

An International Journal of Analytical Chemistry

ΤΑΛΑΝΤΑ

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**PERGAMON PRESS**

LONDON NEW YORK PARIS LOS ANGELES

VOLUME 7

NUMBERS 1/2

NOVEMBER-DECEMBER 1960

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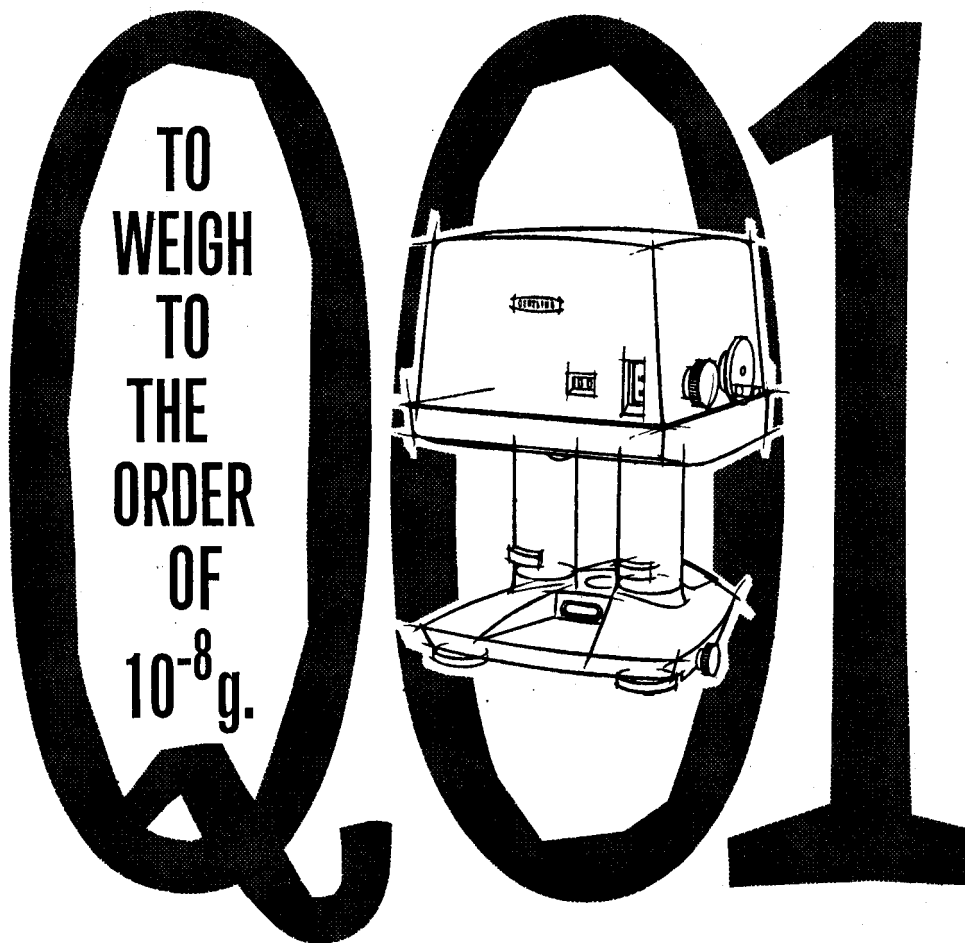
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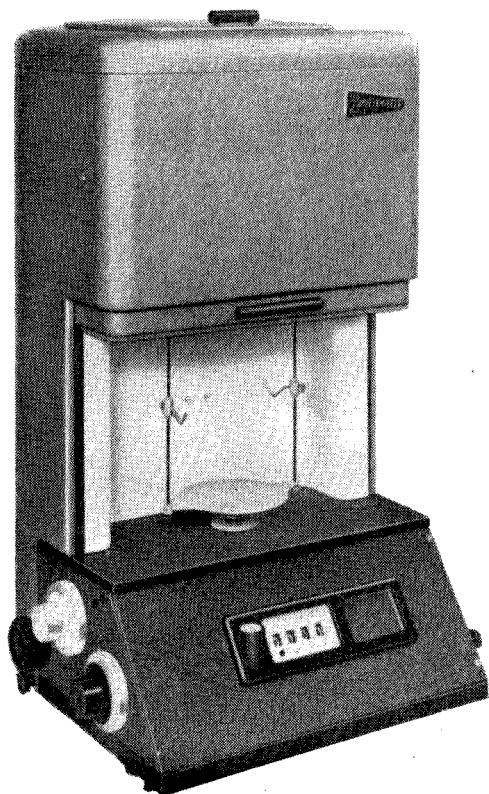
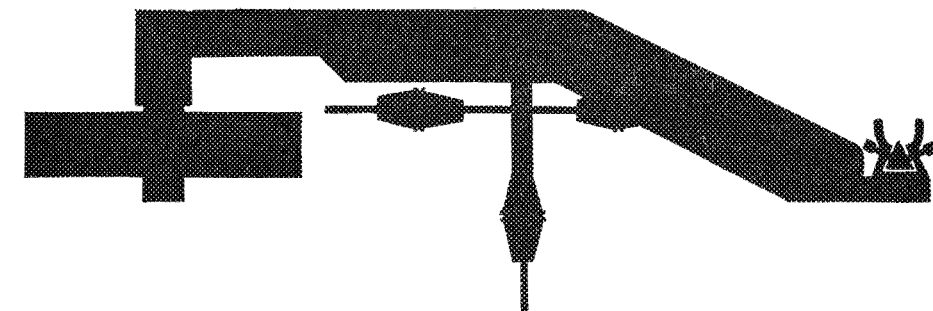
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# LIQUID-LIQUID EXTRACTION OF IRON<sup>III</sup> WITH TRIBUTYLPHOSPHATE

## SEPARATION FROM MIXTURES

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(Received 14 March 1960)

**Summary**—A method is presented for rapid solvent extraction of iron<sup>III</sup> 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<sup>III</sup> have been investigated. The extractable species are FeCl<sub>3</sub>·3TBP and H[FeCl<sub>4</sub>(TBP)<sub>2</sub>] 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.<sup>1,2</sup> But very little work has as yet been done on the extraction of common elements with TBP. Recently Musil and Weidmann<sup>3</sup> reported the separation of cobalt from nickel by extraction with TBP. Specker and Cremer<sup>4</sup> described the solvent extraction of iron<sup>III</sup> 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<sub>4</sub>(TBP)<sub>2</sub>] and from 4*M* acid, FeCl<sub>3</sub>·3TBP. The maximum partition coefficient value obtained from 9*M* hydrochloric acid was 9.27. Aven and Freiser<sup>5</sup> described the removal of iron interference in steel analysis by extraction of ferric thiocyanate with TBP. This work was extended by Melnick *et al.*<sup>6</sup> 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<sup>III</sup> 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<sup>III</sup> 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<sup>III</sup> 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.*<sup>7</sup>

\* Research Fellow, Council of Scientific and Industrial Research (India).

*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<sup>III</sup> 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<sup>III</sup> 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<sup>III</sup> was determined by direct dichromate titration.

## RESULTS AND DISCUSSION

*Effect of acidity*

The system was investigated at concentrations of hydrochloric acid in the range 0.25M–9.6M. The partition coefficients (*D*) were calculated from the concentration ratios:

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

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

The concentration of iron<sup>III</sup> in the organic phase was obtained by titration

TABLE I.—EXTRACTION OF IRON<sup>III</sup> AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION (Fe<sup>III</sup>, 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, <i>D</i>	0	0.22	2.77	9.42	32.33	34.34	34.34	70.4

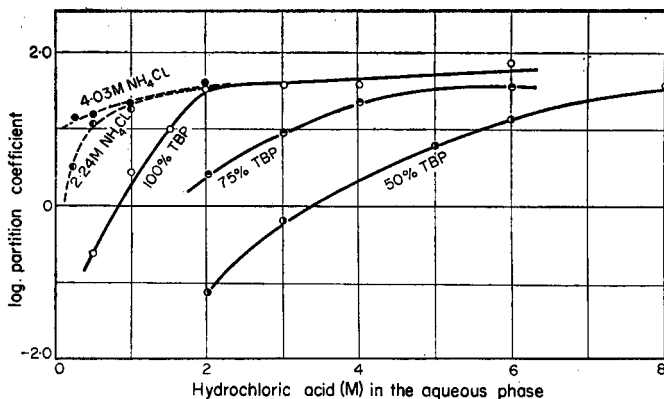


FIG. 1. Extraction of iron<sup>III</sup> with TBP as a function of hydrochloric acid concentration in the aqueous phase.

according to the general procedure; that in the aqueous phase was calculated by difference from the total amount of iron<sup>III</sup> taken. Extraction with 100% TBP starts from about 0.5M hydrochloric acid and becomes almost quantitative (>97%) from 1.92M 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<sup>III</sup> is possible from 3–6M hydrochloric acid. The maximum partition coefficient obtained was 70 (6M acid) which can be compared to the value 9.27 (9M acid) reported by Specker and Cremer.<sup>4</sup> 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 1M 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.*, 0.25M–0.5M, 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% (0.69M) to 75% (2.75M) 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  $\log D - \log C_{\text{TBP}}$  plot (Fig. 2). The best line through the points for 2M hydrochloric acid indicates a slope of 3.1 so that the species involved is  $\text{FeCl}_3 \cdot 3\text{TBP}$ ; whereas the plot at 6M acid corresponds to a slope of 1.7 giving the extractable species approximately as di-solvate, *viz.*,  $\text{H}[\text{FeCl}_4 \cdot (\text{TBP})_2]$ . Presumably at 2M hydrochloric acid the extraction system follows a limiting cube law which holds good up to 4M acid; and a limiting square law from 6M acid onwards. This result agrees fairly well with that of Specker and Cremer<sup>4</sup> who found a cube law at 4M acid and a square law at 7–9M acid.

In order to make Fig. 2B complete, a few runs were made with 30% TBP at 6M hydrochloric acid. The extraction was 55.7% giving  $D = 1.26$ . Extraction was negligible from 2M acid.

#### Diverse ions

The following ions were tested for interference (Table IV):  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Th}^{4+}$ ,  $\text{VO}_3^-$ ,  $\text{Mo}_7\text{O}_{24}^{6-}$ ,  $\text{PO}_4^{3-}$ , citrate, tartrate and EDTA. The aqueous phase in each case was maintained at 4M in hydrochloric acid.

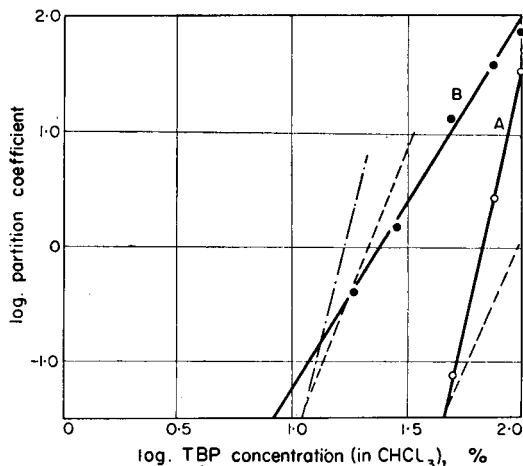


FIG. 2. Partition coefficient as a function of TBP concentration: A. Aqueous phase, 2M HCl. Line of slope 3.1 B. Aqueous phase, 6M HCl. Line of slope 1.7.

TABLE II.—SALTING-OUT AGENTS  
A. NH<sub>4</sub>Cl. Fe<sup>III</sup>, 23.07 mg; TBP, 100%

HCl, M	0.25			0.5			1.0			1.92	
NH <sub>4</sub> Cl, 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<sub>2</sub>·2H<sub>2</sub>O. Fe<sup>III</sup>, 23.07 mg; TBP, 100%

HCl, M	0.25	0.5	1.0
BaCl <sub>2</sub> ·2H <sub>2</sub> O, M	1.24	1.24	1.24
Extraction, %	83.2	88.6	93.4
Partition coefficient, D	4.95	7.77	14.16

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



TABLE III.—EXTRACTION AS A FUNCTION OF TBP CONCENTRATION.  
A. 19% TBP (0.69M) IN CHLOROFORM

HCl, <i>M</i>	4.0	6.0	8.0	9.6
Extraction, %	1.19	28.6	94.6	98.2
Partition coefficient, <i>D</i>	0.01	0.4	17.52	54.55

B. 50% TBP (1.83M) IN CHLOROFORM

HCl, <i>M</i>	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, <i>D</i>	0.07	0.07	0.62	5.58	12.7	32.33

C. 75% TBP (2.75M) IN CHLOROFORM

HCl, <i>M</i>	2.0	3.0	4.0	6.0
Extraction, %	72.2	89.88	95.8	97
Partition coefficient, <i>D</i>	2.6	8.88	22.81	32.33

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

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

#### *Recommended procedure*

The solution should contain about 25 mg of iron<sup>III</sup> as chloride. Adjust to 4M 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<sup>III</sup> from the organic layer by shaking with two 20-ml portions of water and determine iron<sup>III</sup> in the combined aqueous extracts with dichromate.

From ten such runs (iron = 23.07 mg) an average recovery of  $96.7 \pm 2.2\%$  was obtained, so that the standard deviation was  $\pm 2.3\%$ . 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<sup>III</sup>, 23.07 mg

Foreign ion	Amount added, mg	Source	Iron <sup>III</sup> extracted, %	Remarks
Cu <sup>2+</sup>	95	CuSO <sub>4</sub> ·5H <sub>2</sub> O	97	No interference <sup>b</sup>
Hg <sup>2+</sup>	100	HgCl <sub>2</sub>	97	No interference
Co <sup>2+</sup>	25	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	TBP layer coloured green	Interference <sup>a</sup>
Ni <sup>2+</sup>	94	NiSO <sub>4</sub> ·6H <sub>2</sub> O	98.2	No interference
Ba <sup>2+</sup>	100	BaCl <sub>2</sub> ·2H <sub>2</sub> O	95.8	No interference
Bi <sup>3+</sup>	100	BiOCl	97	No interference
Al <sup>3+</sup>	98	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	95.8	No interference
Cr <sup>3+</sup>	100	Cr(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	98.2	No interference
Th <sup>4+</sup>	25	Th(NO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O	97	No interference
UO <sub>2</sub> <sup>2+</sup>	5	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	99	No interference
VO <sub>3</sub> <sup>-</sup>	50	NH <sub>4</sub> VO <sub>3</sub>	V <sup>5+</sup> co-extracted	Interference <sup>a</sup>
Mo <sub>7</sub> O <sub>24</sub> <sup>6-</sup>	50	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O	co-extraction of Mo <sup>6+</sup>	Interference <sup>c</sup>
PO <sub>4</sub> <sup>3-</sup>	100	NaH <sub>2</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	97	No interference
(EDTA) <sup>4-</sup>	100	EDTA (disodium salt)	97	No interference
Tart <sup>3-</sup>	100	Tartaric acid	—	Interference <sup>c</sup>
Cit <sup>3-</sup>	100	Citric acid	—	Interference <sup>c</sup>

<sup>a</sup> Colour interference.

<sup>b</sup> Cu<sup>2+</sup> was also extracted giving a deep yellow TBP phase but there was no interference with analysis of iron<sup>III</sup>.

<sup>c</sup> Interference with iron<sup>III</sup> analysis.

*Acknowledgement*—Thanks are due to the Council of Scientific and Industrial Research (India) for financial support and awarding a fellowship to one of us (S. K. M.).

*Zusammenfassung*—Eine Methode zur schnellen Solventextraktion von Fe(III) mit Tributylphosphate (TBP) wird beschrieben. Die Extraktion ist quantitativ aus Lösungen 3–6 molar in Salzsäure, wenn 100% TBP verwendet wird. Der Einfluss der TBP-Konzentration, Aussalzeffekte sowie Anwesenheit verschiedener Ionen wurde studiert. Die extrahierten Partikeln sind FeCl<sub>3</sub>·3TBP und H[FeCl<sub>4</sub>·(TBP)<sub>2</sub>] 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<sub>3</sub>, 3 T.B.P. et H[FeCl<sub>4</sub>(T.B.P.)<sub>2</sub>] en milieu acide chlorhydrique 2 M et 6 M respectivement.

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## CATION-EXCHANGE STUDIES OF LEAD<sup>II</sup> ON DOWEX 50W-X8

### SEPARATION FROM MIXTURES

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(Received 5 April 1960)

**Summary**—Quantitative studies are reported on the behaviour of lead<sup>II</sup> 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<sup>II</sup> is separated from barium, strontium and aluminium by selective elution with ammonium acetate (1M) and from cerium<sup>IV</sup>, zirconium<sup>IV</sup>, thorium<sup>IV</sup>, bismuth<sup>III</sup> and iron<sup>III</sup>, 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<sup>1</sup> determined the cation-exchange equilibrium involving ions like lead<sup>II</sup> on Dowex 50, and derived a selectivity scale for bivalent ions on the basis of their affinity for the resin. Minami and Ishimori<sup>2</sup> 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.<sup>3</sup> 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<sup>4</sup> 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<sup>II</sup> 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<sup>IV</sup>, zirconium, bismuth, iron<sup>III</sup>, 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.<sup>5,6</sup> 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.<sup>7</sup>

*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 + 0.5M 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, 0.01M 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.<sup>8</sup> 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.<sup>8</sup> 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<sup>9</sup>

$$E = \frac{d \cdot A}{V}$$

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<sup>2</sup>. 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<sup>II</sup> 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

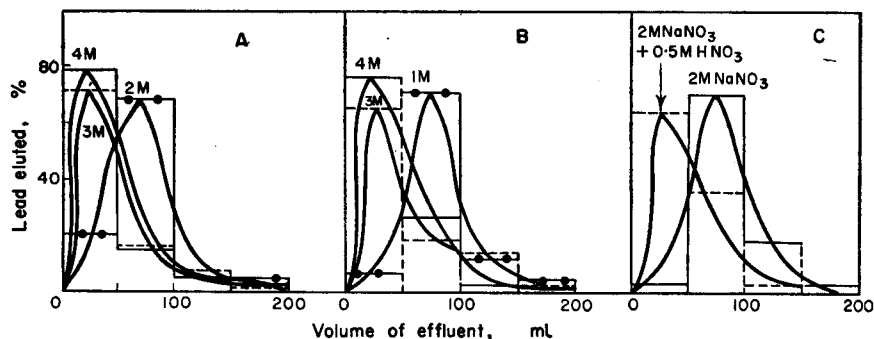


FIG. 1.—Elution of lead<sup>II</sup> on Dowex 50W-X8  
A. HNO<sub>3</sub> B. CH<sub>3</sub>COONH<sub>4</sub> C. NaNO<sub>3</sub>

TABLE I. BEHAVIOUR OF LEAD<sup>II</sup> 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 <sub>3</sub> , 1M	2.3	2.3	5.7	5.1	15.4	—
	HNO <sub>3</sub> , 2M	16.7	70.1	6.2	5.1	98.1	0.390
	HNO <sub>3</sub> , 3M	72.6	16.4	7.0	1.3	97.3	0.693
	HNO <sub>3</sub> , 4M	78.9	15.0	5.1	3.7	102.7	0.693
	HNO <sub>3</sub> , 6M	84.6	7.6	10.1	3.7	106.0	0.693
2	CH <sub>3</sub> COONH <sub>4</sub> , 1M	5.3	74.8	15.1	2.1	97.3	0.390
	CH <sub>3</sub> COONH <sub>4</sub> , 3M	68.1	18.7	16.0	2.1	104.9	0.693
	CH <sub>3</sub> COONH <sub>4</sub> , 4M	78.5	25.1	1.3	0.5	105.4	0.693
3	NaNO <sub>3</sub> , 1M	3.3	3.6	4.6	6.0	17.5	—
	NaNO <sub>3</sub> , 2M	3.5	73.9	18.5	2.9	98.8	0.271
	NaNO <sub>3</sub> , 2M with 0.5M HNO <sub>3</sub>	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 <sub>4</sub> , 2M	...	...	...	...	5.7	—
7	CH <sub>3</sub> COOH, 4M	—	—	—	—	2.5	—
8	EDTA, 0.01M (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<sup>II</sup> but fails to elute some cations like barium, strontium and aluminium. Secondly, lead<sup>II</sup> 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<sup>II</sup> by passage through a cation-exchange column.

#### *Separation from strontium, barium and aluminium*

A mixture of lead<sup>II</sup> and an excess of strontium, barium or aluminium nitrate was adsorbed on the ion-exchange column. After washing with water (50 ml), lead<sup>II</sup> 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<sup>II</sup> 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<sup>IV</sup> (as ceric nitrate) and zirconium<sup>IV</sup> (as zirconyl nitrate) were converted to anionic complexes<sup>10</sup> with 5% citric acid at pH 2.7. The mixture with lead<sup>II</sup>, 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<sup>II</sup> 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 <sup>IV</sup> 132.12		
6	Pb 34.73	34.37	99.0
	Zr <sup>IV</sup> 69.60		
7	Pb 14.88	14.62	98.2*
	Bi <sup>III</sup> 29.0		
8	Pb 34.73	32.82	94.5
	Fe <sup>III</sup> 68.0		
9	Pb 14.88	14.15	95.1*
	Th <sup>IV</sup> 67.50		
10	Pb 14.88	15.10	101.4*
	Th <sup>IV</sup> 140.0		

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

*Separations from bismuth, iron and thorium*

Mixtures of lead<sup>II</sup> with bismuth<sup>III</sup>, iron<sup>III</sup> or thorium<sup>IV</sup> nitrate were treated with 0.01M 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<sup>+</sup> form). In each case the effluent fraction containing lead<sup>II</sup> 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<sup>II</sup>, mercury<sup>II</sup> 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  $\pm 3\%$ .

*Acknowledgements*—The authors are grateful to the Council of Scientific and Industrial Research (India) for sponsoring this project, and to Dow Chemical Co., Midland, Mich., U.S.A., for the gift sample of Dowex 50W-X8 which was used in this work.

*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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(Received 23 April 1960)

**Zusammenfassung**—Es wird über die Existenz eines Komplexes des Peroxytitanylions mit 1,2-Diaminocyclohexan-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 Gegensatz 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<sup>1</sup>, die jedoch nur innerhalb eines relativ geringen pH-Bereiches beständig sind.<sup>2</sup> 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.<sup>3</sup>

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 Titan Komplexe mit diesen Ionen stabiler als das Titan Komplexonat.

Es wurde bereits von Sweetser u. Bricker<sup>4</sup> sowie von Lieber<sup>4</sup> 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<sup>5,6</sup> ist offenbar befähigt mit ÄDTA ein stabileres Chelat zu bilden. Diese Annahme wird durch die Angaben von Musha und Ogawa<sup>7</sup> bestätigt, die für den Komplex  $[\text{TiO}(\text{H}_2\text{O}_2)\text{Y}]^{2-}$  einen log. K-Wert von 20,43 angeben, während für  $[\text{TiY}]$  17,7 bzw.  $[\text{TiOY}]^{2-}$  17,3 gefunden wurden.<sup>1</sup> 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  $[\text{TiO}(\text{H}_2\text{O}_2)\text{Y}]^{2-}$  wird berichtet.

Sajo<sup>8</sup> und Wilkins<sup>9</sup> 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<sup>7</sup> stellten fest, daß dieser Bereich zwischen pH 0,4 und 4 liegt. Im alkalischen Milieu liegt das Titan als  $[\text{Ti}(\text{O}_2)_4]^{4-}$ -Anion vor<sup>5</sup>, welches nicht mehr mit ÄDTA zu reagieren vermag. Dieser Umstand wurde von Wehber<sup>10</sup> zur



Maskierung des Titans bei komplexometrischen Titrationsen anderer Metalle bei pH 10 ausgenutzt.

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<sup>11</sup> bzw. Adler u. Hiskey<sup>12</sup> liegt in schwach saurem

Medium das Niob in Gegenwart von Wasserstoffperoxyd als  $\left[ \begin{array}{c} \text{O} \\ | \\ \text{O} \end{array} \text{Nb-O-OH} \right]^{2-}$ -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 Titrationsmethode des Niobs auszunützen, in dem ein gemessener ÄDTA-Überschuß mit Kupferlösung gegen PAN-Indikator rücktitiert werden sollte, scheiterten an einem über 1 ml Maßlösung schleppendem Umschlag. 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<sup>7</sup> steht die Tatsache, daß die Kurve des  $[\text{TiO}(\text{H}_2\text{O}_2)\text{Y}]^{2-}$  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<sup>8</sup> und Wilkins<sup>9</sup> 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-( $\beta$ -amino-äthyläther-(ÄGTA) und 1,2-Diaminocyclohexan-N,N,N<sup>1</sup>,N<sup>1</sup>-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 Titanchelate zwischen pH 2 und 7 stabil ist.

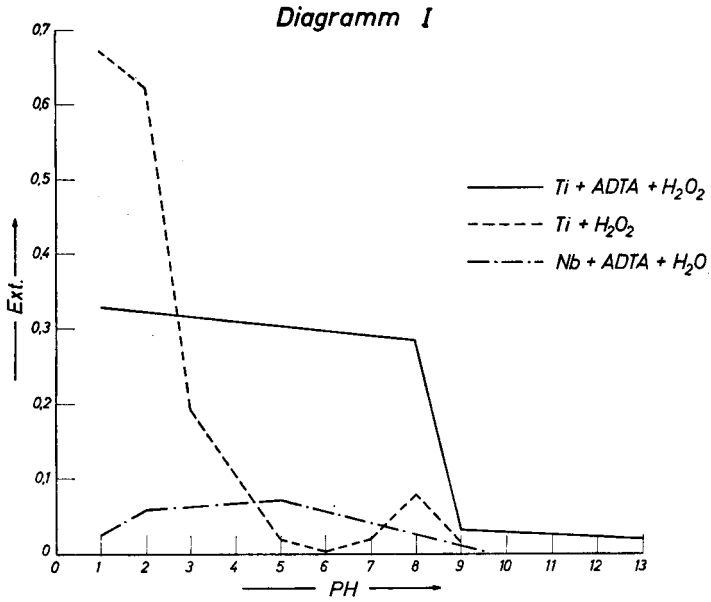


ABB. 1.—2 ml 0,05 m Ti-Lösung, 1 ml 5% ig ÄDTA-Lösung, 1 ml  $H_2O_2$  30% ig in 100 ml. ... ELKO II Photometer, Küvette 2 cm, Filter Hg 436

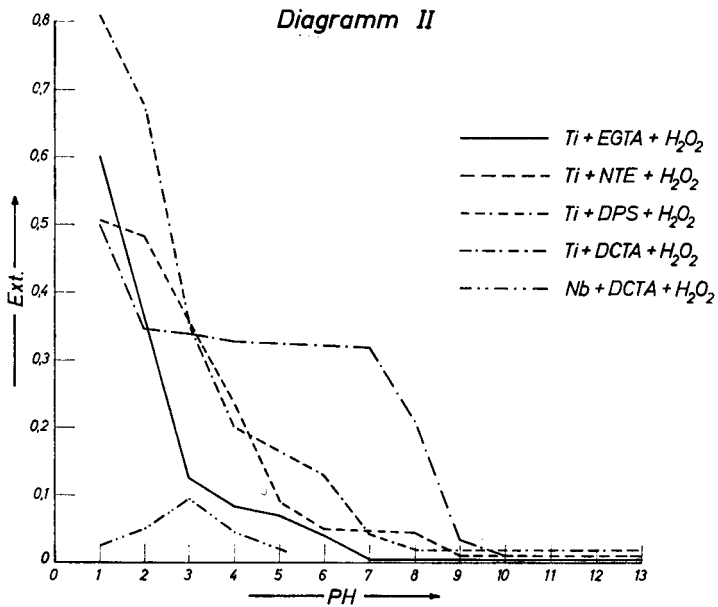


ABB. 2.—2 ml 0,05 m Ti-Lösung, 1 ml 5% ige Aminopolycarbonsäure, 1 ml  $H_2O_2$  30% ig in 100 ml ELKO II Photometer, Küvette 2 cm, Filter Hg 436

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 vollständig 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<sup>13</sup> und der geringen Wasserlöslichkeit des Cu-PAN-Chelats ist einerseits erhöhte Temperatur (70-90°C), andererseits langsames 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 ist bei erhöhter Temperatur zu arbeiten, ist es nicht unbedingt notwendig, Alkohol zur besseren Löslichkeit des Cu-PAN-Chelats zuzusetzen. Bei 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 läßt 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 verdünnter 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  $\pm 0,012$  ml 0,05 m DCTA-Lösung zu rechnen. Dies entspricht einem mittleren absoluten Fehler von  $\pm 0,025$  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 durch mehrmaliges Fällern, 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 peroxy-titanyl 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 tétra-cétique et l'ion peroxytitanyl. Ce chélate 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) à 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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(Received 30 April 1960)

**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 propriété étudiée, au point d'équivalence.

De cette catégorie de titrages, dits linéaires<sup>1</sup>, nous rappelons les titrages conductométriques, réfractométriques, radiométriques<sup>2</sup>, ampérométriques, hétérométriques<sup>3</sup>, chronopotentiométriques<sup>4</sup>, 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<sup>5</sup>, 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 galvanomètre); 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  $\text{NaClO}_4$

$\text{NaClO}_4$ , ml	$\sqrt{n}$	$\text{NaClO}_4$ , ml	$\sqrt{n}$	$\text{NaClO}_4$ , 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

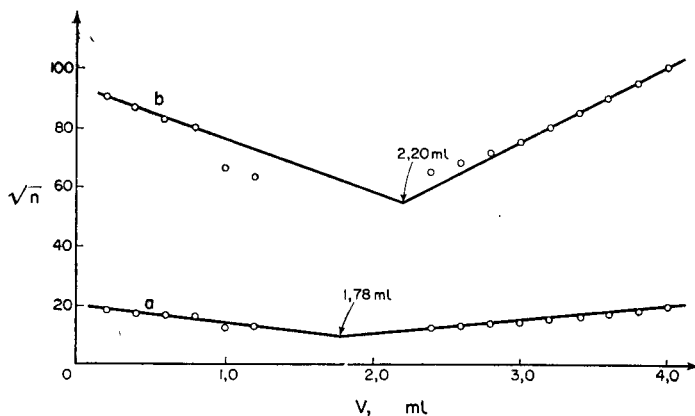


FIG. 1.

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 détermine 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<sup>6</sup>, 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<sup>7</sup> 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<sup>6</sup>, 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<sup>8</sup> emploie la méthode des moindres carrés, d'après le procédé du centre de pesanteur de A. Milasovszky<sup>9</sup>.

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

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



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

$$y = A_0 + A_1x + A_2x^2 + \dots + A_mx^m$$

obtenues en substituant  $x$  par les valeurs expérimentales  $x_k$ .

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

$$y = f(x) = A_0 + A_1x + A_2x^2 + \dots + A_mx^m$$

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

Le phénomène étudié, c'est-à-dire un titrage linéaire, peut être représenté par une équation du premier degré  $y = A_0 + A_1x$ , comme c'est le cas dans le titrage linéaire, après avoir écrit la condition (1) sous la forme:

$$f(x) = [(A_0 + A_1x) - y_1]^2 + [(A_0 + A_1x_2) - y_2]^2 + \dots + [(A_0 + A_1x_m) - y_n]^2 = \text{minimum}$$

on annule les dérivées partielles par rapport à  $A_0$  et  $A_1$ ; on obtient<sup>10</sup> 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 ( $y = A_0 + A_1x$ ) 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:

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

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

respectivement

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

$$A_1' = \frac{n_2 \sum_{k=1}^{n_2} x_k y_k - \sum_{k=1}^{n_2} x_k \sum_{k=1}^{n_2} y_k}{n_2 \sum_{k=1}^{n_2} x_k^2 - \left( \sum_{k=1}^{n_2} x_k \right)^2} \quad (5)$$

On calcule le point d'équivalence analytiquement en mettant

$$A_0 + A_1x = A_0' + A_1'x,$$

d'où

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

### 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<sup>11</sup>;  $V = 11,70$  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<sup>11</sup>.  $V_e = 14,80$  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<sup>12</sup>;  $V_e = 1,065$  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  $H_3PO_4$   $5 \cdot 10^{-2}$  N par NaOH  $5,6 \cdot 10^{-1}$  N<sup>13</sup>  $V_e' = 0,75$  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<sup>14</sup>  $V_e = 4,35$  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 Ermittlung des Schnittpunktes zweier Geraden zum Ziele. Die Koeffizienten in den Gleichungen der beiden Geraden (Ordinatenhöhe für Nullwert der Abszisse 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 beträchtliche 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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(Received 30 April 1960)

**Résumé**—On donne une nouvelle méthode 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.

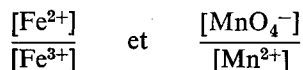
Suivant la méthode décrite, le coefficient réel d'asymétrie est calculé par la méthode des moindres carrés et à l'aide des données de titration éloignées du point d'équivalence; sa valeur a le caractère d'une moyenne arithmétique.

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 titrages dits symétriques<sup>1</sup>.

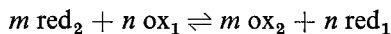
Si on considère le titrage général  $mA + nB$ , c'est-à-dire le titrage de la substance  $A$  par  $B$ , le rapport  $\frac{m}{n} = \mu$  s'appelle coefficient d'asymétrie<sup>1</sup> et il faut en tenir compte dans le calcul du point d'équivalence<sup>1-3</sup>.

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 réactifs soient égales, par exemple  $\text{Cl}^-$  à  $\text{Ag}^+$ , ou les rapports de leurs concentrations à leur produit de réaction soient égaux (réactions rédox), par exemple:



Si on a la titration



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

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

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

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

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

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

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

$$E_0 - E_e = u(E_m - E_n) \quad (1)$$

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<sup>1</sup> 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 moléularité 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<sup>4</sup> l'oxydation de l'électrode de platine pendant la titration rédox a  $\text{Ce}^{4+}$  et  $\text{CrO}_4^{2-}$ .

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<sup>5</sup>, 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  $\Delta V/\Delta E - (V - \frac{1}{2}\alpha \cdot \Delta V)$ ,

$$\text{ou } \alpha = \frac{\Delta V}{|v_i - V|}$$

Le volume d'inflexion  $v_i$  peut être déterminé avec une précision suffisante par l'une des méthodes de calcul connues<sup>6,7,etc.</sup>. Au besoin et surtout au cas d'adjonctions inégales de réactif au voisinage du point d'équivalence, le volume d'inflexion  $v_i$  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,  $y = A_0 + A_1x$  et  $y = A_0' + A_1'x$  en laissant de côté les points trop écartés de la droite.

Puisque  $\frac{E_e - E_n}{E_m - E_e} = u$ , 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,  $y = A_0 + A_1x$ , 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,  $\frac{\Delta V}{u \cdot \Delta E} = y_{\text{sym}}$  au lieu de  $\frac{\Delta V}{\Delta E} = y$ . Par conséquent

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

On obtient ainsi

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

et

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

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  $y = A_0 + A_1x$ . Il en résulte que  $A_1'' = A_1$  et donc

$$u = \frac{|A_1'|}{|A_1|} \quad (5)$$

(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:  $y = A_0 + A_1x$  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.

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

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

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

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

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

$$A_0 + A_1x = A_0' + A_1'x.$$

On obtient

$$x = \frac{A_0 - A_0'}{A_1' - A_1} = V_i \quad (10)$$

$V_i$  ainsi obtenu sert à calculer le coefficient  $\alpha$  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' $\alpha$ , on prend la valeur  $v_i = 3,09$  ml, déterminée d'après F. L. Hahn et G. Weiller<sup>6</sup>

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	$\alpha = \frac{\Delta V}{ v_i - V }$	$\frac{1}{2}\alpha \cdot \Delta V$	$\frac{V + \frac{1}{2}\alpha \cdot \Delta V}{V - \frac{1}{2}\alpha \cdot \Delta V}$ x	$\frac{\Delta V}{\Delta E} \cdot 10^4$ 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	$M = \frac{279,65}{195,87} = 1,42$
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  $\alpha$ ,  $v_i = 3,225$  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  $\text{KMnO}_4$   $10^{-1}\text{N}$  en solution de  $\text{H}_2\text{SO}_4$   $1\text{N}^9$*

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 <sub>4</sub> ml	$\omega$ (ohms comp.)	$\alpha = \frac{\Delta V}{ v_i - V }$	$\frac{1}{2}\alpha \cdot \Delta V$	$\frac{V + \frac{1}{2}\alpha \cdot \Delta V}{V - \frac{1}{2}\alpha \cdot \Delta V}$	$\frac{\Delta\omega}{\Delta V} \cdot 10^4$	Résultats
20,00	200	0,5106	0,1534	20,1534	600,0	$(v_i = 21,175 \text{ ml})$
20,60	210	0,6087	0,1065	20,7065	350,0	
20,95	220	0,4444	0,0222	20,9722	100,0	$A_1 = -603,13$
21,05	230	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					$u = \frac{1053,15}{603,13} = 1,75$
21,25	480	0,5333	0,0107	21,2393	13,3	
21,31	490	0,4444	0,0133	21,2967	60,0	$A_0 = 12 \cdot 776,17$
21,60	500	0,6823	0,0989	21,5011	290,0	
22,80	510	0,7384	0,4430	22,3570	1200,0	$A_0' = -22 \cdot 348,75$

Pour ce même titrage, F. L. Hahn et M. Frommer<sup>10</sup>, 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<sup>1</sup>, 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 Asymmetriekoeffizienten,  $u$ , 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 experimentellen Punkte in einiger Entfernung vom Äquivalenzpunkt herangezogen werden. Die Koeffizienten 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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(Received 30 April 1960)

**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 détermination du point d'équivalence dans les titrages potentiométriques ne fait usage de la méthode des moindres carrés, pourtant seule une méthode de ce genre serait vraiment rigoureuse.

Le fondement théorique de la méthode c'est la transformation de la courbe logarithmique à un point d'inflexion (coordonnées  $E-V$ ), en courbe linéaire d'après le procédé G. Gran<sup>1</sup>, mais pas seulement jusqu'au point d'équivalence, en coordonnées

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

Le volume d'inflexion  $v_i$  peut être déterminé avec une exactitude suffisante par l'une des méthodes connues<sup>2,3</sup>etc. 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.

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

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

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

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

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

$$x = \frac{A_0 - A_0'}{A_1' - A_1} = V_i \quad (5)$$

$x$  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<sup>4-6</sup>. 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  $\frac{y}{u}$ .

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:

$$x = V_e = \frac{u A_0 - A_0'}{A_1' - u A_1} \quad (6)$$

$A_0$ ,  $A_1$ ,  $A_0'$  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,

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

après avoir remplacé, on obtient:

$$x = V_e = \frac{uA_0 - A_0'}{2A_1'} \quad (7)$$

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:

$$y_i = A_0 + A_1V_i = A_0' + A_1'V_i, \quad (8)$$

puis

$$V_i = \frac{y_i - A_0}{A_1} = \frac{y_i - A_0'}{A_1'} \quad (9)$$

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:

$$y_e = A_0 + A_1V_e \quad (10)$$

d'où

$$V_e = \frac{y_e - A_0}{A_1} \quad (11)$$

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

$$V_e - V_i = \frac{y_e - y_i}{A_1} \quad (12)$$

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

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

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

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

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

on obtient

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

respectivement

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

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

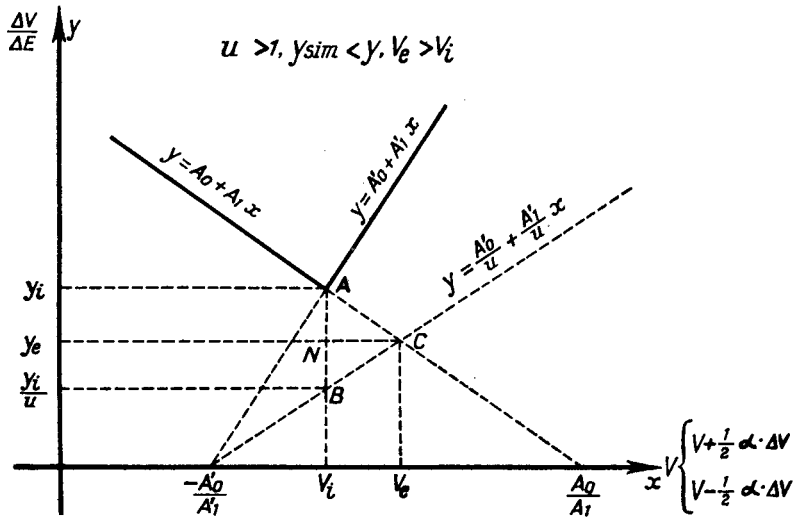


FIG. 1.

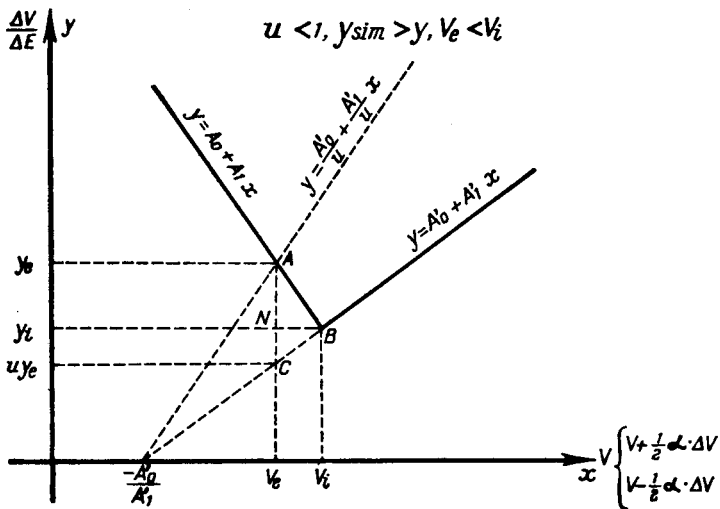


FIG. 2.

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 qui 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

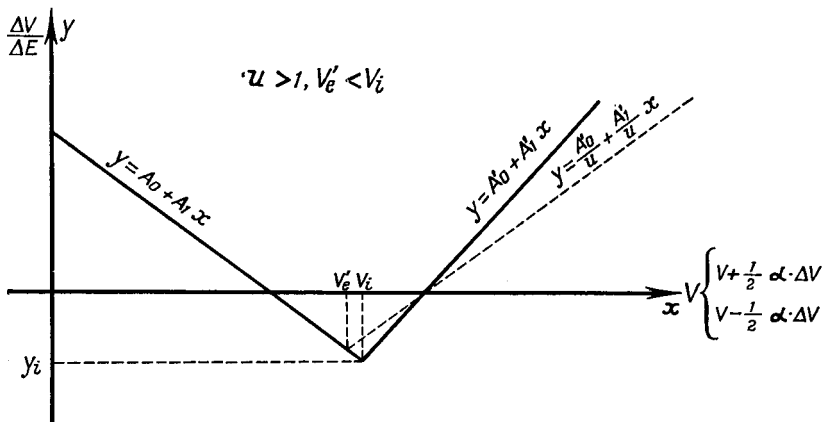


FIG. 3.

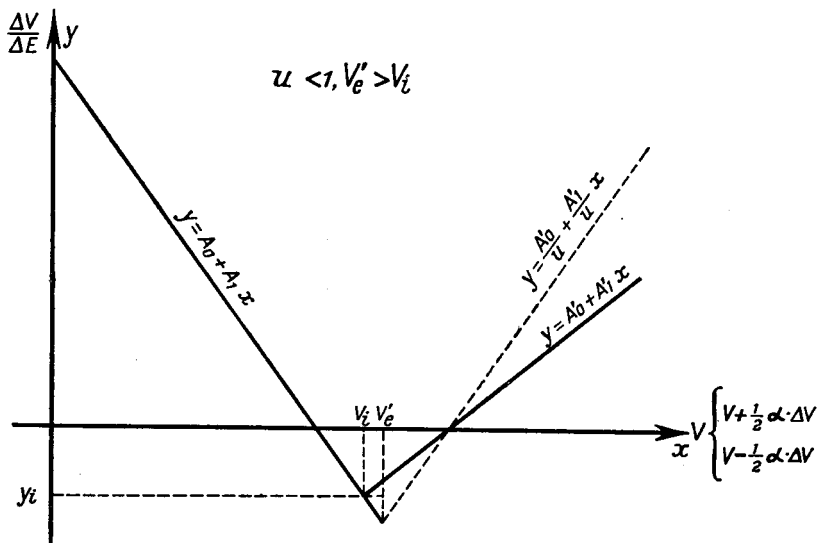


FIG. 4.

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:

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

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

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

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



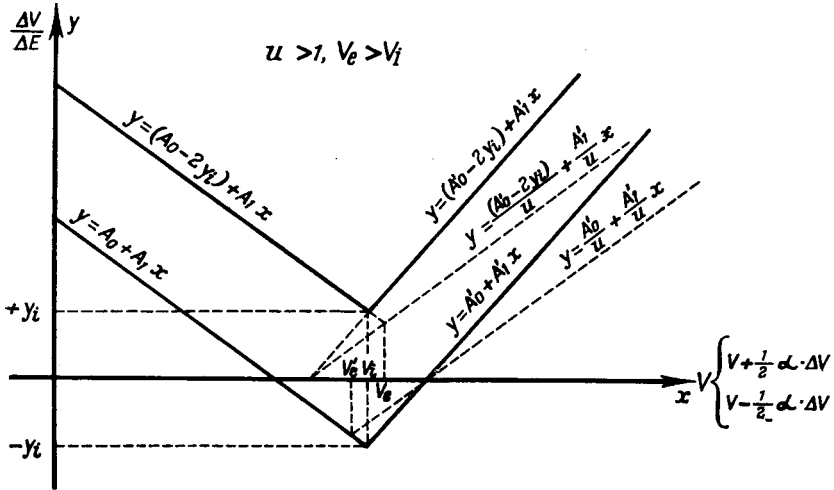


FIG. 5.

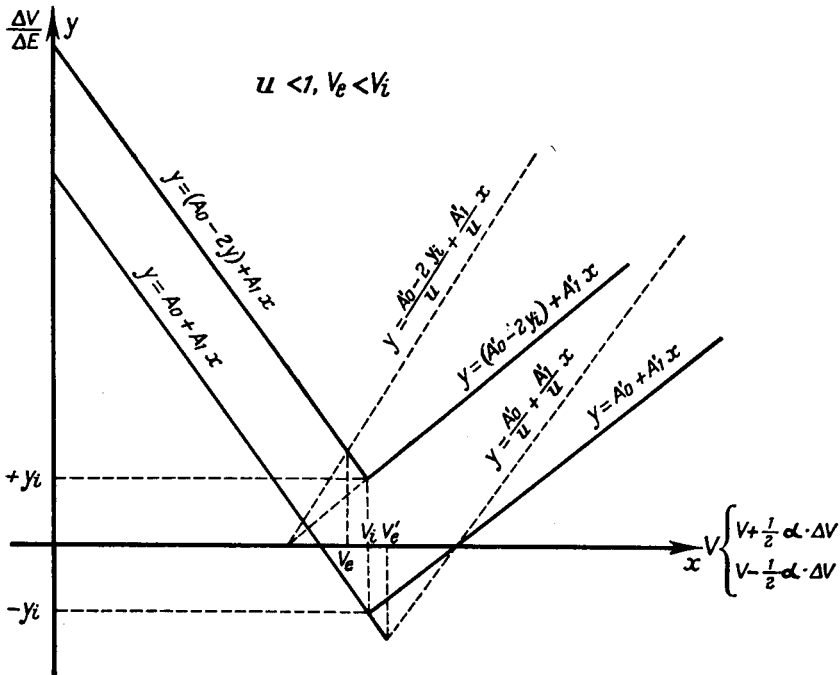


FIG. 6.

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

$$(A_0 - 2y_i) + A_1x = \frac{A_0' - 2y_i}{u} + \frac{A_0'}{u}$$

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

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

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:

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

c'est-à-dire:

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

respectivement

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

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

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

(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<sup>1</sup> 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) *Titration de 10 ml de solution de l'acide gluconique  $7,687 \cdot 10^{-2}$  N par NaOH  $2,5 \cdot 10^{-1}$  N<sup>7</sup>.*

Pour linéariser, on prend  $v_i = 3,08$  ml (calculé d'après Hahn-Weiller)<sup>2</sup>; 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  $\text{KMnO}_4$   $10^{-1}$  N en solution de  $\text{H}_2\text{SO}_4$  1 N<sup>8</sup>.*

TABLEAU II

$\text{KMnO}_4$ 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
$\omega$ , (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'inflexion 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 conséquent 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 Wendepunktolum  $V_i$  der Titrationskurve. Der Assymetriekoeffizient,  $u$ , sowie das dem Äquivalenzpunkte entsprechende Volum  $E$  werden schliesslich errechnet.

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## THE FORMATION OF INTERHALOGENS

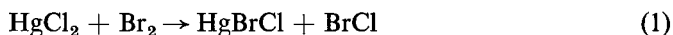
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(Received 23 May 1960)

**Summary**—The formation of interhalogen compounds has been investigated in the reactions between elementary bromine or iodine with mercury<sup>II</sup> 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<sup>1</sup> used a standard reagent which was freshly prepared by combining a separately stored ethanolic iodine solution with an ethanolic solution of mercury<sup>II</sup> chloride. This method was examined later by Schweissinger,<sup>2</sup> Ephraim<sup>3</sup> and Wijs.<sup>4</sup> Schweissinger presumed mercury<sup>II</sup> 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<sup>5</sup> for the determination of the iodine bromine number, and he recommended also the addition of a minute amount of mercury<sup>II</sup> 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,<sup>6</sup> the heterolytic dissociation of the elementary halogen ( $\text{Br}_2 \rightleftharpoons \text{Br}^+ + \text{Br}^-$ ) is promoted by a mercury<sup>II</sup> 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:

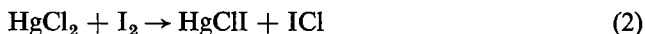


represents the active component.

The order of the degree of dissociation of the halides of mercury<sup>II</sup> ( $\text{HgCl}_2 > \text{HgBr}_2 > \text{HgI}_2$ ; the dissociation constants are  $K_{\text{HgCl}_2}: 2.6 \times 10^{-15}$ ;  $K_{\text{HgBr}_2}: 8 \times 10^{-20}$ ;  $K_{\text{HgI}_2}: 3.2 \times 10^{-29}$ ) 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<sup>II</sup> 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<sup>II</sup> 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<sup>II</sup> 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:



Solutions of bromine and iodine, respectively, in glacial acetic acid behaved similarly with mercury<sup>II</sup> chloride, although to a smaller degree.\*

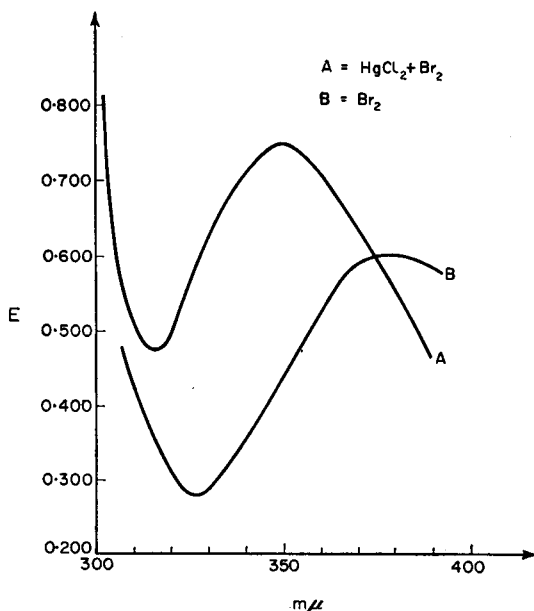


FIG. 1

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<sup>II</sup> chloride (1M HCl, 0.1M HgCl<sub>2</sub>, 0.01M Br<sub>2</sub>) was established. As can be seen in Fig. 1, a curve characteristic of bromine chloride<sup>7</sup> 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<sup>II</sup> salt; this can be ascribed to the fact that the major part of the chloride content of the solution is bound by mercury<sup>II</sup> 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<sup>II</sup> 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.)

\* Presumably the heterolytic dissociation of elementary iodine is markedly lower in acetic acid of low dielectric constant ( $\epsilon = 9.7$ ) than in water ( $\epsilon = 80.3$ ).

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,<sup>8,9</sup> but this method involves the removal,

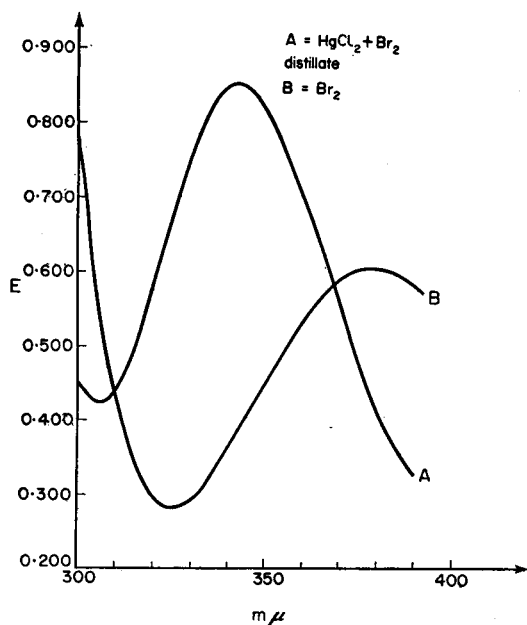


FIG. 2

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.†

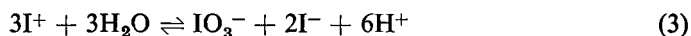
With the use of this method, the composition was determined of the mixture of halogens which forms when mercury<sup>II</sup> chloride and elementary bromine react in a hydrochloric acid medium and the products are distilled into hydrochloric acid. Under optimum conditions, the distillate contained 85% 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

† The amount of elementary bromine formed by the homolytic decomposition of bromine chloride ( $2 \text{BrCl} \rightleftharpoons \text{Br}_2 + \text{Cl}_2$ ) 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<sup>II</sup> 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<sup>II</sup> chloride and mercury<sup>II</sup> 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<sup>II</sup> salt. Thus, antipyrine could be iodinated in an acidic medium by elementary iodine in the presence of mercury<sup>II</sup> 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<sup>13</sup> in a hot solution in the presence of mercury<sup>II</sup>:



Iodide ions formed according to equation (3) are bound by mercury<sup>II</sup> 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<sup>10</sup> 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<sup>I</sup> halides (the solubility products in decreasing order are  $Hg_2Cl_2$ :  $2 \times 10^{-18}$ ;  $Hg_2Br_2$ :  $1.5 \times 10^{-21}$ ;  $Hg_2I_2$ :  $1.2 \times 10^{-29}$ ). Thus, oxidation is actually carried out by the electrophilic halogen ions formed ( $I^+$  and  $Br^+$ , respectively). Elementary chlorine does not react with mercury<sup>I</sup> 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 0.005M 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 0.01N 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 0.01N 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 0.01N  $\text{Na}_2\text{S}_2\text{O}_3 \equiv 0.79916 \text{ mg of Br}$ ).

#### Preparation of iodo-antipyrine

One hundred ml of saturated aqueous iodine (about 0.1N with respect to sulphuric acid) was treated with 2 ml of 1N mercury<sup>II</sup> 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.<sup>12</sup> 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<sup>II</sup> 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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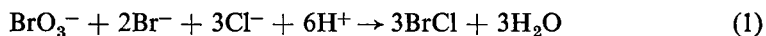
(Received 23 May 1960)

**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<sup>1,2</sup> that bromine chloride, owing to its electrophilic nature, reacts with nucleophilic reaction partners such as aromatic compounds,<sup>1</sup> unsaturated double bonds,<sup>2</sup> *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<sup>3</sup> markedly exceeding that of elementary bromine ( $E_{\text{BrCl}} = 1.3 \text{ V}$ ;  $E_{\text{Br}_2} = 1.07 \text{ V}$ ), and that the redox potential of the hydrochloride complex of bromine chloride can be varied by changing the concentration of hydrochloric acid<sup>4</sup> 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  $\text{Br}^+$  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.<sup>5</sup>

In the present investigations, three readily available unsaturated aldehydes, acrolein, crotonic aldehyde and cinnamic aldehyde, were used, whilst a 0.1*N* solution of potassium bromate served as a standard solution which contained, according to equation (1), an equivalent amount of bromide ions:<sup>6</sup>



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,<sup>6</sup> prepared according to (1), was used.

It was found that:

1. the bromine chloride addition takes place completely and almost instantaneously

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

Substance	Content present, %	BrCl excess, %	Content found, %	Deviation, %
<i>Crotonic aldehyde</i>	93.00	9.5	92.83	-0.17
		4.0	93.22	+0.22
		115.0	93.00	+0.0
<i>Acrolein</i>	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, <i>min</i>	Content found, %	Deviation, %
<i>Crotonic aldehyde</i>	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
<i>Acrolein</i>	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

when only a small excess (5 to 10%) of bromine chloride is present (*cf.* Table 1);

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  $\pm 0.5\%$  (*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<sup>7</sup> was applied. In the case of cinnamic aldehyde, the aldehyde

bisulphite was decomposed by hydroxylamine hydrochloride.<sup>8</sup> 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

TABLE III. BROMINE CHLORIDE ADDITION OF UNSATURATED ALDEHYDES

Substance	Amount weighed, mg	Consumed 0.1N BrCl, ml	Amount found, mg	Content found, %	Deviation, %
<i>Cinnamic aldehyde</i> (Content: 99.00%)	43.44	6.49	42.88	98.71	-0.29
		6.51	43.01	99.01	+0.01
	85.50	12.86	84.97	99.38	+0.38
		12.86			
<i>Crotonic aldehyde</i> (Content: 93.00%)	17.86	4.74	16.61	93.00	+0.00
		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			
<i>Acrolein-</i> (Content: 86.00%)	12.28	3.77	10.57	86.07	+0.07
		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			

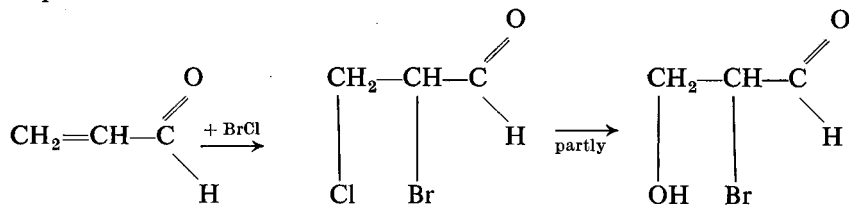
chloride addition. When, however, the determination of aldehyde was carried out after the addition of bromine chloride, results on the basis of the aldehyde content were in accordance with those obtained with bromine chloride.

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.<sup>9</sup>

## EXPERIMENTAL

### *Determination of the Bromine Chloride Addition to Saturated Aldehydes*

#### *Reagents*

0.1N 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.

0.1N 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.

0.1N 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 0.1N 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 0.1N 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 0.1N standard sodium thiosulphate solution in the presence of starch as indicator.\* The titre of 0.1N bromine chloride solution should be checked iodometrically.

\* 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  $\pm 0.5\%$  (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<sup>10</sup> by bromine addition at the temperature of melting ice and also by the hydroxylamine hydrochloride method,<sup>11</sup> 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 liaison des aldéhydes non saturées. Le réactif, qui est électrophile, réagit très 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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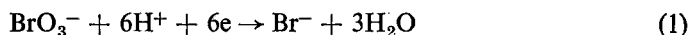
(Received 20 June 1960)

**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.

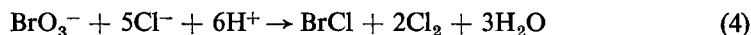
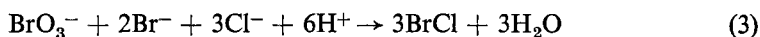
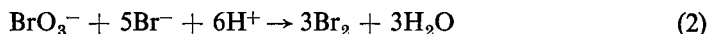
It is pointed out that in redox titrations with potassium bromate, in place of bromate or bromic acid, actually elementary bromine, or bromine chloride, or bromine chloride and elementary chlorine act as agents. Thus, bromine and bromine chloride form a complex with the halide content (bromide and chloride, 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:



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:



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<sup>2</sup> 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<sup>II</sup> ions (as poorly dissociated mercury<sup>II</sup> bromide), to prevent the formation of bromine.<sup>3</sup> 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
$\text{BrO}_3^-/\text{Br}_2$	1.52
$\text{BrO}_3^-/\text{Br}^-$	1.42
$\text{Br}_{2\text{aq}}/\text{Br}^-$	1.087
$\text{BrCl}_{\text{complex}}/\text{Br}^-$	1.3
$\text{Cl}_{2\text{aq}}/\text{Cl}^-$	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.<sup>4</sup>

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<sup>5</sup> of aromatic compounds of nucleophilic nature and the halogen addition<sup>6</sup> 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.

\* 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.<sup>17</sup>



Taking into account the above considerations, the phenomenon which was pointed out by Zöllner and Varga,<sup>7</sup> 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<sup>8</sup>), 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<sup>8</sup> or hydroxylamine<sup>9</sup>), 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 aforementioned 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  $\text{BrO}_3^- : \text{Br}^-$ ) 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.<sup>1</sup> 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,<sup>10</sup> the addition of bromine chloride to unsaturated double bonds<sup>6,11,16</sup> and many oxidation reactions with bromine chloride<sup>2,12,13,15</sup> were subjected to a thorough examination. In all cases, as expected, a marked increase of reaction rates was observed.

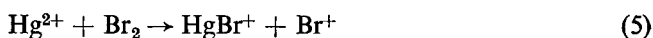
The standard solution of bromine chloride suggested by us was applied with success to the determination of reducing substances which can be oxidised only extremely slowly or non-stoichiometrically by elementary bromine. The bromatometric determination of these substances was previously only possible 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<sup>13</sup> 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<sup>12</sup> and hydroxylamine.<sup>2</sup>

On using a standard solution of bromine chloride, it was possible to determine unsaturated compounds as well, *e.g.* maleic acid and fumaric acid,<sup>6</sup> 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.

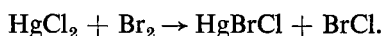
Considering the higher reaction rates of brominations carried out with bromine chloride and with  $\text{Br}^+$  cations developed during the dissociation of this compound, respectively, it was possible to interpret the mechanism of action of mercury<sup>II</sup> ions *i.e.* of the "catalyst" generally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

Thus, it was assumed that the heterolytic dissociation of elementary halogen is completed by mercury<sup>II</sup> ions, with the formation of poorly dissociated mercury<sup>II</sup> halides:



The increase in reaction rate is due to the formation of  $\text{Br}^+$  cations.

In order to prove the validity of this assumption, bromine water was treated with mercury<sup>II</sup> chloride and, since  $\text{HgBrCl}$  is less dissociated than  $\text{HgCl}_2$ , bromine chloride should be formed<sup>21</sup> according to the equation:



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 Redox-titrationen 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 brome 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 contrôlés 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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(Received 21 June 1960)

**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<sup>8,10,16,18</sup> and benzene-methanol solutions.<sup>6,12</sup> Acidic compounds have been titrated in benzene-methanol solutions,<sup>5,7</sup> pyridine,<sup>13</sup> dimethylformamide,<sup>3,14</sup> and solvent mixtures of dimethylformamide, diethylamine, and triethylamine.<sup>9</sup> Conductance titrations have been carried out in dimethylformamide, methanol, and pyridine, and binary mixtures of these solvents.<sup>14,15</sup>

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.<sup>14</sup> 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.

\* Work partially supported by United States Atomic Energy Commission.

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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.<sup>2</sup> 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.*<sup>14</sup> 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

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

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,

$$\text{then } C_s = \frac{C_1(C_2^2\omega^2 + k^2)}{\omega^2C_2^2 + \omega^2C_1C_2 + h^2}.$$

At a given frequency  $\omega$  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  $k$ .

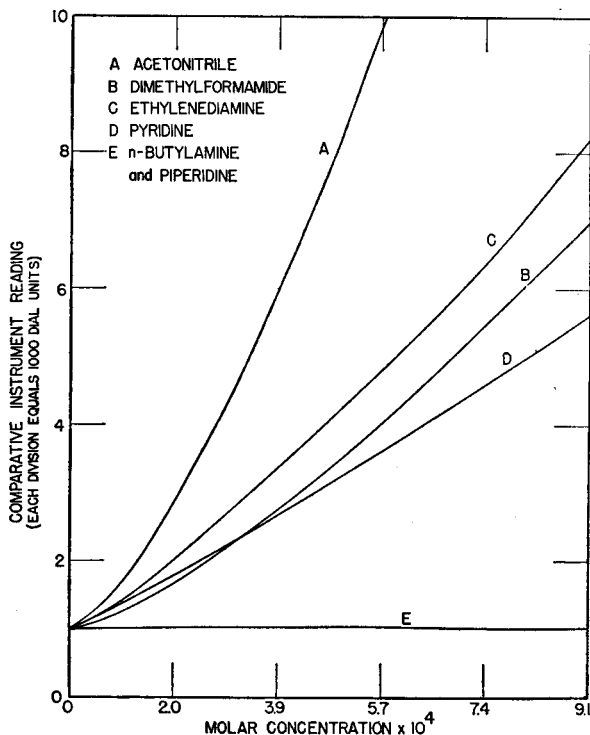


FIG. 1. HF response curves for ammonium iodide.

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.

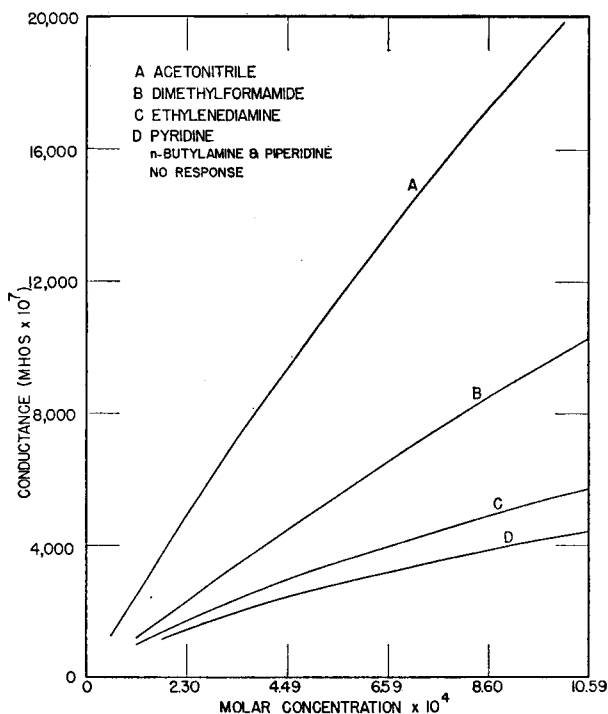
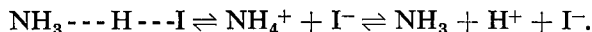


FIG. 2. Conductance curves for ammonium iodide.

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



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

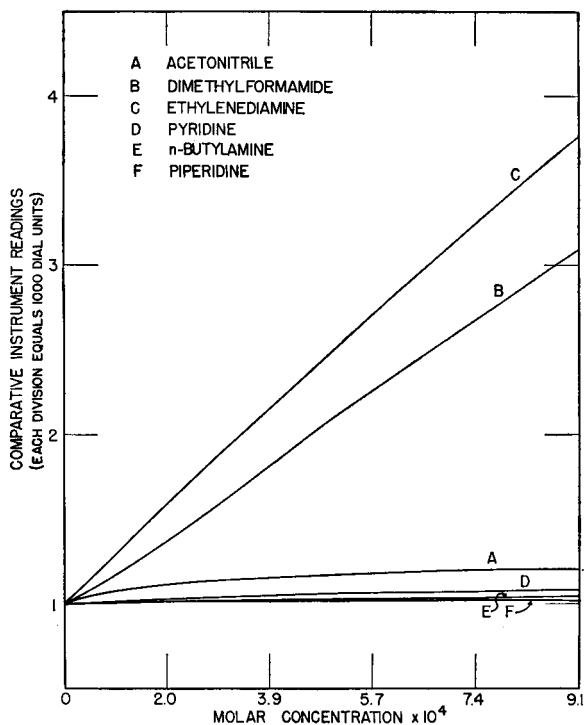


FIG. 3. HF response curves for 3:5-dinitrobenzoic acid.

dielectric constants.<sup>15</sup> The lack of response of conductance when this acid was added to acetonitrile may be due to the formation of a strongly bound complex.

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.<sup>4</sup>

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.

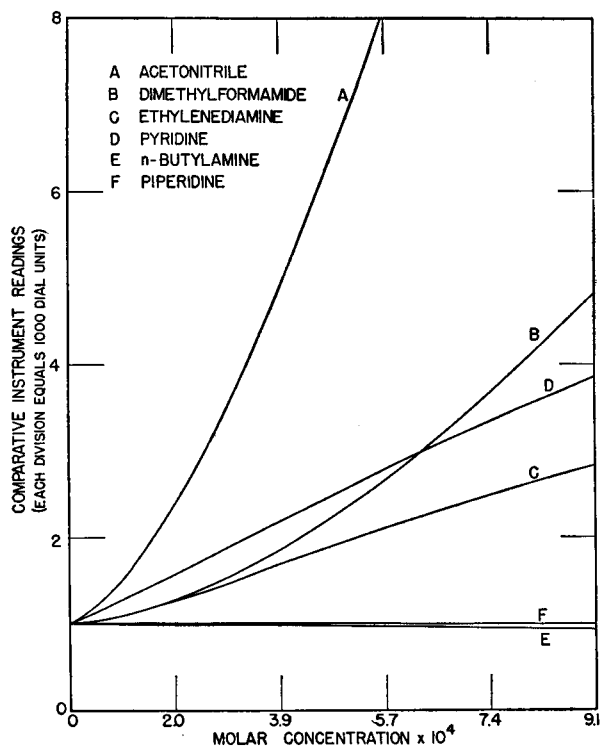
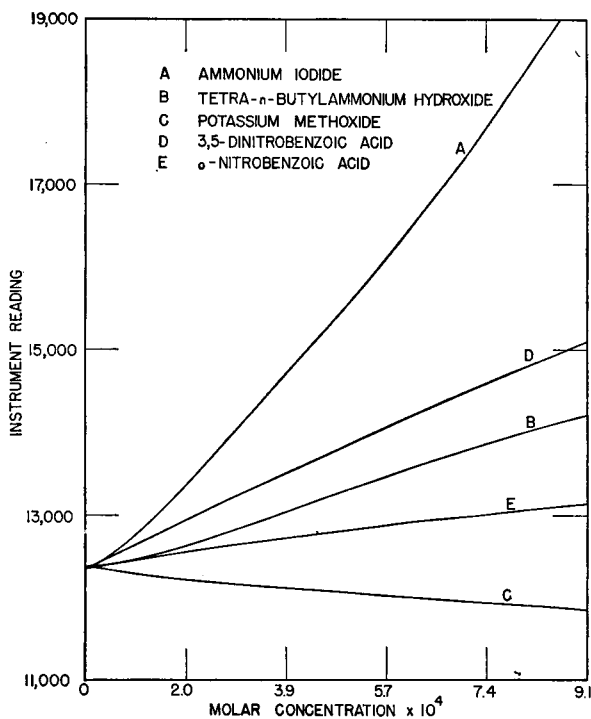


FIG. 5. HF response curves for tetrabutylammonium hydroxide.

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.<sup>17</sup> However, the negative slope for the

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		<i>o</i> -Nitrobenzoic acid		Tetrabutylammonium acid		Potassium methoxide	
	$\rho$	pKb	$\epsilon$	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
<i>n</i> -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.

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.

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<sup>1</sup> in their work with phenols, and Maryott<sup>11</sup> 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

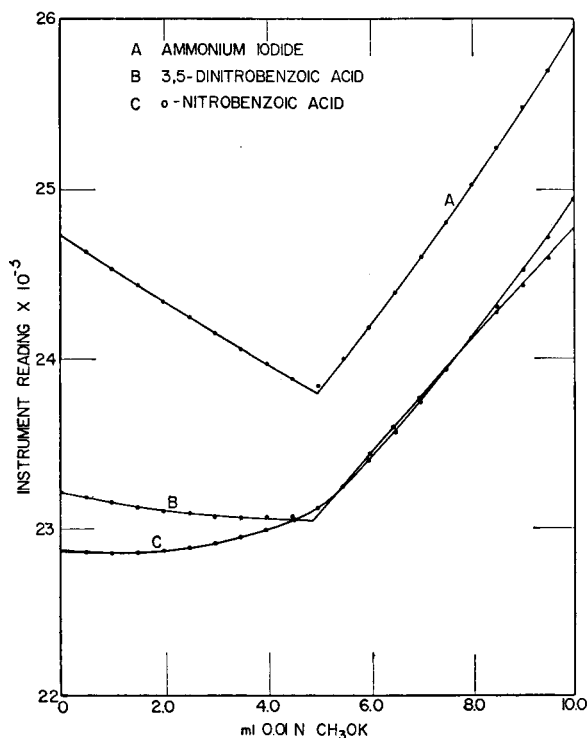


FIG. 6. HF titrations in dimethylformamide.

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.

*Acknowledgement*—The authors wish to acknowledge the help and advice received from Dr. R. B. Scott of the University of Alabama during the time this work was in progress.

**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 Leitfähigkeits-titrations 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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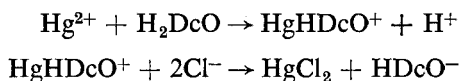
## MICRODETERMINATION OF CHLORIDE IN WATER

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(Received 30 June 1960)

**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  $\mu\text{g}$  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.<sup>1-6</sup> This method involves the following fundamental reactions:



where  $\text{H}_2\text{DcO}$  and  $\text{HDcO}^-$  represent, respectively, the molecule and the anion of diphenylcarbazone, and  $\text{HgHDcO}^+$  the coloured complex cation with mercury.<sup>2-7</sup> In the presence of an excess of diphenylcarbazone, an inner complex salt of the type  $\text{Hg}(\text{HDcO})_2$  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<sup>3</sup> we have eliminated the influence of copper in a concentration of less than 10<sup>-3</sup>% 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  $\mu\text{g}$  (Fig. 1).

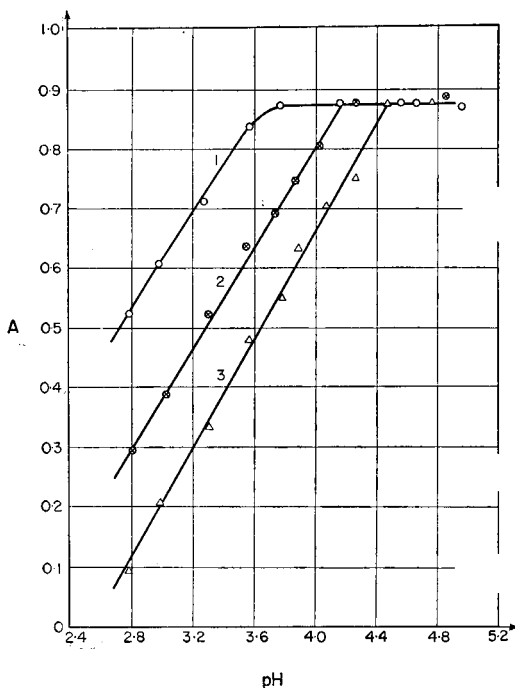


FIG. 1.—Change of absorption with pH for solutions of mercury-diphenylcarbazone complex: 1—in the absence of Cl<sup>-</sup>; 2—in the presence of 25  $\mu\text{g}$  Cl<sup>-</sup>; 3—in the presence of 50  $\mu\text{g}$  Cl<sup>-</sup>.

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.<sup>8</sup> 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  $\mu\text{g}$  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, $\mu\text{g}$	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<sup>II</sup> 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<sup>II</sup> nitrate, 0.01*F*:* Dissolve 1.083 g of pure mercury<sup>II</sup> 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  $\text{m}\mu$ . 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  $\mu\text{g}$  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<sup>II</sup> nitrate solution. After dilution to 50 ml, bring the solution to a constant temperature (*e.g.* 20°) and measure its absorption at 520  $\mu\text{m}$ . 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  $\mu\text{g}$  of chloride ion. The calibration curve is linear within the range 0 to 60  $\mu\text{g}$  of chloride ion.

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

Chloride ion, added, $\mu\text{g}$	Chloride ion found, $\mu\text{g}$	Standard deviation, $\mu\text{g}$	Coefficient of variation, %	Accuracy, $\mu\text{g}$
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, $\mu\text{g}$	Chloride ion found, $\mu\text{g}$	Difference, $\mu\text{g}$	Remarks
10	12.0	+2.0	50 $\mu\text{g}$ Cu <sup>II</sup> added
25	28.5	+3.5	
50	50.3	+0.3	
10	8.5	-1.5	200 $\mu\text{g}$ Cu <sup>II</sup> added
25	23.5	-1.5	
50	45.0	-5.0	
10	8.5	-1.5	100 $\mu\text{g}$ Ni <sup>II</sup> added
25	24.2	-0.8	
50	49.5	-0.5	
10	8.8	-1.2	100 $\mu\text{g}$ Cd <sup>II</sup> added
25	25.0	0	
50	46.5	-3.5	
10	8.5	-1.5	100 $\mu\text{g}$ Co <sup>II</sup> added
25	26.3	+1.3	
50	51.5	+1.5	
10	10.0	0	100 $\mu\text{g}$ Pb <sup>II</sup> added
25	27.5	+2.5	
50	54.0	+4.0	
10	10.0	0	100 $\mu\text{g}$ Zn <sup>II</sup> 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<sup>II</sup> 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*N* 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  $\pm 1.0 \mu\text{g}$  (Table II). Greater errors are obtained in the presence of interfering cations (Table III). In this case an error of  $5.0 \mu\text{g}$  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  $1.6 \mu\text{g}$  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  $60 \mu\text{g Cl}^-$  waren gegeben. Bei Anwesenheit des Überschusses von Kupfer, Nickel, Kobalt, Zink, Kadmium und Blei soll man diese Kationen durch  $\text{CHCl}_3$ -Extraktion als Diphenylkarbazonaten beseitigen.

**Résumé**—Une méthode indirecte pour la détermination des ions de chlorure est présentée: on exploite la diminution de la densité optique du complexe de mercure avec diphenylcarbazone en présence des ions du chlorure. On a étudié l'influence de pH et de la température, en précisant les conditions dans lesquelles il est possible de déterminer de 10 à  $60 \mu\text{g de Cl}^-$ . Cuivre, nickel, cobalt, zinc, cadmium et plomb peuvent être extraits sous la forme des diphenylcarbazonates.

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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 alkoxy 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 alkoxy groups is still based on Zeisel's classical method,<sup>1</sup> an iodometric procedure<sup>2</sup> 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,<sup>11,12</sup> developed recently for the quantitative determination of substances in the vapour phase, has been used to study certain stages of the alkoxy determination. Milligram-quantities of the lower alkyl iodides can be trapped quantitatively in liquid nitrogen<sup>11</sup> 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<sup>35</sup> 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.

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

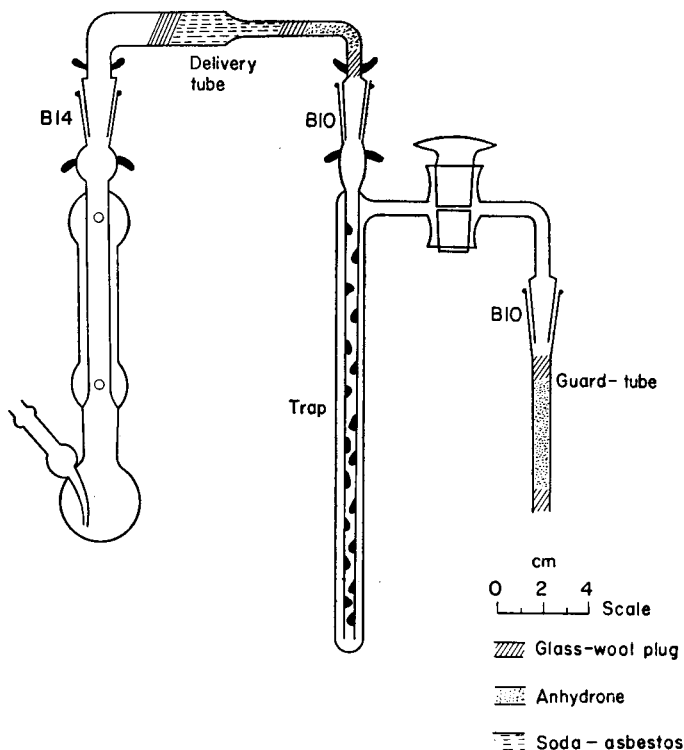


FIG. 1. Assembled apparatus.

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.

*Anhydrous calcium chloride*: 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 anhydrous calcium chloride 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.<sup>11</sup> 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

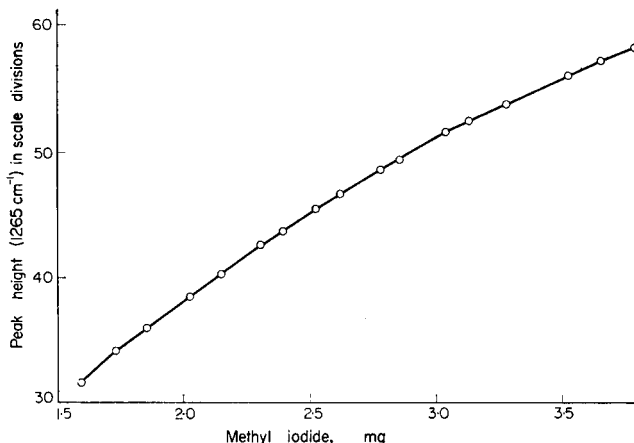


FIG. 2. Calibration curve for determination of methyl iodide.

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.

### Weighing of samples

For solids, a long-handled weighing-spoon<sup>10</sup> was used. Volatile liquids were conveniently weighed in a long-handled micro weighing-bottle<sup>10</sup> 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<sup>13</sup> still report difficulty with "bumping", although electrical heating was earlier reported to be advantageous.<sup>14</sup>

### 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<sup>7</sup>,<sup>15</sup> and 25<sup>8</sup> 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<sup>8</sup> (25 ml per min) and by Inglis<sup>9</sup> (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<sup>10</sup> 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.	Alkoxy 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
$\alpha$ -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,<sup>16</sup> and the addition of a few drops of this concentration to the constant-boiling acid suggested.<sup>5</sup> Reflux for 30 min over red phosphorus before use has been recommended.<sup>6,17</sup> 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<sup>4</sup> stated that the use of fresh colourless acid was essential. Steyermark,<sup>18</sup> however, found that the colour was not critical if the acid was refluxed before use: more recently it was observed<sup>19</sup> that the presence of free iodine in the hydriodic acid was in fact advantageous. Belcher<sup>7</sup> 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,<sup>8</sup> 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<sup>20</sup> which liberate alkyl iodides continuously for several hours.

### 3. Determinations on volatile liquids

Earlier investigations found double distillation<sup>9,18,21</sup> or the use of modified apparatus<sup>8</sup> 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 alkoxy 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 alkoxy 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.<sup>22,23</sup>

An interaction between hydrogen sulphide and alkyl iodides, resulting in mercaptan formation,<sup>1,24</sup> is considered to cause the low results; Bethge and Carlson<sup>25</sup> 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: alkoxy 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<sup>10</sup> that aqueous sodium thiosulphate is unsatisfactory because of reaction with methyl iodide.<sup>26,27</sup> 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.*,<sup>10</sup> 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  $42^\circ \pm 1^\circ$ , but this adds a complicating factor to the scrubber design. Moreover, whilst heated scrubbing solutions have been recommended,<sup>1,6,28</sup> Colson<sup>21</sup> 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,<sup>23,29</sup> 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.<sup>30</sup>

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 =  $20^{\circ} \pm 1^{\circ}$ .

† 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<sup>30</sup> found a preliminary water scrubber essential (to remove hydrogen iodide vapour), since otherwise the scrubber acidity increased

\* 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.<sup>26,27</sup>

Many other aqueous scrubbers have been proposed, *e.g.* red phosphorus suspensions,<sup>1,2,4,28</sup> solutions of organic compounds,<sup>27</sup> acetic acid<sup>8</sup> and hydrochloric acid.<sup>25</sup> 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.*<sup>10</sup> 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.*,<sup>31</sup> but their use in alkoxy determinations attracted little attention until recently.<sup>13,32,33,34</sup>

We have found soda-asbestos (M.A.R.) to be a very efficient solid scrubber, although Večera and Spěvák<sup>34</sup> 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	∴ Alkoxy present, <i>mEquivs</i>	Wt. of sodium sulphate added, mg	∴ Sulphur present, <i>mEquivs</i>	Range of alkoxy 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 alkoxy determinations in which the standard gravimetric or iodometric finish is employed.

Details of the investigation of reaction conditions for determination of propoxy and butoxy groups, of the differentiation of ester from ether groups, and of the infrared method for analysis of compounds containing methoxy and ethoxy groups will be given shortly in further parts of this series.

*Acknowledgements*—We thank Professor E. L. Hirst, C.B.E., F.R.S., for his interest; the Carnegie Trust for the award of a Scholarship (to J. L. D.); Messrs. I.C.I. Ltd., and the Rockefeller Foundation for research grants; and Messrs. I.C.I. (Dyestuffs Division) Ltd., for supplying zone-refined vanillin.

**Zusammenfassung**—Eine empfindliche Infrarotmethode zur quantitativen Bestimmung von Dämpfen wurde verwendet um die Reaktionsvariablen der Alkoxybestimmung nach Zeisel zu studieren. Verschiedene Widersprüche in der Literatur wurden klargestellt. Die Reaktionsbedingungen 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 wässrigen Lösung und gibt exzellente 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 alkoxy 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'amianté 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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(Received 6 July 1960)

**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,<sup>1</sup> and an examination of the one most used is described in associated papers.<sup>2–4</sup> Colorimetric procedures have been described by Sandell<sup>7</sup> and current methods are surveyed in a review article.<sup>8</sup>

### *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<sup>9,10</sup> 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.<sup>11</sup> The most recent of these methods<sup>10</sup> 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<sup>12-14</sup> or isobutyl acetate,<sup>15</sup> extraction of ferric thiocyanate with amyl alcohol-ether,<sup>16</sup> extraction of the iron-sodium diethyldithiocarbamate complex with chloroform<sup>15</sup> and selective extraction of aluminium oxinate in the presence of EDTA after first converting the iron to ferrocyanide.<sup>17</sup>

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.<sup>18</sup> Using this procedure Rooney<sup>15</sup> 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<sup>19</sup> 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,<sup>20</sup> 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.<sup>19,20-32</sup> 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,<sup>19</sup> by extraction with an organic solvent of the iron cupferrate,<sup>13-16,25</sup> the oxinate<sup>10</sup> or the 8-hydroxyquinaldinate,<sup>31</sup> or by fusion with sodium carbonate.<sup>24</sup>

Using the method of Scholes and Smith,<sup>19</sup> 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,<sup>29</sup> Jean,<sup>28</sup> and Fogelson *et al.*<sup>25</sup> 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  $-1.7$  V (vs. S.C.E).<sup>33</sup> 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<sup>34</sup> 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.<sup>1-4,15,18,19,35,36</sup>

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.*<sup>37</sup> and others<sup>5,6,38,39</sup> 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.<sup>15</sup> The polarograph used was a Tinsley MK.15 model with the following centre settings:—

sensitivity	4 $\mu$ A 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  $\mu$ g, 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  $\mu$ A 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,<sup>12,13,16,32,40-46</sup> alizarin S,<sup>47-50</sup> morin,<sup>51,52</sup> quercetin,<sup>53</sup> haematoxylin<sup>54,55</sup> Eriochrome Cyanine R,<sup>10,14,51,56-62</sup> oxine,<sup>17,24,27,63</sup> cupferron,<sup>29</sup> quinizarin sulphonic acid,<sup>64</sup> stilbazo<sup>28</sup> and arsenazo.<sup>65</sup>

In addition, two other reagents which, like Eriochrome Cyanine R are hydroxy-triphenylmethane dyes, have been proposed<sup>66</sup> 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.<sup>51</sup> It forms a red-violet complex in an acetate buffer solution, and has been shown to be superior to aluminon,<sup>11</sup> especially with respect to complex formation at room temperature and stability to temperature change. Richter<sup>59</sup> 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<sup>10,14,19,56,57,61,62</sup> are convinced that a pH value nearer to 6 is the optimum for colour development.

Hill<sup>10</sup> 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.<sup>19</sup>

A cell similar to the one described by Center *et al.*<sup>67</sup> 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<sup>2</sup>.

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<sup>19,24,27-30,48,67,68</sup> employ an electrolyte containing sulphuric acid, and observe special precautions for the satisfactory deposition of chromium. Hynek and Wrangell<sup>51</sup> 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<sup>13</sup> 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.

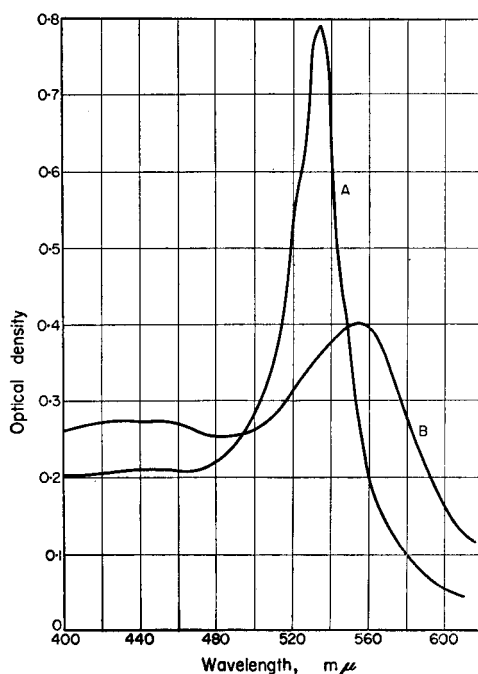


FIG. 1. Absorption spectra for nitrated Solochrome R complexes.  
Curve A. Test solution containing 50  $\mu\text{g}$  of aluminium measured against water.  
Curve B. Test solution containing 200  $\mu\text{g}$  of iron measured against water.

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  $\mu\text{g}$  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  $m\mu$ . In addition, the absorption spectrum of the corresponding iron complex was plotted over the same range and showed a maximum absorption at 556  $m\mu$ . 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.<sup>10,15,19</sup> 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<sup>15</sup> 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  $\mu\text{g}$  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*, 0.2N: Dilute 20 ml of AnalaR grade hydrochloric acid (sp.gr. 1.16) to 1 litre with water.

*Sodium hydroxide*, 2N: 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  $\equiv$  10  $\mu$ g 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 2N sodium hydroxide from a polythene wash bottle. Titrate until colourless with 0.2N 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 m $\mu$ , 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<sup>19</sup> 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  $\mu$ g 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, $\mu\text{g}$	Optical density	Aluminium found, $\mu\text{g}^*$
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 0.5 $\mu\text{g}$ .

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.

*Acknowledgement*—The authors are indebted to the National Coal Board for permission to publish this work.

**Zusammenfassung**—Eine Methode für 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 Volumen gebracht und aus einem Aliquot wird das verbliebene Eisen, zusammen mit Vanadin und Titan durch Extraktion als Kupferronat entfernt. Nach Zerstörung des überschüssigen Kupferrons wird die Lösung neutralisiert und ein Säureüberschuss zugegeben. Sodann wird der Aluminiumkomplex des nitrierten Solochrome 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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(Received 9 July 1960)

**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<sup>1</sup> 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:

$$P_r = G_r - J(Q_r - G_r) - J^2(Q_r - G_r - Q_r^d) \quad (1)$$

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

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

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

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

$P_r$  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.<sup>2,3</sup>

$Q_r$  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

$$u = U/(U + V + W) \quad (3a)$$

$$v = V/(U + V + W) \quad (3b)$$

$$w = W/(U + V + W) \quad (3c)$$

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:

$$J = E \cdot C \cdot l \quad (4)$$

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 similarity 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

$$J = (U + V + W) \times \kappa. \quad (5)$$

$\kappa$  is constant, having the numerical value  $2.303/3.1616 = 0.72843$  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.<sup>1</sup> Then the coefficient  $E$ , which may be called the overall absorptivity, is related to the equivalent parameter  $\varepsilon$  (extinction coefficient) in the Lambert-Beer law by the relationship  $\sum K_r \cdot \varepsilon_i = E$ , 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  $J^2 \cdot Q_r^d$  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<sup>II</sup> and nickel<sup>II</sup> 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<sup>II</sup>.

#### 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

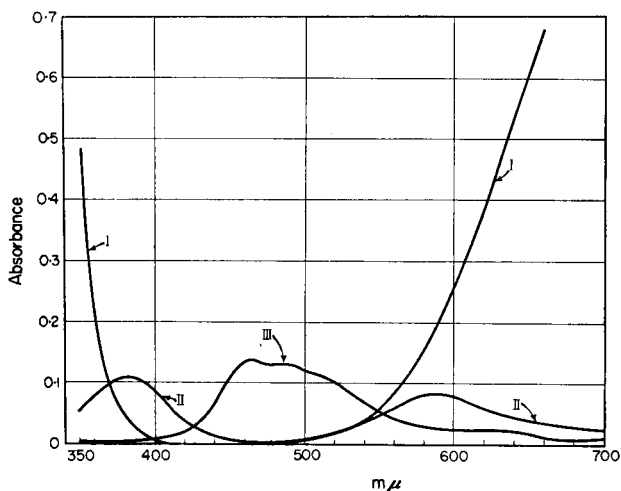


FIG. 1. Absorbance curves of the EDTA-complexes of I, Cu; II, Ni; III, Co.

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.

By employing the ten selected ordinate method, the complementary colour points,  $Q_c$ , for the two (pure) colorants can be calculated from the absorbance curves in Fig. 1. For the copper-EDTA complex under the prevailing conditions,  $u = 0.616$  and  $v = 0.377$ , and for the nickel complex  $u = 0.465$  and  $v = 0.429$ . 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  $m\mu$  and for the  $v$ -range, 580, 590, 600, 610, and 620  $m\mu$ . 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

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

$$U = 0.511$$

$$V = 1.323$$

$$W = 0.007$$

$$J = U + V + W = 1.841$$

$$u = U/J = 0.2776$$

$$\text{Check } u + v + w = 1$$

$$v = V/J = 0.7184$$

$$E = J/Cl = 1.841/10 = 0.1841$$

$$w = W/J = 0.0040$$

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

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  $U = 0.511$  and that for the  $v$ -range,  $V = 1.325$ . According to the definition of complementary tri-stimulus colorimetry and equation (5) with  $W = 0$ , the sum of the

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

$$J = (U + V) \kappa = 0.511 + 1.325 = 1.834.$$

The constant  $\kappa$  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 0.1M 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  $E_{\text{Cu}} = J/C = 1.834/10 = 0.1834$  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,  $u = U/J = 0.511/1.834 = 0.2786$  and  $v = V/J = 1.325/1.834 = 0.7214$ . 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

\* The numerical value of  $\kappa$  in the present case (when related to the hypothetical eye) would be 2.303/15 = 0.15353 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 m $\mu$ . 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).

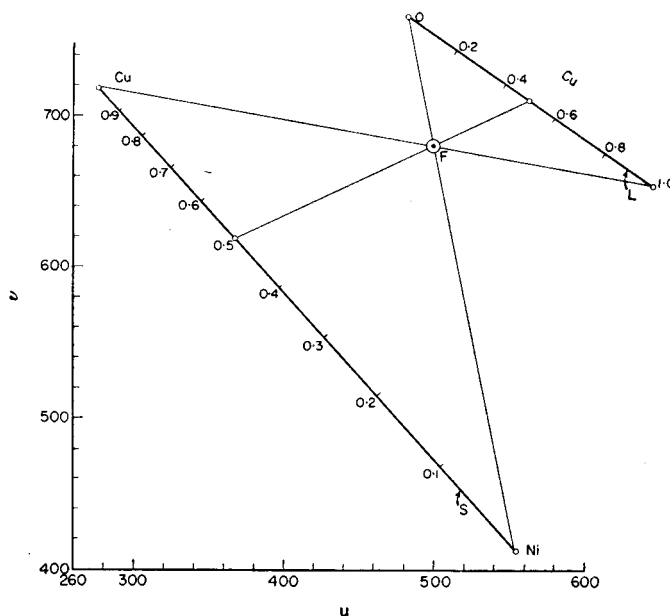


FIG. 2.  $u$ - $v$  Plot containing the linear and non-linear calibration for the binary system Cu-Ni.

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

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

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:

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

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

$$q = C_a/(C_a + C_b) \quad (8)$$

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

For unit concentration the following formula is valid

$$U_{a,1} = u_a \cdot E_a \quad (9)$$

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:

$$u_m = \frac{q \cdot u_a \cdot E_a + (1 - q) \cdot u_b \cdot E_b}{q \cdot E_a + (1 - q) \cdot E_b} \quad (10)$$

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

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

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

$$U_a = C_a \cdot u_a \cdot E_a \quad (12)$$

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)

$$u_m' = (U_m + U_m') / (U_m + V_m + W_m + U_m' + V_m' + W_m') \quad (13)$$

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

$$q = C_a / (C_a + C_b) \quad (14)$$

$$q' = (C_a + C_a') / (C_a + C_b + C_a' + C_b') \quad (14a)$$

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  $q = 0.1$  and  $q = 0.2$  will *not* equal in general the distance between  $q = 0.8$  and  $q = 0.9$ . 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

$$E_a = U_a + V_a + W_a \quad (15)$$

$$E_b = U_b + V_b + W_b \quad (16)$$

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

$$p \cdot U_a + V_a + W_a = p \cdot U_b + V_b + W_b \quad (17)$$

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  $q = 0$ ,  $q = 0.5$  and  $q = 1$  on the system line (it should be appreciated that only the point  $q = 0.5$  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:

$$U_m = C_a \cdot u_a \cdot E_a + C_b \cdot u_b \cdot E_b \quad (18a)$$

$$V_m = C_a \cdot v_a \cdot E_a + C_b \cdot v_b \cdot E_b \quad (18b)$$

$$W_m = C_a \cdot w_a \cdot E_a + C_b \cdot w_b \cdot E_b \quad (18c)$$



This set can be written in summation notation:

$$R_{i,m} = \sum_j C_j \cdot r_{ij} \cdot E_j \quad (19)$$

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  $i \geq j$ . 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

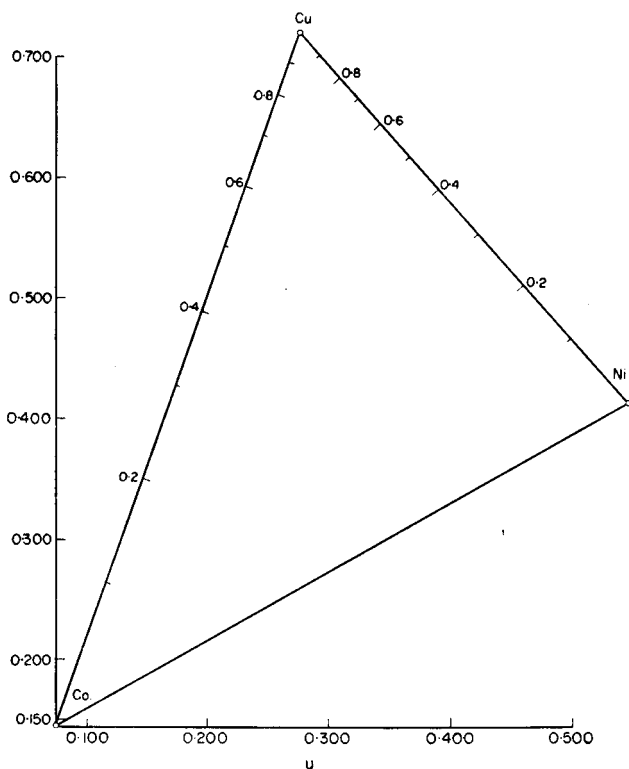


FIG. 3.  $u$ - $v$  Plot containing the calibration triangle for the ternary system Cu-Ni-Co.

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,  $c$ .

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  $C_c \cdot u_c \cdot E_c$ ,  $C_c \cdot v_c \cdot E_c$  and  $C_c \cdot w_c \cdot E_c$ , 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

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

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

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

0.1M 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 0.10M 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 0.10*M* in copper<sup>II</sup>, nickel<sup>II</sup> and cobalt<sup>II</sup> 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 0.4*M* in disodium ethylenediaminetetraacetate and 0.3*M* 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 0.1*M*. 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.

*Acknowledgements*—The author is indebted to A. J. Barnard Jr., Phillipsburg, N.J., for helpful criticism of the manuscript. The author also thanks Messrs. A. L. Chason and A. J. Shingler, The Coca Cola Co., Atlanta, Ga., for arranging use of the Cary recording spectrophotometer of that company and for valuable discussions.

**Zusammenfassung**—Complémentaire 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 Musterbeispiele 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<sup>II</sup> WITH BENZOHYDROXAMIC ACID

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(Received 15 July 1960)

**Summary**—Manganese<sup>II</sup> reacts with benzohydroxamic acid in ammoniacal solution to form a stable reddish-brown complex ( $\lambda_{\max}$  500 m $\mu$ ). 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  $\mu$ g of manganese per cm<sup>3</sup> for log  $I_0/I = 0.001$ ; the spot-plate sensitivity is 0.2  $\mu$ g 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<sup>II</sup> in ammoniacal 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 0.07M to 7M. In solutions exceeding 0.5M 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.<sup>5</sup> The separation is accomplished by adsorption on Dowex-1,8X anion-exchange resin from 12M 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<sup>II</sup>.

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<sup>III</sup> with these acids in dilute hydrochloric acid<sup>2</sup>. Benzohydroxamic acid has been used by Wise and Brandt<sup>8</sup> 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<sup>II</sup>:* 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 m $\mu$ . At this wavelength the complex obeys Beer's law over a manganese

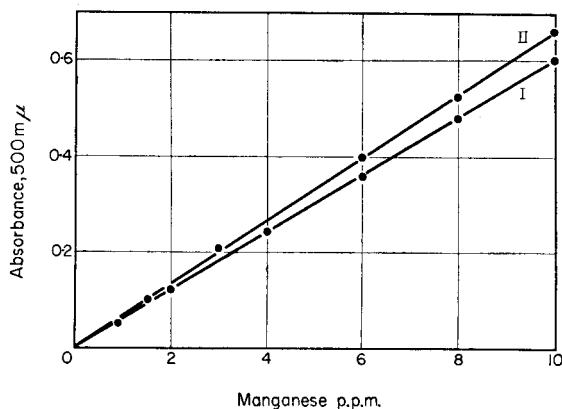


FIG. 1. (I) Mn-complex formed after ion-exchange separation; (II) Mn-complex formed directly from standard manganese solution

concentration range from 0.4 to 10 ppm. The optimum concentration range is 3 to 10 ppm.

The sensitivity is 0.015  $\mu g$  of manganese per  $cm^2$  for  $\log I_0/I = 0.001$ . The molar absorptivity is 3,630.

The spot-plate sensitivity is 0.2  $\mu g$  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 0.5M, 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 0.35M 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<sup>II</sup> 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  $m\mu$  in water, but the addition of dimethylformamide causes a displacement of the absorbance curve below 500  $m\mu$  (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  $m\mu$  and 700  $m\mu$ .

At 360  $m\mu$  and at 500  $m\mu$ , the manganese-complex in DMF obeys Beer's law. At 500  $m\mu$ , 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

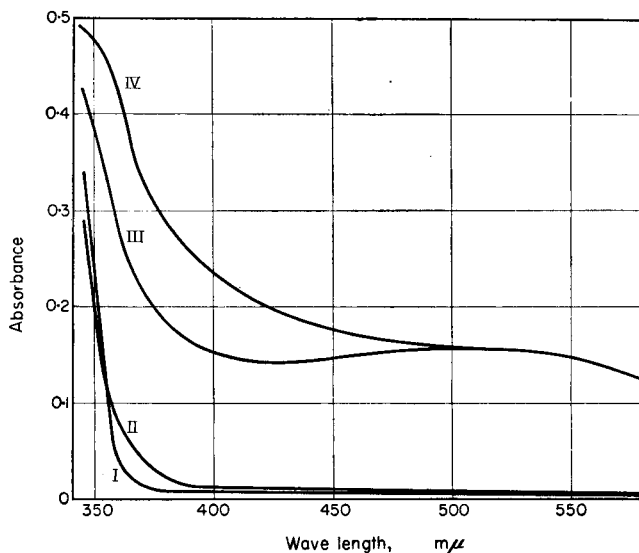


FIG. 2. (I) Benzohydroxamic acid in aqueous ammonia, (II) in ammoniacal dimethylformamide, (III) the Mn-complex in aqueous ammonia, (IV) in ammoniacal dimethylformamide.

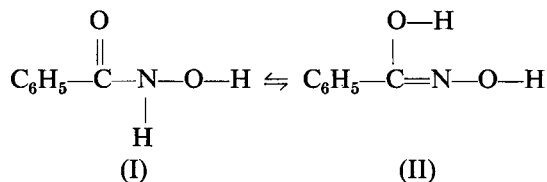
anhydrous system, but the absorbance at 500  $m\mu$  was shown to be independent of the concentration of water in the solvent system from 1 to 100% water. Although the complex follows Beer's law at 360  $m\mu$ , this wavelength is not recommended for three reasons:

- (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  $m\mu$  but do not interfere at 500  $m\mu$ .

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.

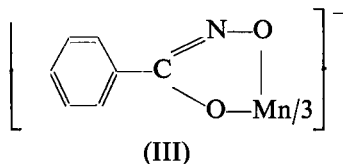
#### STRUCTURE

There are two possible structures of the reagent molecule:

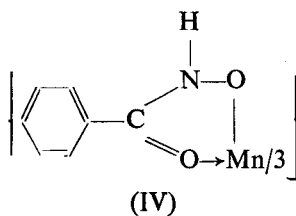


On the basis of an ultraviolet absorption study of several hydroxamic acids, Plapinger<sup>7</sup> concluded that benzohydroxamic acid exists predominately in the keto-form (I). In basic solution, however, it was shown that a considerable portion of the acid exists in the enol-form (II).

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.



If the reaction proceeds through the keto-form, the following structure is possible:



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 ( $\text{CH}_2=\text{N}-\text{OH}$ ) also reacts with manganese<sup>II</sup> to form a manganese<sup>III</sup> complex, whose colour is almost identical with manganese-benzohydroxamic acid complex.<sup>3</sup> Manganese<sup>II</sup> 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<sup>4</sup> 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;<sup>1</sup> consequently, it seems likely that the empirical formula is  $\text{R}_3\text{Mn}$ .

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<sup>II</sup> complexes, in which the six co-ordinate positions of the cobalt are satisfied, is well known.<sup>6</sup> The phenomenon mentioned above can be explained by assuming that the cobalt<sup>II</sup> complex is more easily oxidised than the manganese<sup>II</sup> 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<sup>III</sup> 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<sup>II</sup>, Fe<sup>III</sup>, Co<sup>II</sup> and Cu<sup>II</sup>. Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Be<sup>2+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup>, Sn<sup>2+</sup>, Sn<sup>4+</sup>, Cr<sup>3+</sup>, Pt<sup>6+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>1-</sup>, SO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, SiO<sub>3</sub><sup>2-</sup>, MoO<sub>4</sub><sup>2-</sup> and WO<sub>4</sub><sup>2-</sup> show no interference.

When the ratio of interfering ions to manganese is increased, ions such as aluminium<sup>III</sup> and chromium<sup>III</sup> interfere by precipitating. However, if the weight ratio is decreased to 1:1, the ions listed in Table I can be tolerated. Iron<sup>III</sup> 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<sup>II</sup>, iron<sup>III</sup>, cobalt<sup>II</sup> and copper<sup>II</sup>, these ions were separated from manganese<sup>II</sup> by an ion-exchange technique developed by Kraus and Moore.<sup>5</sup> 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 <sup>a</sup>	Effect on A <sub>s</sub> , ± %
Ni <sup>II</sup>	-1
Ti <sup>III</sup>	+0.5
Cu <sup>II</sup>	+8
Co <sup>II</sup>	+31 after exposure to air
PO <sub>4</sub> <sup>3-</sup>	-0.6

<sup>a</sup> One mg of interfering ion and 0.1 mg of manganese<sup>II</sup> 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  $\mu$ g to 100  $\mu$ g).

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  $m\mu$  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  $\mu$ g 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 m $\mu$ ). 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  $\mu$ g Mn/ccm for  $\log I_0/I = 0.001$ ; Die Empfindlichkeit auf der Tüpfelplatte ist 0.2  $\mu$ g Mn per 0.05 ml. Beer's Gesetz ist hinauf bis zu 10 ppm in 1-cm Absorptionsgefäßen 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, Stabilität 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 m $\mu$ ). 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  $\mu$ g de Mn par cm<sup>3</sup> pour  $\log I_0/I = 0,001$ ; la sensibilité "spot plate" est de 0,2  $\mu$ g 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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(Received 12 August 1960)

**Summary**— $^{192}\text{Ir}$  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  $^{192}\text{Ir}$  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,<sup>1</sup> and (b) the new method of Payne.<sup>2</sup> 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<sup>III</sup> in a sulphuric acid medium. Each separated element is finally determined gravimetrically as the metal.

In the procedure of Payne,<sup>2</sup> 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.*<sup>3</sup>

Ayres and Berg<sup>4</sup> have pointed out some of the difficulties inherent in the precipitation separations and gravimetric determinations. These workers<sup>5</sup> have used spectrographic methods to study the separation of palladium with dimethylglyoxime from platinum, iridium and rhodium. Ayres and Maddin<sup>6</sup> have reported a similar investigation of the separation of rhodium from iridium by the reduction of the rhodium in solution to metal, using titanium<sup>III</sup> as reducing agent.

### EXPERIMENTAL

#### *Reagents*

$^{192}\text{Ir}$  tracer was supplied as  $(\text{NH}_4)_2\text{IrCl}_6$  in hydrochloric acid solution from the Radiochemical Centre, Amersham. The material was of high specific activity—250 millicuries  $^{192}\text{Ir}/\text{g}$  of iridium. Nuclear data for  $^{192}\text{Ir}$  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  $H_2RhCl_6$  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.<sup>7</sup>

The concentrations of the respective platinum metals in the stock solutions were confirmed by gravimetric analysis.<sup>8</sup>

TABLE I.—NUCLEAR DATA FOR IRIIDIUM-192  
HALF-LIFE: 74.4 DAYS

Type of radiation	$\beta^-$	EC	$\gamma$
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 IRIIDIUM 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.<sup>1</sup> In runs G3–6 (Table II) the reduction of rhodium by titanium<sup>III</sup> chloride was followed potentiometrically using the technique of Ayres and Maddin.<sup>5</sup> This enabled the amount of excess titanium<sup>III</sup> 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.<sup>9</sup>

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)  $\gamma$ -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  $^{192}\text{Ir}$  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

TABLE III.—SEPARATION OF RHODIUM AND PLATINUM FROM IRIIDIUM 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

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.

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.<sup>2</sup>

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.<sup>6</sup>

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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- <sup>4</sup> G. H. Ayres and E. W. Berg, *Analyt. Chem.*, 1952, **24**, 465.
- <sup>5</sup> *Idem*, *ibid.*, 1953, **25**, 980.
- <sup>6</sup> G. H. Ayres and C. M. Maddin, *ibid.*, 1954, **26**, 671.
- <sup>7</sup> D. N. Sunderman and W. W. Meinke, *ibid.*, 1957, **29**, 1578.

## SHORT COMMUNICATIONS

### Effect of chloride ions on the determination of nitrate by Leithe's method

(Received 30 July 1960)

DURING an ion-exchange study<sup>1</sup> requiring exact nitrate determinations, we attempted to use the method developed by Leithe,<sup>2</sup> based on the reduction of the nitrate by iron<sup>II</sup> sulphate and titration of the excess of iron<sup>II</sup> sulphate with potassium dichromate, using ferroin 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

1N HCl, ml added	0	3	4	5	10	15	20	150
0.1N K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , 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<sup>II</sup> sulphate used was about 0.1N and not 0.2N. 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 ferroin as an indicator for the titration of iron<sup>II</sup> 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 ferroin decreases from 1.06V to 0.76V while that of dichromate rises<sup>3</sup> 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<sub>4</sub> 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<sup>II</sup> 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.<sup>2</sup>

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 1N hydrochloric acid between 3 and 15 ml have the greatest influence, yet no stoichiometric relation exists between hydrochloric acid and iron<sup>II</sup> sulphate. It can also be concluded from these experiments that the chloride ions react with the iron<sup>II</sup> 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<sup>III</sup> 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<sup>II</sup> with dichromate in 1–2N hydrochloric acid.

An attempt was made to find the theoretical reason for the chloride effect. A possibility taken

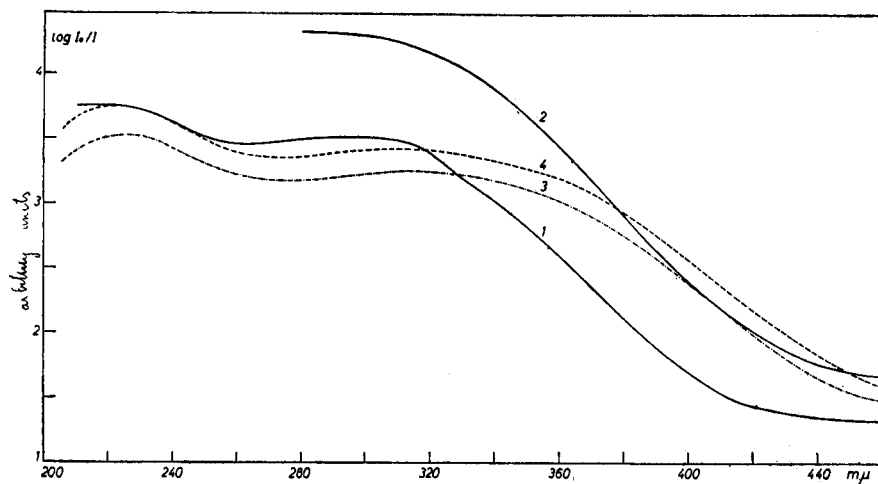


FIG. 1. Absorption spectra of iron solutions in 50%  $H_2SO_4$ :

1. 25 ml 0.1M  $FeSO_4$  + 25 ml  $H_2O$ .
2. 25 ml 0.1M  $FeSO_4$  + 25 ml 1N HCl.
3. 0.6 ml 0.1M  $FeCl_3$  + 25 ml 1N HCl + 24.4 ml  $H_2O$ .
4. 0.8 ml 0.1M  $FeCl_3$  + 25 ml 1N HCl + 24.2 ml  $H_2O$ .

TABLE II.—EFFECT OF CHLORIDE CONCENTRATION ON NITRATE DETERMINATIONS

$NO_3^-$ , mg present	1N HCl, ml added	0.1N $K_2Cr_2O_7$		$NO_3^-$ , 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<sup>II</sup> and chloride ions. Such complexes are known to exist and three species are cited,  $[FeCl]^+$ ,<sup>4,5</sup>  $[FeCl_3]^-$ , and  $[FeCl_4]^{2-}$ .<sup>6</sup> 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<sup>II</sup> 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<sup>III</sup> 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.<sup>6</sup> 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<sup>III</sup> by air may occur, but the absorption spectra obtained from these solutions did not show the presence of iron<sup>III</sup> ions (Fig. 1). Potentiometric titrations (using a Beckman H-2 pH meter with a platinum electrode) of iron<sup>II</sup> 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<sup>III</sup> 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  $\pm 1\%$ .

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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<sup>II</sup> 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 Äquivalenzpunkt 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 Abwesenheit 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 méthode 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 à analyser doivent contenir la même quantité des ions chlore.

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## 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,<sup>1</sup> 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 this 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.<sup>1</sup> 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

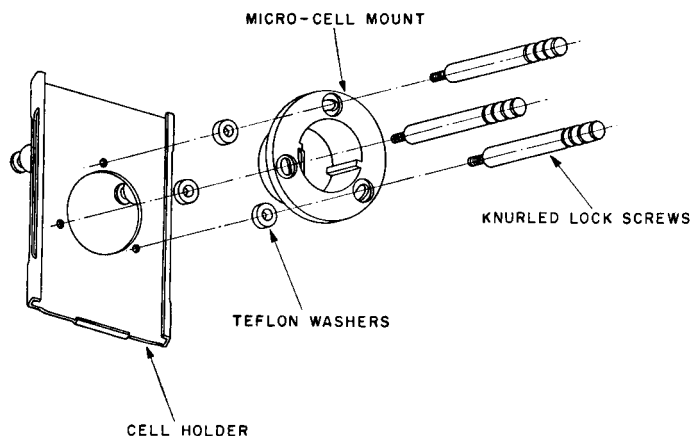


FIG. 1.

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.

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  $2500\text{ cm}^{-1}$  ( $4\ \mu$ ), 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.

\* 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  $4\ \mu$ , 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.

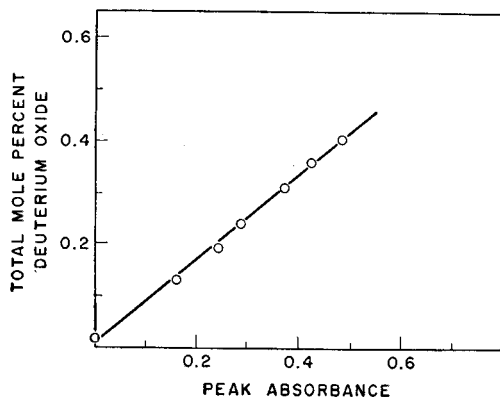
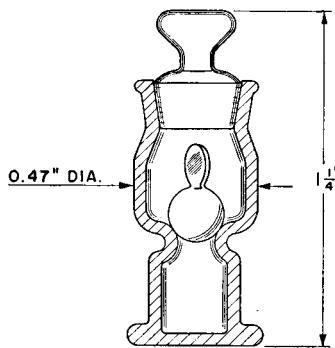


FIG. 2.



WEIGHING BOTTLE

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  $3.5\ \mu$  to  $4.5\ \mu$  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

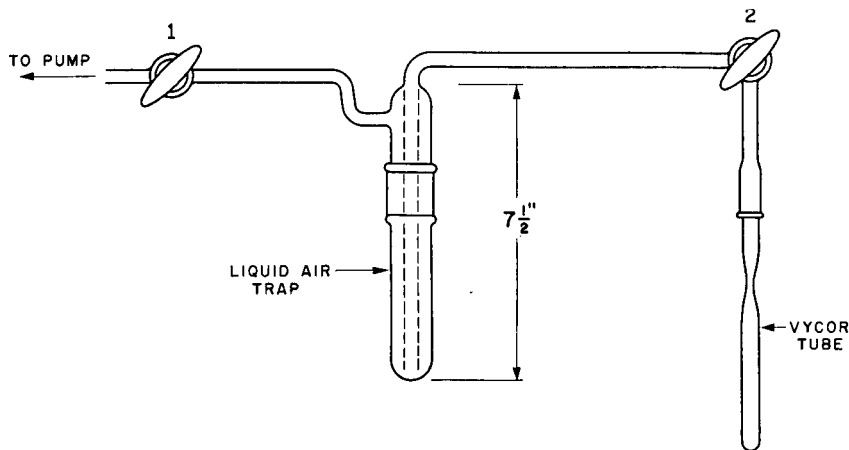


FIG. 4.

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.

Using these weighing and transfer techniques it has been found possible to obtain satisfactory analyses of *cyclo-pentanone- $\alpha$ ,  $\alpha$ - $d_4$*  (b.p.  $760\text{mm}$ ,  $160^\circ$ ) and *diacetyl- $d_6$*  (b.p.  $760\text{mm}$ ,  $88^\circ$ ), 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.

**Zusammenfassung**—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.

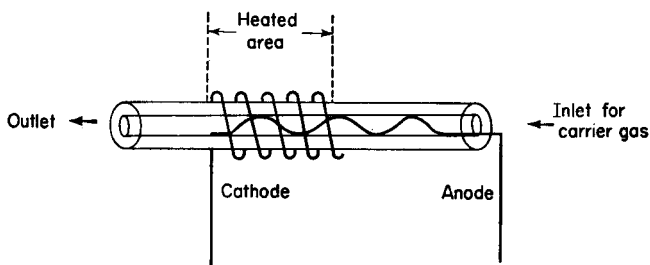
## LETTER TO THE EDITOR

### 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°.

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  $\mu\text{g}$  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  $245 \pm 10$  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.

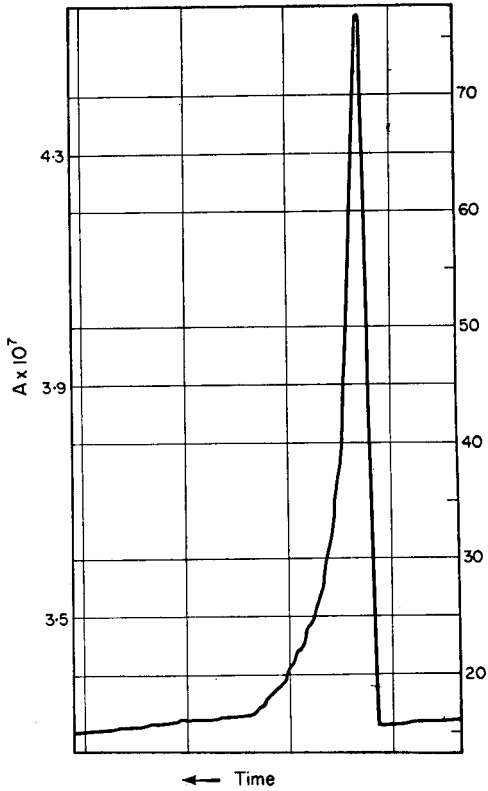


FIG. 2.

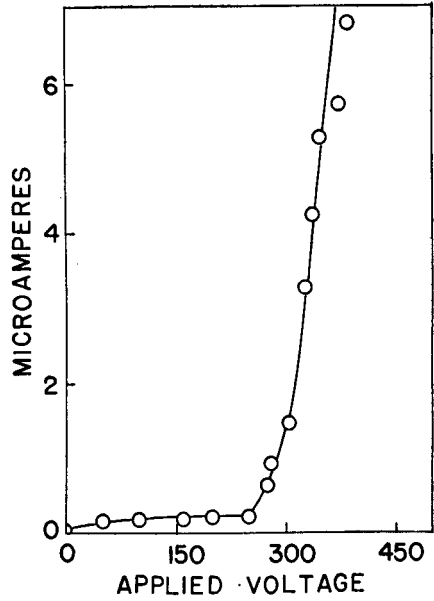


FIG. 3.

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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GERALD J. PAPARIELLO

## 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).

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

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122 EAST 55TH STREET, NEW YORK 22, N.Y.

Printed in Northern Ireland at The Universities Press, Belfast