays of 1·17 and 1·33 MeV.[4]

The following study was made to develop a procedure for the determination of radioactive cobalt in the presence of other radionuclides. No attempt was made to distinguish between the various radioactive isotopes of cobalt. Cobalt-60 was used as tracer in all experiments.

Several methods have been devised for the radiochemical determination of ^{60}Co. Duncan and coworkers[2] extracted the cobalt thiocyanate complex from acid solution using amyl alcohol. Cobalt was stripped from the organic solvent with ammonium hydroxide, then precipitated as cobalt ferrocyanide for β-counting. The ferrocyanide is a bulky precipitate of indefinite composition and not entirely satisfactory for weighing and counting. Meinke[6] gives several procedures for the determination of radioactive cobalt in various targets after bombardment. The cobalt was weighed and counted in various forms: as cobalt$^{\mathrm{II}}$ sulphide, as potassium cobaltinitrite, or as the 1-nitroso-2-naphthol compound. None of these compounds is of constant composition, hence they are not suitable for accurate analyses.

The best general radiochemical method is that devised by Burgus.[1] Cobalt is separated from other activities by a series of precipitations and solvent extractions. It is finally electroplated as the metal for weighing and counting. The electroplating, however, is tedious and time-consuming and a simple precipitation method would be more desirable. Various precipitants for cobalt, therefore, were investigated.

Duval[3] studied about thirty different precipitates and two of these, cobalt mercury$^{\mathrm{II}}$ thiocyanate, $CoHg(SCN)_2$, and cobalt anthranilate, $Co(C_7H_6O_2N)_2$, appeared most promising for radiochemical use. These were carefully investigated.

EXPERIMENTAL

Reagents

Cobalt carrier: Dissolve 49·4 g of C.P. $Co(NO_3)_2{\cdot}6H_2O$ in distilled water and dilute to 1 litre. Standardise by the following procedure:

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Take 5 ml of the solution and dilute to 50 ml with water, then add 25 ml of 0·1 *M* ammonium mercurithiocyanate reagent. Stir the solution and scratch the walls of the beaker to promote crystallisation. Digest the resulting precipitate for 1 hr at room temperature, then filter through a tared, sintered-glass crucible, using a rubber policeman to ensure complete transfer. Wash with 5 ml of a 0·01 *M* solution of the reagent, followed by 1-2 ml of 95% ethyl alcohol, then dry at 120° for 30 min and weigh.

Nickel carrier, 10 mg/ml: Dissolve 5 g of C.P. $Ni(NO_3)_2 \cdot 6H_2O$ in 100 ml of distilled water.

Palladium carrier, 10 mg/ml: Dissolve 2 g of C.P. $PdCl_2 \cdot 2H_2O$ in 100 ml of distilled water.

Copper carrier, 10 mg/ml: Dissolve 2·7 g of C.P. $CuCl_2 \cdot 2H_2O$ in 100 ml of distilled water.

Ammonium mercurithiocyanate, 0·1*M* with a 10% excess of ammonium thiocyanate: Dissolve 27 g of C.P. $HgCl_2$ and 34 g of C.P. NH_4CNS in distilled water and dilute to 1 litre.

Anthranilic acid, 2%: Dissolve 20 g of $C_6H_4 \cdot NH_2 \cdot COOH$ in 160 ml of 1*N* sodium hydroxide and dilute with 800 ml of distilled water. Filter this solution, and bring the pH to 6 by adding 5% acetic acid.

Thioacetamide, 1M: Dissolve 7·6 g of $CH_3 \cdot CS \cdot NH_2$ in 100 ml of distilled water.

Potassium hydroxide, 10*M*: Dissolve 560 g of potassium hydroxide in 1 litre of distilled water. Store in a polyethylene bottle.

Amyl alcohol-ether mixtures, 35% amyl alcohol, 65% diethyl ether by volume.

Ethyl alcohol, 95%.

Ammonium thiocyanate, solid.

Potassium nitrite, solid.

Acetic acid, 6*M*.

Hydrochloric acid, concentrated, 37·6% by weight.

Nitric acid, concentrated, 70% by weight.

Ammonium hydroxide, concentrated, 28% by weight.

Precipitation as cobalt anthranilate

Anthranilic acid (o-aminobenzoic acid) was investigated as a precipitant for cobalt by Wenger and coworkers.[7] A 2% solution of the reagent is used and cobalt is precipitated as the corresponding salt from neutral or weakly acid solution. Cobalt anthranilate is a pink-coloured, light, flaky precipitate which is easily filtered and washed. This precipitant was investigated for radiochemical use by adding a known amount of ^{60}Co tracer to a solution of cobalt nitrate as carrier, then precipitating the mixture with a 2% solution of anthranilic acid. The resulting cobalt anthranilate precipitate was filtered, weighed, then γ-counted in a well-type scintillation counter. The results are given in Table I and show an average recovery of 99·2% of the radioactive cobalt.

TABLE I. RECOVERY OF ^{60}Co AS COBALT ANTHRANILATE

Sample*	Gravimetric yield, %	Observed counts, *cpm*	Counts corrected for yield, *cpm*	Recovery, %
1	96·2	4361	4533	98·0
2	97·1	4424	4556	98·5
3	93·6	4433	4736	102·4
4	94·8	4293	4528	97·9

* 10·41 mg of cobalt carrier and 4625 cpm of ^{60}Co were added to each sample.

Precipitation as cobalt mercurithiocyanate

Lamure[5] reported the compound, cobalt^{II} tetrathiocyanatomercurate (commonly called cobalt mercurithiocyanate), to be a quantitative precipitate for cobalt. It has the formula $CoHg(SCN)_4$, and contains 11·98% of cobalt. It is a blue-coloured, dense, crystalline precipitate which is easily filtered and washed.

A preliminary study was made to determine whether cobalt activity would be carried completely on this precipitate. A known amount of ^{60}Co tracer was added to a solution of cobalt nitrate carrier and the mixture precipitated by the addition of ammonium mercurithiocyanate reagent. The resulting precipitate of cobalt mercurithiocyanate was filtered, weighed, and γ-counted. The results are given in Table II and show an average recovery of 100·1 % of the cobalt activity.

TABLE II. RECOVERY OF ^{60}Co AS COBALT MERCURITHIOCYANATE

Sample*	Gravimetric yield, %	Observed counts, *cpm*	Counts corrected for yield, *cpm*	Recovery, %
1	96·9	4392	4533	98·0
2	96·4	4503	4671	101·0
3	95·9	4433	4623	100·0
4	95·8	4497	4694	101·5

* 10·21 mg of cobalt carrier and 4625 cpm of ^{60}Co were added to each sample.

Comparison of the mercurithiocyanate and anthranilate methods

On the basis of the previous experiments, both the mercurithiocyanate and anthranilate methods are satisfactory for the determination of radioactive cobalt. In order to gain additional information in regard to the relative merits of these two precipitates, it seemed advisable to study their selectivity for radioactive cobalt. A series of determinations was performed to study the effectiveness of the separation of cobalt activity from foreign activities. Samples, containing known amounts of foreign activities, were analysed by both methods, using the procedures described previously except that no cobalt activity was added to the samples. Both β- and γ-counting were employed. The results, summarised in Table III, are the average of four determinations for each activity tested.

TABLE III. EFFICIENCY OF SEPARATION FROM FOREIGN ACTIVITIES—THE TWO PRECIPITATES COMPARED

Activity added	Radiation measured	Percentage activity carried down	
		Mercurithiocyanate method	Anthranilate method
^{134}Cs	γ	1·1	0·2
^{90}Sr —^{90}Y	β	0·1	58·0
^{95}Zr —^{95}Nb	γ	0·0	8·3
^{106}Ru —^{106}Rh	γ	13·0	44·0
^{32}P	β	0·5	0·2
^{144}Ce —^{144}Pr	β	1·1	82·0
^{131}I	γ	17·0	13·0

The major contaminants in the mercurithiocyanate method were ^{106}Ru —^{106}Rh and ^{131}I, 13 % of the former and 17 % of the latter being recovered on the cobalt mercurithiocyanate precipitate. ^{90}Sr —^{90}Y, ^{106}Ru —^{106}Rh, ^{144}Ce, and ^{131}I activities were carried down quite appreciably on the cobalt anthranilate precipitate. The results of these experiments show the mercurithiocyanate method to be more selective for cobalt. On the basis of these experiments, and also because the mercurithiocyanate precipitate is denser and therefore easier to manipulate, it seemed advisable to employ the cobalt mercurithiocyanate precipitate in the following procedures.

Determination of radioactive cobalt in mixtures of activities

The decontamination procedure for the determination of radioactive cobalt was adapted from a procedure given by Burgus.[1] In this procedure cobalt is separated from fission products and from nickel by precipitation as potassium cobaltinitrite from acetic acid solution, followed by appropriate scavenging steps and extraction of the blue cobalt thiocyanate complex into an amyl alcohol-ether mixture. The cobalt is then precipitated as the sulphide, which is dissolved, and the cobalt finally electroplated from an ammoniacal solution. Certain modifications of Burgus' procedure were made, the most significant being the final form in which the cobalt is counted. Thioacetamide is used in this modified procedure to replace hydrogen sulphide as a precipitant in the scavenging steps. The excess thioacetamide can be destroyed very easily by heating with nitric acid. If hydrogen sulphide gas is employed in place of thioacetamide, the sample must be evaporated to dryness to ensure complete removal of the excess reagent. Nickel "holdback" carrier is added initially to reduce the co-precipitation of radioactive nickel with the cobalt. The entire analysis takes about 3 hr. The procedure finally adopted is as follows:

Step 1. Place a known volume of the radioactive solution to be analysed in a 40-ml centrifuge tube. Add sufficient water to make the volume about 20 ml. Add 2·0 ml of standard cobalt nitrate carrier (10 mg of cobalt per ml) and 1 ml of nickel nitrate carrier. Add $10M$ potassium hydroxide until the solution is basic. Stir thoroughly. Centrifuge, decant and discard the supernate. Wash the precipitate with 20 ml of water. Discard the supernate and washings.

Step 2. Dissolve the precipitate in 3 ml of $6M$ acetic acid. Dilute to 15 ml with water.

Step 3. Precipitate potassium cobaltinitrite by adding 10 ml of a solution of $3M$ acetic acid saturated with potassium nitrite* to the above solution. Stir thoroughly and let stand for 5 min. Centrifuge, discard the supernate, and wash the precipitate with 10 ml of water. Discard the washings.

Step 4. Dissolve the precipitate of potassium cobaltinitrite in 4-5 ml of concentrated hydrochloric acid and evaporate the solution almost to dryness. Add 2 drops of palladium chloride and 4 drops of copper^{II} chloride carriers. Dilute to 20 ml and make about $0{\cdot}1M$ in hydrochloric acid. Add 2 ml of $1M$ thioacetamide and immerse the centrifuge tube in a beaker of boiling water. When the sulphide precipitate begins to settle in the tube, remove the tube from the boiling water and filter through a Whatman No. 40 filter paper. Catch the filtrate in a 50-ml beaker. Discard the precipitate.

Step 5. Add 2-3 ml of concentrated nitric acid to the filtrate in the beaker, and heat to boiling to decompose the excess thioacetamide.

Step 6. Cool the mixture and add 4 drops of iron^{III}chloride carrier. Add concentrated ammonium hydroxide until basic, then add 1 ml in excess. Pour the mixture into a 40-ml centrifuge tube and centrifuge. Decant the supernate into a 50-ml beaker and discard the precipitate.

Step 7. Acidify the supernate from step 6 with concentrated hydrochloric acid, adding 1 ml in excess. Add 15 g of solid ammonium thiocyanate and stir until dissolved. Pour the solution into a 125-ml separatory funnel and extract the cobalt thiocyanate complex into 50 ml of amyl alcohol-ether mixture. Discard the aqueous layer.

Step 8. Back-extract the cobalt into 20 ml of water to which 4-6 ml of concentrated ammonium hydroxide has been added. The organic layer should now be almost colourless. If it is not, add more ammonium hydroxide. Discard the organic layer into a 50-ml beaker.

Step 9. Heat the solution from step 8 to boiling and add slowly, with constant stirring, about 10 ml of $10M$ potassium hydroxide to precipitate cobalt hydroxide. Continue boiling the mixture for about 10 min, stirring frequently. Transfer the mixture to a 40-ml centrifuge tube and centrifuge. Wash the precipitate with 20 ml of water. Centrifuge and discard the washings.

Step 10. Dissolve the cobalt hydroxide precipitate in 5-6 drops of concentrated hydrochloric acid.

Step 11. Transfer the solution to a 50-ml beaker using 10 ml of water. Add 10 ml of $0{\cdot}1M$ ammonium mercurithiocyanate reagent. Stir and scratch the walls of the beaker to promote crystallisation. Allow the precipitate to digest at room temperature for about 30 min.

Step 12. Filter the cobalt mercurithiocyanate precipitate through a previously weighed filter paper disc in a Hirsch funnel. Wash with 10 ml of $0{\cdot}01M$ ammonium mercurithiocyanate solution followed by 5 ml of 95% ethyl alcohol. Dry the precipitate and filter paper disc in a drying oven for about 30 min at 110°. Cool in a desiccator, weigh, then count in a well-type scintillation counter.

Testing the procedure for separation of foreign activities.

The above procedure was tested to determine its efficiency in separating radioactive cobalt from other activities. Two samples were analysed which did not contain any radioactive cobalt, but which

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* This solution should be prepared immediately before use by adding solid potassium nitrite to 10 ml of $3M$ acetic acid until some solid remains undissolved.

did contain the following counts per min (γ) of other activities: $1{\cdot}5 \times 10^4$ cpm ^{134}Cs, $8{\cdot}0 \times 10^4$ cpm ^{95}Zr —^{95}Nb, $1{\cdot}1 \times 10^4$ cpm ^{131}I, $15{\cdot}0 \times 10^4$ cpm ^{144}Ce —^{144}Pr, and $15{\cdot}7 \times 10^4$ cpm ^{106}Ru —^{106}Rh. With both samples less than 40 cpm were recovered after correction for carrier yield. The procedure, therefore, gives successful decontamination from these activities.

Testing the procedure for recovery of cobalt activity.

Several samples containing a known amount of ^{60}Co were analysed in order to obtain statistics concerning the accuracy and precision of the method. Table IV summarises the results of these determinations.

TABLE IV. DETERMINATION OF RADIOACTIVE COBALT

Sample*	Gravimetric yield, %	Observed counts, *cpm*	Counts corrected for yield, *cpm*	Recovery, %
1	76·79	3561	4626	100·0
2	79·48	2651	4593	99·3
3	80·41	3710	4614	99·8
4	76·79	3426	4462	96·5
5†	62·05	2848	4590	99·2
6†	52·74	2491	4724	102·1

* 20·42 mg of cobalt carrier and 4625 cpm of ^{60}Co were added to each sample.

† Two scavenging steps with palladium chloride and copper$^{\mathrm{II}}$ chloride carriers were performed on these samples using H_2S gas. This accounts for the lower gravimetric yields of these samples.

Zusammenfassung—Eine detaillierte Beschreibung der Trennung Von Radiokobalt von anderem aktiven Material wird mitgeteilt. Die Fällung als Quecksilberthiocyanate wird der als Anthranilat vorgezogen. Das Kobalt wird in der Quecksilberverbindung gezahlt.

Résumé—Les auteurs donnent une méthode détaillée de séparation chimique du radio-cobalt des autres radio éléments. La précipitation à l'état de mercurithiocyanate est préférée à la précipitation à l'état d'anthranilate, et le cobalt est finalement dosé par comptage sous forme de mercurithiocyanate

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SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF OSMIUM—I*

EXTRACTION AND ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM TETROXIDE

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Summary—An ultraviolet spectrophotometric method is presented for the determination of milligram quantities of osmium in solutions of uranyl sulphate. Osmium is first oxidised to the octovalent state and the osmium tetroxide which is formed, is selectively extracted with chloroform. The ultraviolet absorption spectrum of osmium tetroxide in chloroform has a series of absorption bands with peak absorbancies at 282, 289, 297, 304 and 312 mμ and molar absorbancy indexes of 1870, 1760, 1640, 1400 and 1000, respectively. For each wavelength, the optimum concentration range for the determination of osmium was evaluated. From 0·4 to 3·3 mg of osmium can be determined with a coefficient of variation of 3%. Of the elements tested only chloride and octovalent ruthenium interfere; however, both of these interferences can be eliminated.

METHODS were desired for the determination of milligram and microgram quantities of osmium in solutions of uranyl sulphate which contain copper, nickel, iron, and chromium as minor components. The existing methods[4] are not sufficiently selective for the direct determination of osmium without a prior separation. Moreover, osmium can exist in solution in many different valency states and therefore, a further problem was that of obtaining all of the osmium in a single valency state. Accordingly, an extremely selective separation procedure suggested by Sauerbrunn and Sandell[5] was tested whereby osmium is oxidised to the octovalent state and the osmium tetroxide which is formed, is then extracted with chloroform. In the work presented in this paper the osmium is determined by measuring the ultraviolet absorbancy of the extracted osmium tetroxide. Although the ultraviolet absorption spectrum of osmium tetroxide in organic solvents has been previously reported in studies of the vibrational frequencies of the osmium tetroxide molecule,[1] the absorbancy of osmium tetroxide has not been utilised previously for analytical purposes.

In a second method[7] the osmium is oxidised and extracted as before, then the extract is added to an ethanolic solution of 1:5-diphenylcarbohydrazide and a blue-violet coloured complex is formed. This method is also extremely selective for osmium and is about 15 times more sensitive than the method described here.

A further method[8] involves the formation of the osmium complex with 1:5-diphenylcarbohydrazide in an aqueous medium rather than in the organic extract.

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The complex is then extracted with chloroform and the absorbancy of the extract is measured. Although this method is not as selective for osmium as the two previously described methods, it provides an extremely sensitive means of determining osmium. The molar absorbancy index is about 150,000.

EXPERIMENTAL

Reagents

Osmium tetroxide, 0·38 mg of osmium per ml, in 0·1M sulphuric acid: A vial containing 0·5 g of osmium tetroxide was broken under 500 ml of 0·1M sulphuric acid. After the osmium tetroxide had dissolved completely, the solution was filtered into a 1-litre volumetric flask and diluted to volume with 0·1M sulphuric acid. This solution was standardised by the gravimetric benzotriazole method.[6] More dilute osmium solutions were prepared by appropriate dilution of the standard solution.

Apparatus

Beckman Model DU spectrophotometer, equipped with ultraviolet accessories.

Procedure

Transfer a sample aliquot which contains between 0·4 and 3·3 mg of osmium to a 60-ml separatory funnel. If the osmium is not in the octovalent state, dilute to 5 ml with 6N sulphuric acid and oxidise the osmium by the dropwise addition of a 5% potassium permanganate solution until a permanent pink colour persists. Discharge the pink colour with a few drops of a 2% ferrous ammonium sulphate solution. Immediately add 3 ml of 15M nitric acid and 2 ml of water and extract the osmium tetroxide with two 10-ml portions of chloroform. Drain the extracts into a second 60-ml separatory funnel which contains 10 ml of 0·1M sulphuric acid, and wash to remove any traces of nitric acid. Drain the chloroform phase into a 25-ml volumetric flask containing about 1 g of anhydrous sodium sulphate and dilute to volume with chloroform. Measure the absorbancy of the solution against a chloroform blank at the appropriate wavelength using 1-cm cells.

Prepare a calibration curve by adjusting suitable aliquots of a standard osmium tetroxide solution to a 10-ml volume containing 30 volume per cent of nitric acid and extracting them by the same procedure. The oxidation step is not necessary.

RESULTS AND DISCUSSION

Oxidation and extraction of osmium tetroxide

These procedures are essentially the same as those proposed by Sauerbrunn and Sandell[5] and they are discussed by Sandell.[4] Since osmium is extracted from a nitric acid solution, many elements besides osmium can also be extracted if the solvent is polar and has an oxygen-containing functional group.[2] Therefore a nonpolar solvent is necessary for the selective extraction of osmium. The distribution ratio of osmium tetroxide into chloroform is slightly greater than into carbon tetrachloride. More than 99% of the osmium is extracted into the chloroform phase.

Ultraviolet absorption spectrum of osmium tetroxide

The absorption spectrum of osmium tetroxide in chloroform (Fig. 1) exhibits the same features as the spectra previously reported in carbon tetrachloride and in hexane.[1] Above 320 mμ the absorbancy of the osmium tetroxide solution is very small. Below 260 mμ the absorbancy increases rapidly. However, the absorbancy of the chloroform blank also becomes appreciable below 260 mμ.

Adherence to Beer's law

Calibration data for the determination of osmium were obtained for the 5 absorption bands which centre at 282, 289, 297, 304 and 312 mμ. The molar absorbancy indexes are presented in Table I.

The absorbancies at all of the wavelengths adhere to Beer's law. In addition, the optimum concentration range for the determination of osmium was evaluated for each wavelength by the method of Ringbom[3] and these are shown in Table I. A range of from 0·4 to 3·3 mg of osmium can be determined by proper choice of the wavelength, with a coefficient of variation of about 3%.

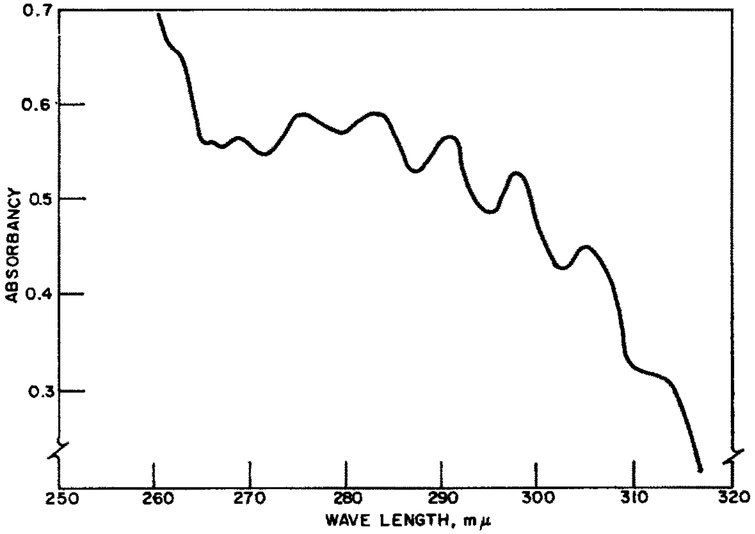

FIG. 1.—Ultraviolet absorption spectrum of osmium tetroxide in chloroform
Osmium, M, $3{\cdot}20 \times 10^{-4}$
Cells, cm, 1

Effect of foreign substances

The effect of various cations and anions was evaluated by treating solutions containing 1·14 mg of osmium and the foreign substance to be tested by the recommended procedure. The results of these tests are shown in Table II.

Neither the uranyl ion nor the other cations which are normally found as minor components in uranyl sulphate solutions—iron^{III}, copper^{II}, nickel,^{II} chromium^{VI}—interfere appreciably in the determination of osmium. When more than 500 mg of chromium^{VI} was present high results were obtained. The platinum group elements, in their lower valency states, do not interfere. Ruthenium in the octovalent state is

TABLE I—DATA FOR THE ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

Wavelength, mμ	Molar absorbancy index	*Optimum concentration range*[a]	
		$M \times 10^4$	*mg/25 ml*
282	1870	0·8 – 3·7	0·4 – 1·8
289	1760	0·9 – 4·0	0·4 – 1·9
297	1640	0·9 – 4·3	0·5 – 2·0
304	1400	1·1 – 5·0	0·5 – 2·4
312	1000	1·5 – 7·0	0·7 – 3·3

[a] 1-cm cell

TABLE II.—EFFECT OF FOREIGN SUBSTANCES

Conditions:	Volume, ml	25
	Wavelength, mμ	289
	Cells, cm	1
	Osmium, mg	1·14

Foreign substance		Osmium, *mg*	
Element	*mg*	Found	Error
U^{VI}	1000	1·19	0·05
Fe^{III}	1000	1·22	0·08
Ni^{II}	1000	1·18	0·04
Cu^{II}	1000	1·19	0·05
Th^{IV}	500	1·17	0·03
Cr^{VI}	500	1·19	0·05
Cr^{III}	500	1·16	0·02
Mo^{VI}	500	1·14	0·00
Pd^{II}	6	1·20	0·06
Au^{III}	5	1·12	−0·02
Rh^{III}	2	1·10	−0·04
Pt^{II}	2	1·17	0·03
Ir^{III}	1	1·16	0·02
Ru^{III}	1	1·19	0·05

an interference since ruthenium tetroxide extracts along with osmium tetroxide[4] and has a similar absorption spectrum.[1] However, osmium can be separated from ruthenium by a modification of the extraction procedure.[4] Of the anions which were tested, perchlorate, sulphate and phosphate did not interfere. When the osmium was initially in a reduced state in the presence of chloride, low results were obtained, since chloride forms complex ions with osmium^{IV} and ^{VI} and inhibits the complete oxidation and subsequent extraction of osmium.[4] For this application, however, the chloride concentration in uranyl sulphate sample solutions is very small and therefore, chloride interference is not significant.

CONCLUSION

The recommended procedure provides a simple and rapid method for the determination of milligram amounts of osmium in solutions of uranyl sulphate. This method is probably applicable to many other types of sample solutions. Of the elements tested only chloride and octovalent ruthenium were found to interfere; however, procedures are available for elimination of both of these interferences.[4]

Acknowledgments—The authors acknowledge the assistance of H. P. House and M. A. Marler in the preparation of this manuscript.

This work was abstracted from a thesis submitted by Gerald Goldstein in partial fulfillment of the requirements for the degree of Master of Science, 1959

Zusammenfassung—Eine uv-spektrophotometrische Methode zur Bestimmung von Milligrammengen Osmium in Uranylsulfatlosungen wird beschrieben. Osmium wird erst in die achtwertige Oxydationstufe gebracht und das Osmiumtetroxyd selektiv mittels Chloroform ausgezogen. Das UV-Spektrum von Osmiumtetroxyd hat mehrere Absorptionsmaxima: 282, 289, 297, 304 und 312 mμ mit den dazugehörigen Absorptionskoeffizienten von 1870, 1760, 1640, 1400 und 1000. Fur jede der genannten

Wellenlängen wurde der optimale Konzentrationsbereich ermittelt. Für Mengen von 0·4–3·3 mg kann die Bestimmung mit einem Variationskoeffizienten von 3 % ausgeführt werden. Von den untersuchten Ionen stören nur Ruthenium(III) und Chloride, jedoch sind diese Störungen auszuschaltbar.

Résumé—Les auteurs présentent une méthode spectrophotométrique ultra-violette de dosage de quantités d'osmium de l'ordre du milligramme en solution de sulfate d'uranyle. L'osmium est d'abord oxydé à l'état octavalent, et le tétroxyde d'osmium formé est extrait sélectivement par le chloroforme. Le spectre ultra-violet du tétroxyde d'osmium dans le chloroforme a une série de bandes d'absorption avec des maxima à 282, 289, 297, 304 et 312 mμ, et des coefficients d'extinction molaires de 1870, 1760, 1640, 1400 et 1000 respectivement Pour chaque longueur d'onde, le domaine de concentration le meilleur pour le dosage de l'osmium a été évalué. De 0.4 à 3,3 mg d'osmium peuvent être dosés avec un coefficient de variation de 3 pour cent. Parmi les éléments essayés, seuls le chlorure et le ruthénium octavalent gênent; ces deux interférences peuvent cependant être élimineés.

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SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF OSMIUM—II*

EXTRACTION AND DETERMINATION OF OSMIUM *IN SITU* WITH 1·5-DIPHENYLCARBOHYDRAZIDE

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Summary—A method has been developed for the spectrophotometric determination of microgram quantities of osmium in uranyl sulphate solutions. The osmium is oxidised to osmium tetroxide, then extracted with chloroform. The extracts are added to an ethanolic solution of 1:5-diphenylcarbohydrazide. A blue-violet coloured reaction product is formed which exhibits maximum absorbancy at 560 mμ. After a period of 2 hr for colour development the molar absorbancy index is about 31,000. Beer's law is adhered to over a range of 30 to 100 μg of osmium with a coefficient of variation of about 4%. A study was made of the effects of foreign substances and only chloride and octovalent ruthenium were found to interfere. Both of these interfering ions can be eliminated.

THE previously reported method[2] for the determination of osmium by extraction of osmium tetroxide and measurement of its ultraviolet absorbancy was suitable for milligram quantities of osmium. Since it was also necessary to determine microgram quantities, a survey was made of various chromogenic reagents to determine if any would react with osmium tetroxide in chloroform to form a coloured product and provide a more sensitive method. It was desirable for the chromogenic reagent to react with the osmium tetroxide in the chloroform phase because of the selectivity of the extraction procedure. It was found that 1:5-diphenylcarbohydrazide (DPC) reacted to give a blue-violet coloured product.

EXPERIMENTAL

Reagents

Osmium tetroxide, 12 μ*g of osmium per ml:* Prepared as previously described.[2]

1:5-*Diphenylcarbohydrazide* (sym-*diphenylcarbazide; DPC*), 0·2%, *in ethanol:* Dissolve 100 mg of the reagent in 50 ml of ethanol. This reagent is not stable and should be prepared freshly each day.[1]

Apparatus

Beckman Model DU spectrophotometer.

Procedure

Transfer a sample aliquot, containing from 30 to 100 μg of osmium, to a 60-ml separatory funnel. Oxidise, extract, and wash the osmium as previously described.[2] Drain the washed extract into a 25-ml

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volumetric flask containing 5 ml of 0.2% DPC and about 1 g of anhydrous sodium sulphate and, if necessary, dilute to volume with additional chloroform. After a 2-hr colour-development period, measure the absorbancy of the solution at 560 mμ *vs.* a reagent blank, using 1-cm cells.

Prepare a calibration curve by carrying aliquots of a standard osmium tetroxide solution through the procedure. The oxidation step is not necessary in this case.

RESULTS AND DISCUSSION

Absorption spectrum of the osmium-DPC complex

The absorption spectrum of the product of the reaction between osmium tetroxide and DPC (Fig. 1) was obtained by treating 48 μg of osmium by the recommended procedure and measuring the absorbancy *vs.* a reagent blank. There is a broad absorption band between 500 and 600 mμ with peak absorbancy at about 560 mμ. Since freshly prepared DPC reagent does not absorb appreciably between 400 and 700 mμ, its spectrum is not shown.

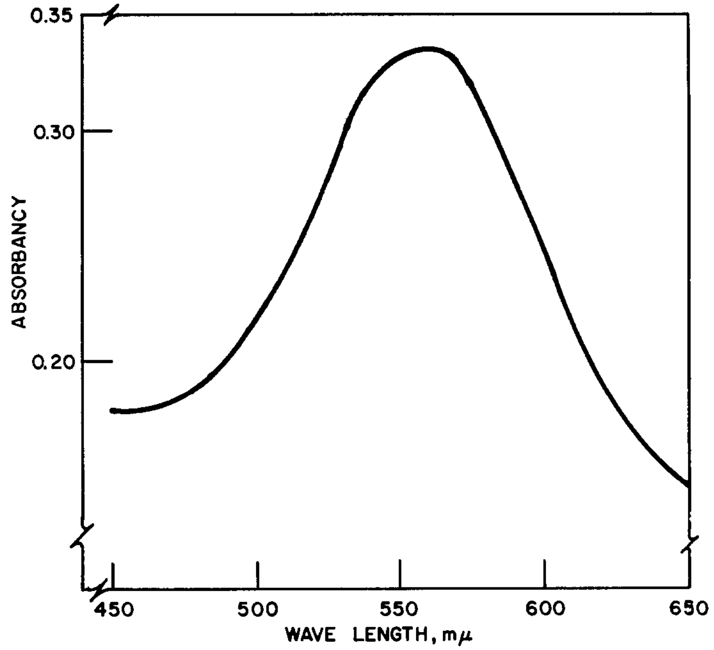

FIG. 1.—Absorption spectrum of the osmium-DPC complex formed in a chloroform medium.

Volume, ml	25
DPC, 0·2%, ml	5
Osmium, μg	48
Colour development	
Time, hr	2
Cells, cm	1

Effect of DPC reagent concentration

Tests were made of the reagent concentration necessary to produce maximum absorbancy by adding extracts containing 96 μg of osmium to various amounts of DPC reagent. From the results, which are shown in Fig. 2, it is indicated that 3 ml of 0·2% DPC in the final 25-ml volume is sufficient for complete colour development. To assure an adequate excess of reagent, however, a 5-ml volume was utilised. This represents approximately an 80:1 molar ratio of reagent to osmium.

Effect of DPC reagent solvent

The DPC reagent can be dissolved in numerous solvents and the effect of several of these on the absorbancy of osmium-DPC solution was tested. A discussion of the solubility and stability of DPC in various solvents is given by Allen.[1] When methanol or acetic acid was utilised as the solvent instead of ethanol, higher absorbancy values were obtained; however, the reproducibility of the measurements was poor. An acetone solution of the reagent gave about the same result as an ethanol solution.

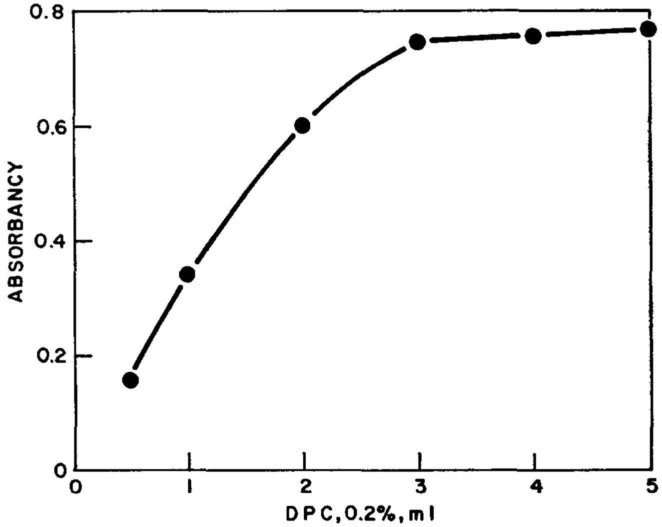

FIG. 2.—Effect of DPC reagent concentration

Volume, ml	25
Osmium, μg	96
Wavelength, mμ	560

The effect of the ethanol concentration was also investigated and it was established that the absorbancies are constant when between 1 and 5 ml of ethanol are present.

Time of colour development

Fig. 3 shows the absorbancy as a function of time, of a typical final solution obtained by treating a solution containing 48 μg of osmium by the recommended procedure. Although the absorbancy increased continually over a period of at least 24 hr, the rate of increase was small after the first hr. For instance, between 30 and 60 min the absorbancies increased by about 5%, between 60 and 120 min by about 3%, and between 120 and 180 min by about 1%. Therefore, within reasonable limits, the time of colour development is not a critical factor for reproducible measurements after the first 2 hr, even though the maximum absorbancy has not yet been attained.

Attempts were made to increase the rate of colour development but these were unsuccessful. When the organic extracts were heated, erratic results were obtained. In some cases the DPC reagent was apparently oxidised, giving the solutions a deep red colour, and in other cases the solutions were completely decolorised.

Order of addition of reagents

The order of addition of the reagents also affected the colour development. If the reagent was added to the extracts, initial absorbancies were very low and the absorbancy increased gradually over a period of about 3 days. Therefore, it is important to add first the reagent solution to the volumetric flasks, then to drain the extracts into the reagent.

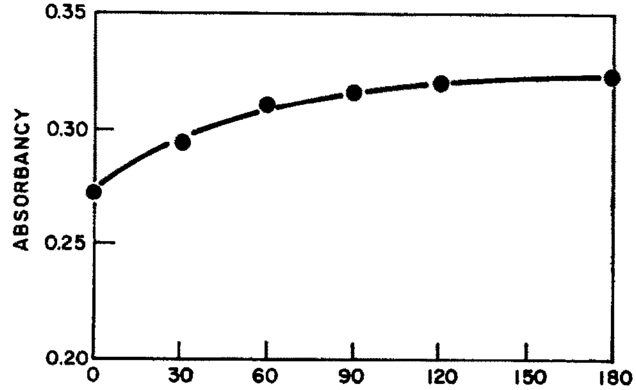

FIG. 3.—Effect of time of colour development

Volume, ml	25
Osmium, μg	48
DPC, 0·2%, ml	5
Wavelength, mμ	560

Adherence to Beer's law

Five calibration curves were prepared on separate days by the recommended procedure (Table I).

TABLE I.— ADHERENCE OF ABSORBANCY OF OSMIUM-DPC SOLUTIONS TO BEER'S LAW

Conditions:		
	Volume, ml	25
	DPC, 0·2%, ml	5
	Colour-development time, hr	2
	Wavelength, mμ	560
	Cells, cm	1

Osmium, μg	Absorbancy for different series					Average
	I	II	III	IV	V	
12	0·079	0·082	0·080	0·079	0·078	0·080
24	0·162	0·165	0·151	0·164	0·173	0·163
48	0·322	0·314	0·300	0·329	0·342	0·321
72	0·462	0·440	0·450	0·473	0·470	0·459
96	0·615	0·592	0·611	0·650	0·642	0·622
Molar absorbancy index	30,900	30,100	30,400	31,900	32,300	31,300
Coefficient of variation, %	2	6	3	2	5	3

Statistical analysis of the five sets of data showed that there was no significant difference in the molar absorbancy indexes or the coefficients of variation. In no case was the coefficient of variation more than 6%; the average was 3%. The optimum range for the determination of osmium, evaluated by the Ringbom method,[3] is from 30 to 100 µg, in the sample taken for analysis, with a coefficient of variation over this range of about 4%.

Experiments to determine the mole ratio of DPC to osmium in the complex were unsuccessful because of the difficulty in obtaining maximum absorbancy values, and because of the varying rate of colour development when the ratio of DPC to osmium was varied.

Effect of foreign substances

The effect of various elements was evaluated by treating solutions which contained 38 µg of osmium and the appropriate quantity of the foreign substance by the recommended procedure. These results are presented in Table II. The elements commonly found in uranyl sulphate solutions do not interfere in the determination of osmium.

TABLE II.—EFFECT OF FOREIGN SUBSTANCES ON THE DETERMINATION OF OSMIUM

Foreign Substance		Osmium, µg[a]	
Element	*mg*	Found	Error
$\mathrm{U^{VI}}$	500	38·7	0·7
$\mathrm{Th^{IV}}$	500	40·0	2·0
$\mathrm{Fe^{III}}$	1	39·9	1·9
$\mathrm{Cr^{VI}}$	1	38·5	0·5
$\mathrm{Cr^{III}}$	1	39·7	1·7
$\mathrm{Ni^{II}}$	1	40·3	2·3
$\mathrm{Cu^{II}}$	1	39·9	1·9
$\mathrm{Co^{II}}$	1	38·2	0·2
$\mathrm{Mo^{VI}}$	1	37·6	−0·4
$\mathrm{Zr^{IV}}$	1	38·8	0·8
$\mathrm{Au^{III}}$	1	39·0	1·0
$\mathrm{Pt^{II}}$	1	39·3	1·3
$\mathrm{Pd^{II}}$	1	38·7	0·7
$\mathrm{Ir^{III}}$	1	37·1	−0·9
$\mathrm{Rh^{III}}$	1	37·9	−0·1
$\mathrm{Ru^{III}}$	1	38·8	0·8
$\mathrm{Ru^{VIII}}$	0·3	49·3	11·3

[a] 38·0 µg present.

Accurate results were obtained even in the presence of 500-mg quantities of uranium and thorium. Of the platinum group metals, only ruthenium$^{\mathrm{VIII}}$ interferes and does so because ruthenium tetroxide is co-extracted with osmium tetroxide[4] and reacts with the DPC reagent to give a violet coloured product. Although it is possible that some of the other elements tested will react with DPC, the extraction procedure selectively separates the osmium. Of the common anions, perchlorate, sulphate and phosphate do not interfere, while chloride hinders the complete extraction of osmium. The interference of both ruthenium^{VIII} and chloride can be eliminated.[4]

CONCLUSION

The procedure presented here is a rapid, selective, and reasonably precise method for the determination of osmium. In addition, the molar absorbancy index of the final solution is about 31,000 so that the sensitivity of this method is 15 times that previously obtained,[2] and about 10 times the sensitivity of the conventional thiourea method.[4]

Since this method also involves the oxidation and extraction of osmium, the discussion of these procedures in the previous paper[2] also applies here.

Acknowledgment—The authors acknowledge the assistance of H. P. House and M. A. Marler in the preparation of this manuscript.

This work was abstracted from a thesis submitted by Gerald Goldstein in partial fulfillment of the requirements for the degree of Master of Science, 1959.

Zusammenfassung—Eine Methode zur Bestimmung von Osmium in Uranylsulfatlösungen wurde entwickelt. Osmium wird erst zur achtwertigen Stufe oxydiert und das Osmiumtetroxyd mit Chloroform ausgezogen. Der Chloroformextrakt wird einer alkoholischen Lösung von 1,5 Diphenylcarbohydrazid zugesetzt. Ein blauviolett gefärbtes Produkt wird gebildet, mit einem Absorptionsmaximum bei 560 mμ. Nach zweistündiger Farbentwicklung beträgt der Absorptionskoeffizient 31000. Für Mengen von 30–100 μg wird Beer's Gesetz befolgt. Die einzigen Störungen werden durch Chlorid und Ruthenium (VIII) verursacht, können jedoch behoben werden.

Résumé—Les auteurs ont développé une méthode de dosage spectrophotométrique de quantités d'osmium de l'ordre du microgramme dans des solutions de sulfate d'uranyle. L'osmium est oxydé en tétroxyde d'osmium et ensuite extrait par le chloroforme. Les extraits sont ensuite ajoutés à une solution éthanolique de 1-5-diphénylcarbohydrazide. Un produit de la réaction bleu violet est formé, il présente un maximum d'absorption à 560 mu. Après une période de 2 heures pour le développement de la couleur, le coefficient d'extinction molaire est environ 31000. La loi de Beer est suivie dans le domaine de 30 μg à 100 μg d'osmium avec un coefficient de variation d'environ 4 pour cent. Une étude des effets des substances étrangères a été faite, et seuls le chlorure et le ruthénium octavalent ont été trouvés gênants. Ces deux interférences peuvent être éliminées.

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SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF OSMIUM—III*

REACTION OF OSMIUM TETROXIDE WITH 1:5-DIPHENYLCARBOHYDRAZIDE IN AQUEOUS SOLUTIONS FOLLOWED BY EXTRACTION OF THE COMPLEX

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Summary—A spectrophotometric method has been developed which is applicable to the determination of extremely small quantities of osmium. Osmium is oxidised to the octovalent state, then added to an acidic aqueous solution containing 1:5-diphenylcarbohydrazide (DPC). After heating the aqueous solution to 65°, the osmium-DPC complex is extracted with chloroform. A molar absorbancy index of about 150,000 is obtained. From 7 to 25 μg of osmium can be determined with a coefficient of variation of 6%. It was established that Fe^{III}, Cu^{II}, Ru^{III} and Au^{III} seriously interfere in the determination of osmium by this method, while Cr^{VI}, Ni^{II}, Mo^{VI}, Ir^{III} and chloride interfere only when present in relatively high concentrations.

IN previous work on the determination of osmium with 1:5-diphenylcarbohydrazide (DPC), osmium tetroxide was extracted with chloroform and added to the DPC reagent.[2] Under these conditions a molar absorbancy index of about 31,000 was obtained. From preliminary experiments it was observed that when the DPC was added to aqueous solutions containing octovalent osmium, a blue-violet compound was formed which could be extracted with chloroform. The intensity of the colour of the extract was much greater than the colour intensity of the aqueous solution. It appeared that much greater sensitivity could be obtained by adding the DPC reagent to the aqueous osmium tetroxide solutions, then extracting the complex, rather than adding the DPC to the osmium which had been extracted into chloroform.

EXPERIMENTAL

Reagents

Osmium tetroxide, 5 μg of osmium per ml: Prepared as described previously.[1]

1:5-Diphenylcarbohydrazide (sym-diphenylcarbazide, DPC), 0·2%: Prepared as described previously.[2]

Apparatus

Beckman Model DU spectrophotometer.

Procedure

Transfer a sample aliquot which contains between 7 and 25 μg of osmium, as osmium tetroxide, to a 50-ml beaker containing 2·5 ml of perchloric acid, 2 ml of glacial acetic acid, and 3 ml of 0·2%

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* Work carried out under Contract No. W-7405-eng-26 at Oak Ridge National Laboratory, operated by Union Carbide Nuclear Co., division of Union Carbide Corp., for the Atomic Energy Commission.

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DPC. Dilute to exactly 25 ml. Heat the solution to 65° over a period of about 5 min, then allow it to cool to room temperature. Transfer the solution to a 60-ml separatory funnel and extract with two 10-ml portions of chloroform. Drain the extracts into a 25-ml volumetric flask which contains about 1 g of anhydrous sodium sulphate, and dilute to volume with chloroform. Measure the absorbancy at 560 mμ *vs.* a reagent blank, using 1-cm cells.

Prepare a calibration curve by treating suitable aliquots of a standard osmium tetroxide solution by the same procedure.

RESULTS AND DISCUSSION

Absorption spectrum of the osmium-DPC extract

The absorption spectrum of the osmium-DPC complex formed in an aqueous medium and then extracted is shown in Fig. 1. Compared with the spectrum of the complex formed in a chloroform medium,[2] the two spectra show the same general features. There is a broad absorption band between 500 and 600 mμ, with maximum absorbancy at 560 mμ. However, the absorption at 560 mμ is much higher when the complex is extracted with chloroform rather than formed in the chloroform solution, and the absorbancies at wavelengths below 500 mμ and above 600 mμ are lower. All further measurements were made at 560 mμ.

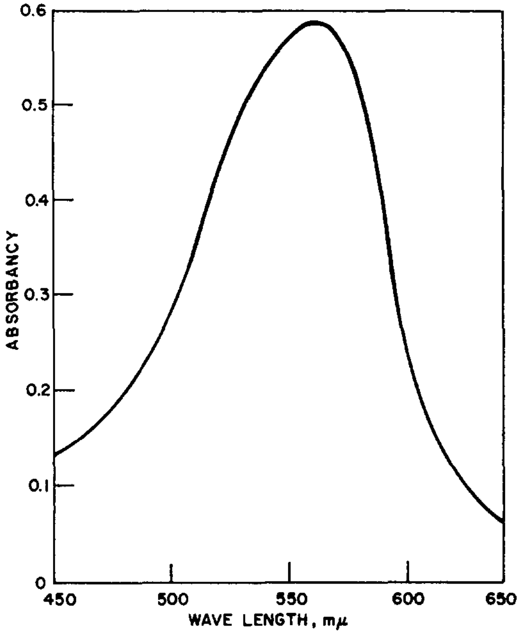

Fig. 1.—Absorption spectrum of the osmium-DPC complex extracted with chloroform from an aqueous medium.

Volume, ml	25
DPC, 0·2%, ml	3
Osmium, μg	19
Cells, cm	1

Organic extractant

Several solvents besides chloroform were tested for the extraction of the osmium-DPC complex. The absorbancy of the extracts at 560 mμ was essentially the same when either chloroform, carbon tetrachloride, or xylene was utilised as the extractant. Lower absorbancies were obtained with bromobenzene, *iso*amyl alcohol, and *iso*amyl acetate, and only a very small absorbancy was observed with methyl *iso*butyl ketone.

Since the extractions were performed with two successive portions of the solvent, the efficiency with which each solvent extracted the osmium-DPC complex could be compared by noting the intensity of the colour in the second extract. In this respect, chloroform was clearly a more efficient extractant than either carbon tetrachloride or xylene, for the second chloroform extract was almost colourless while the second carbon tetrachloride and xylene extracts were substantially coloured. The absorbancies of the reagent blank extracts were about the same in all cases.

Effect of time and temperature

When the osmium-DPC complex is formed in an aqueous solution, then extracted with chloroform, the final absorbancy depends on the temperature of the aqueous solution and on two time factors: (1) the period of time for colour development in the aqueous phase, and (2) the period of time between the extraction of the complex into chloroform and the subsequent absorbancy measurement. Of the two time factors, the former was the more critical. The absorbancy of the extracts depends on the extent to which the osmium-DPC complex forms before the extraction. When the aqueous solutions were heated to 35°, or 50°, then cooled to room temperature, the

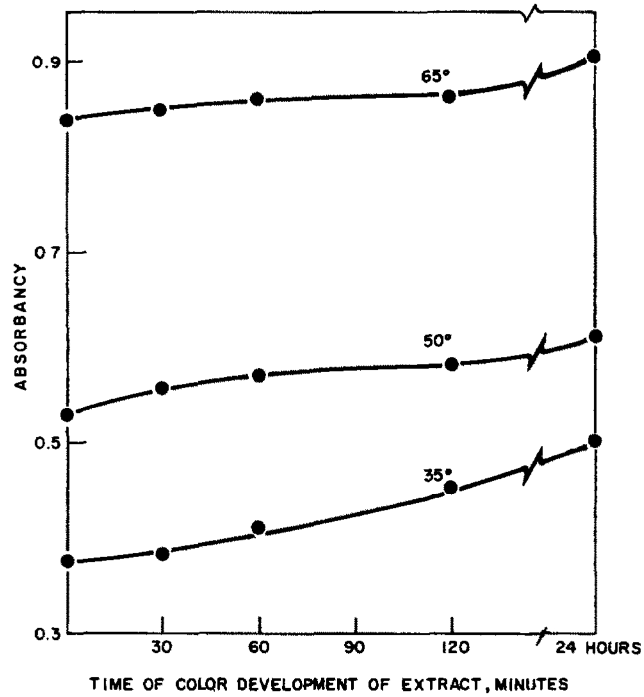

FIG. 2.—Effect of heating the aqueous solutions before extraction

Volume, ml	25
Osmium, μg	28
Wavelength, mμ	560

absorbancy of the extracts was not constant but depended on the time allowed for continuing colour development in the organic phase (Fig. 2). However, when the solutions were heated to 65° over a period of 5 min, and cooled to room temperature before the extraction, much higher absorbancies were obtained and the absorbancy remained reasonably constant. For example, the set heated to 65° exhibited an increase of about 8% over a period of 24 hr.

Although no specific tests were made, it is probable that maximum absorbancy can also be obtained by heating the aqueous solutions at a lower temperature for a longer period of time. At temperatures higher than 65°, there was some tendency for the reagent to oxidise.

Effect of perchloric acid concentration

The absorbancies of the chloroform extracts were found to depend on both the perchloric and the acetic acid concentrations of the aqueous phase as illustrated in Fig. 3. As the perchloric acid concentration was increased up to about 1*M*, the absorbancy also increased and became constant when the perchloric acid concentration was between 1 and 1·5*M*. Further increase in the perchloric acid concentration resulted in a change in the colour of the extracts from blue-violet to red-violet, and an increase in the absorbancy at 560 mμ. Similar results were obtained for all acetic acid concentrations. These absorbancy readings were not as dependent on the perchloric

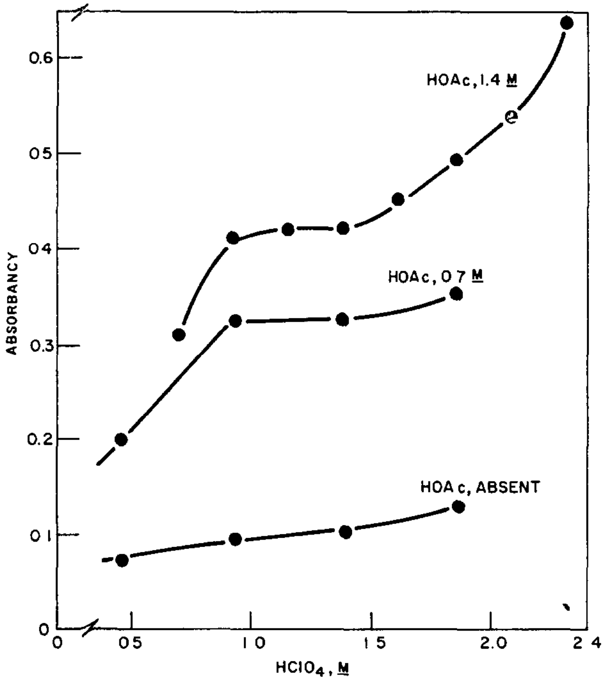

FIG. 3.—Effect of perchloric acid concentration

Volume, ml	25
DPC, 0·2%, ml	4
Osmium, μg	19
Wavelength, mμ	560

acid concentration when acetic acid was absent. The recommended concentration of perchloric acid is $1{\cdot}2 \pm 0{\cdot}1M$.

Effect of acetic acid concentration

The absorbancies of the extracts are increased by addition of acetic acid to the aqueous phase. The increase in absorbancy is almost linear with respect to the acetic acid concentration, and occurs at all perchloric acid concentrations (Fig. 4). The sensitivity of the method, therefore, can be increased by increasing the acetic acid concentration. On the other hand, small variations in the acetic acid concentration of the aqueous phase seriously affect the absorbancy of the extracts and, therefore, the acetic acid concentration must be carefully controlled. A concentration of $1{\cdot}4M$ was chosen for use in further work because this concentration is conveniently prepared and the molar absorbancy index of the extract is sufficiently high so that very small quantities of osmium can be determined.

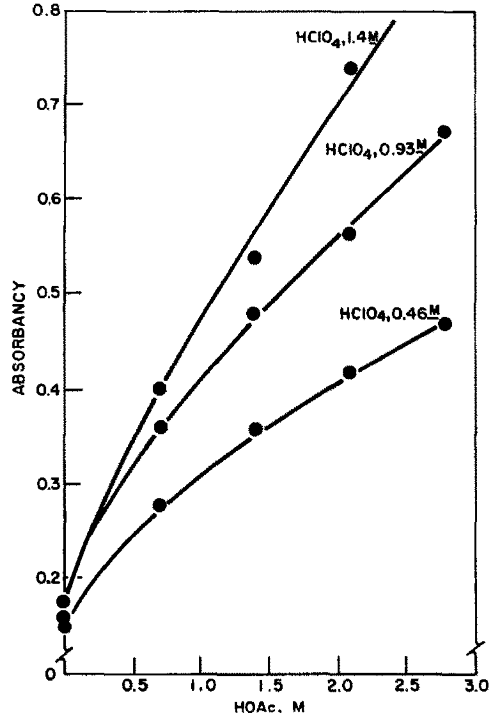

FIG. 4.—Effect of acetic acid concentration

Volume, ml	25
DPC, 0·2%, ml	4
Osmium, μg	19
Wavelength, mμ	560

Effect of reagent and ethanol concentrations

Both the concentration of the chromogenic reagent and ethanol affect the absorbancy. The two effects are interdependent. The effect of varying the DPC concentration at two levels of ethanol concentration is illustrated in Fig. 5. In both cases the absorbancy increases as the amount of DPC added is increased up to 6 mg, after which it decreases somewhat. The absorbancies are higher, however, when 2 ml of ethanol are present than when 5 ml are added, except in the case where 6 mg of DPC were present. This indication that the ethanol concentration affects the absorbancies at certain concentration levels of DPC was confirmed. The results in Fig. 6 show that when 6 mg of DPC are added the absorbancy does not vary with ethanol concentration. If, however, only 2 mg of DPC are added the absorbancy decreases with an increase in ethanol content.

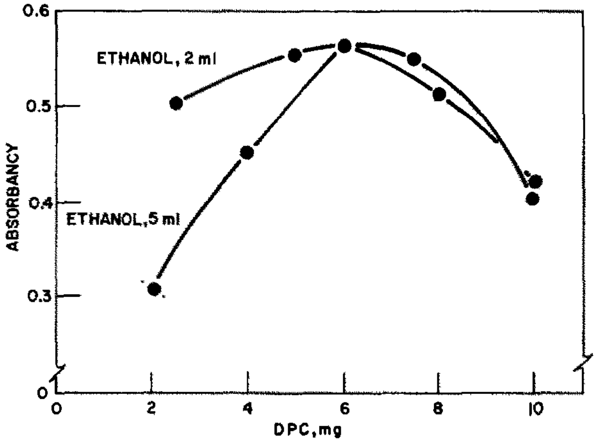

FIG. 5.—Effect of reagent concentration

Volume, ml	25
$HClO_4$, *M*	1·2
HOAc, *M*	1·4
Osmium, μg	19
Wavelength, mμ	560

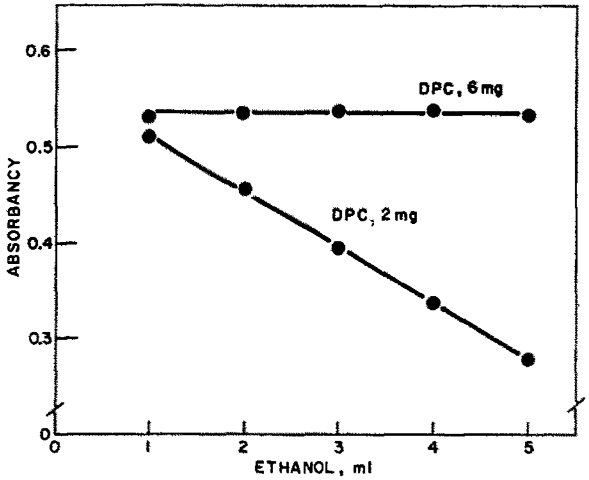

FIG. 6.—Effect of ethanol concentration

Volume, ml	25
$HClO_4$, *M*	1·2
HOAc, *M*	1·4
Osmium, μg	19
Wavelength, mμ	560

In general, the optimum quantity of reagent is 6 mg. At this concentration level, the absorbancy of the extracts is at a maximum and does not depend on the ethanol concentration. If higher or lower DPC concentrations are utilised, not only are the absorbancies smaller but they are also dependent on the quantity of ethanol present.

Adherence to Beer's law and effect of order of addition of reagents

The order of addition of the reagents to the aqueous solutions had a substantial effect on the absorbancies of the extracts. Table I shows calibration data obtained by three procedures: in *A* the order of addition of reagents was osmium, acids, DPC; in *B*, acids, osmium, DPC; and in *C*, acid, DPC, osmium. In each case the aqueous solutions were then heated and extracted as described in the recommended procedure. Absorbancies were highest when the osmium was added to acidic aqueous solutions containing the DPC reagent; somewhat lower absorbancies were observed when the osmium was added to the acidic solution before the DPC reagent; the lowest absorbancies were found when the acids and then the DPC were added to aqueous osmium solution. In all three cases the absorbancies adhered to Beer's law with a coefficient of variation of about 6%. No fading of colour was observed over a 24-hr period.

TABLE I.—ADHERENCE TO BEER'S LAW AND EFFECT OF ORDER OF ADDITION OF REAGENTS

Conditions:		
	Volume, ml	25
	$HClO_4$, *M*	1·2
	HOAc, *M*	1·4
	DPC, 0·2%, ml	3
	Wavelength, mμ	560
	Cells, cm	1

Osmium		Absorbancy		
		Order of reagent addition[a]		
μg	$M \times 10^6$	A	B	C
7·6	1·60	0·137	0·195	0·225
11·4	2·40	0·230	0·293	0·335
15·2	3·20	0·288	0·452	0·483
19·2	4·00	0·387	0·531	0·617
22·8	4·80	0·479	0·632	0·771
Molar absorbancy index		93,600	129,000	148,000
Coefficient of variation, %		6	6	6

[a] See text, p. 312.

To attain maximum sensitivity, therefore, the recommended procedure provides that the sample containing the osmium be added to an aqueous solution of proper acidity which contains the DPC reagent. The optimum concentration range for the determination of osmium by this procedure was evaluated by the method of Ringbom[4] and extends from 7 to 25 μg of osmium in the final 25-ml volume.

Effect of foreign substances

To determine whether other elements also produced coloured extracts, 1-mg quantities of various cations were treated by the recommended procedure. The effects of various anions were determined by preparing osmium tetroxide solutions containing 19 μg of osmium per ml in 0·1*M* hydrochloric acid, nitric acid, hydrofluoric acid and phosphoric acid, individually. After a period of 24 hr, 1-ml aliquots of these solutions were withdrawn and the osmium determined by the recommended procedure.

TABLE II.—EFFECT OF FOREIGN SUBSTANCES

Conditions:	Volume, ml	25
	$HClO_4$, *M*	1·2
	HOAc, *M*	1·4
	DPC, 0·2%, ml	3
	Wavelength, mμ	560
	Cells, cm	1

Foreign substance		Osmium, μg		Amount of substance (μg) equivalent to 1 μg of Os
Element(s)	*mg*	Present	Found	
U^{VI}, Th^{IV}, Cr^{III} Co^{II}, Ti^{IV}, Mn^{II} Cd^{II}, Zr^{IV}, La^{III} Pt^{II}, Pd^{II}, Rh^{III}	1	0	0	—
Fe^{III}	1	0	54	19
Cr^{VI}	1	0	6·6	150
Ni^{II}	1	0	3	330
Cu^{II}	1	0	14	70
Mo^{VI}	1	0	2·5	400
Ru^{III}	1	0	18	55
Ir^{III}	1	0	4	250
Au^{III}	1	0	25	40
Cl^-	[a]	19·0	12·8	—
NO_3^-	[a]	19·0	20·1	—
PO_4^{3-}	[a]	19·0	19·2	—
F^-	[a]	19·0	19·8	—

[a] 0·1*M*

The results of these tests are presented in Table II. The cations iron^{III}, chromium^{VI}, nickel^{II}, copper^{II}, molybdenum^{VI}, ruthenium^{III}, iridium^{III} and gold^{III} formed extractable complexes with DPC which would interfere in the determination of osmium. In the case of chromium^{VI} the aqueous solution was intensely red-violet in colour; however, the coloured complex was only partially extractable under these conditions. The other interfering elements produced a brown colour in the aqueous solutions, and red-violet extracts. Palladium^{II} produced yellow-coloured aqueous solutions and extracts which showed no absorbancy at 560 mμ.

Osmium was recovered completely in the presence of perchlorate, sulphate, phosphate, fluoride and nitrate. In the presence of chloride the absorbancies were significantly lower, which was probably due to the formation of osmium chloro-complexes which in turn prevented the complete reaction of osmium with the DPC.

CONCLUSION

The formation of the osmium-DPC complex in the aqueous phase, followed by its extraction with chloroform, provides an extremely sensitive means of determining osmium. With the exception of the catalytic method[3] the proposed procedure is by far the most sensitive means of determining osmium. The molar absorbancy index of 150,000 is 50 times greater than that of the thiourea complex and at least 5 times greater than in most other spectrophotometric methods.

Although it is necessary to sacrifice some of the selectivity for osmium which can be achieved through the extraction of osmium tetroxide, in order to obtain the greater sensitivity, the substances interfering in the determination are no more numerous than in most other methods and they are fewer than those which interfere with the catalytic method. Of the elements tested, iron$^{\mathrm{III}}$, copper$^{\mathrm{II}}$, ruthenium$^{\mathrm{III}}$ and gold$^{\mathrm{III}}$ interfere seriously while chromium$^{\mathrm{VI}}$, nickel$^{\mathrm{II}}$, molybdenum$^{\mathrm{VI}}$ and indium$^{\mathrm{III}}$ interfere only when the weight ratio of these elements to osmium is greater than 100:1. High concentrations of chloride (about $0{\cdot}1M$) prevent the complete formation of the complex.

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Zusammenfassung—Eine spektrophotometrische Bestimmung für extrem kleine Osmiummengen wurde entwickelt. Osmium wird zur achtwertigen Stufe oxydiert und die Lösung einer sauren wassrigen Lösung von 1,5-Diphenylcarbohydrazid zugesetzt. Nach Erwärmen auf 65°C wird der Osmium-DPC-Komplex mit Chloroform extrahiert. Ein molarer Extinktions Koefficient von etwa 150,000 resultiert. 7–25 μg Osmium Können mit einer Genauigkeit entsprechend einem Variationskoeffizienten von 3% bestimmt werden. Es wurde gefunden, dass Fe(III), Cu, Ru(III) und Au(III) sehr stark stören. Cr(VI), Ni, Mo(VI), Ir(III) und Chlorid stören nur, wenn in grösseren Konzentrationen anwesend.

Résumé—Les auteurs ont développé une méthode spectrophotométrique applicable au dosage de quantités d'osmium extrêmement faibles. L'osmium est oxydé à l'état octavalent et ensuite ajouté à une solution aqueuse acide contenant de la 1-5-diphénylcarbohydrazide. Après chauffage de la solution aqueuse à 65°, le complexe osmium-DPC est extrait par le chloroforme. Un coefficient d'extinction molaire d'environ 150 000 est obtenu. De 7 à 25 μg d'osmium peuvent être dosés avec un coefficient de variation de 6 pour cent. Les auteurs ont établi que Fe (III), Cu (II), Ru (III) et Au (III) gênent sérieusement dans le dosage de l'osmium par cette méthode, cependant que Cr (VI), Ni (II), Mo (VI), Ir (III) et Cl^- gênent seulement quand ils sont présents à des concentrations relativement grandes.

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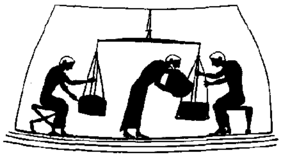

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