

An International Journal of Analytical Chemistry

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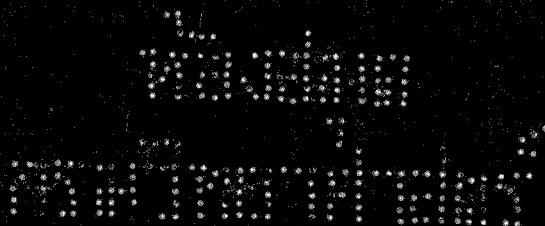
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1. Belcher, R. and Ingram, G., *Analyt. Chim. Acta*, 1950, **4**, 118, 401
2. Clark, S. J., "Quantitative Methods of Organic Analysis", pp42-76, Butterworth's Scientific Publications, 1956

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1. Whitehead, T. H., *J. Chem. Educ.*, 1959, **36**, 297
2. Williams, T. R. and Harley, J. D., *Chemist-Analyst*, 1961, **50**, 114
3. Davies, M. T., *Analyst*, 1959, **84**, 248

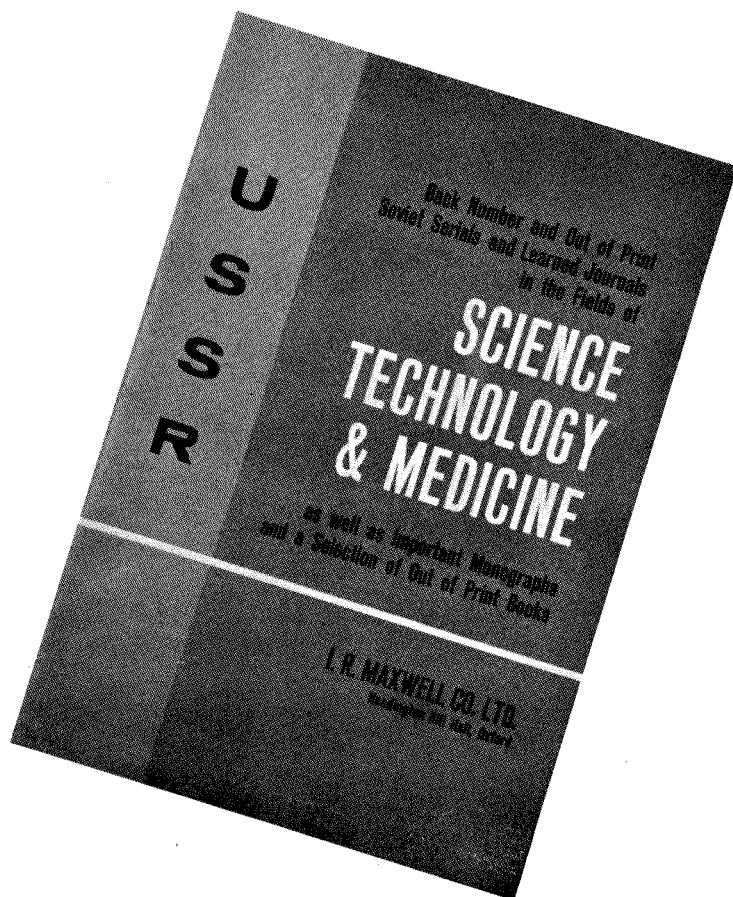
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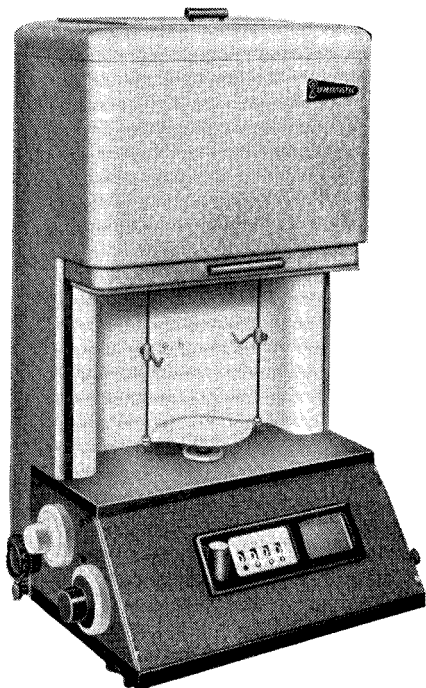
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**Reaction of cadmium with oxine:** ROGER D. WHEALY and B. J. BLAND. *Talanta*, 9, 823.

**Summary**—The stepwise reaction of cadmium with oxine has been studied and equilibrium constants calculated by polarographic and gravimetric methods.

**Determination of antimony in lead by neutron activation analysis:** F. ADAMS and J. HOSTE, *Talanta*, 1962, 9, 827.

**Summary**—Activation analysis of antimony in lead has been studied in the concentration range of 10.03%. Gold is used as a standard so as to avoid self-shielding problems of the antimony standard. The proposed technique is possible by making use of net photospectra and computing the antimony content directly from the ratio of the 0.40- and 0.56-gamma peaks of  $^{198}\text{Au}$  and  $^{122}\text{Sb}$ .

**Ammonium hexanitratocerate(IV) as an oxidising agent:** G. GOPALA RAO, P. V. KRISHNA RAO and K. S. MURTY, *Talanta*, 1962, 9, 835.

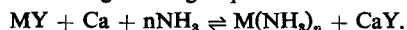
**Summary**—The use of ammonium hexanitratocerate(IV) in oxidimetry has been very little studied, although the salt can be obtained in a high degree of purity. Conditions have now been established for the titration of oxalic and mandelic acids with this reagent at room temperature in a nitric or hydrochloric acid medium using ferroin as indicator. The procedures developed give precise results and they constitute definite improvements over those involving cerium<sup>IV</sup> sulphate.

**Identification of polyatomic anions by infrared spectroscopy:** FARAJ R. HABA and CECIL L. WILSON, *Talanta*, 1962, 9, 841.

**Summary**—Mixtures of ferrocyanide, ferricyanide and cobalticyanide, and of chromate, vanadate and sulphate, may be identified by the characteristic infrared spectra of the anions. The relation between the intensity of the band and the concentration of anion enables quantitative measurements to be made on microgram amounts.

**Quantitative treatment of exchange equilibria involving complexans—I:**  
GENKICHI NAKAGAWA and MOTOHARU TANAKA, *Talanta*, 1962, 9,  
847.

**Summary**—In order to find optimum conditions for the indirect polarographic determination of calcium, a quantitative consideration is made of the following exchange equilibrium:



The use of Cd-EGTA is proposed for the selective determination of calcium in the presence of a large excess of magnesium.

**Potentiometric determination of vanadium<sup>IV</sup> with cerium<sup>IV</sup> sulphate at room temperature:** L. S. A. DIKSHITULU and G. GOPALA RAO, *Talanta*, 1962, 9, 857.

**Summary**—The use of orthophosphoric acid as a catalyst has enabled the potentiometric titration of vanadium<sup>IV</sup> to be carried out with cerium<sup>IV</sup> sulphate in 1.0–2.0*N* sulphuric acid medium at room temperature. Using the same catalyst a method has also been developed for the simultaneous differential potentiometric titration of iron<sup>II</sup> and vanadium<sup>IV</sup> with cerium<sup>IV</sup> sulphate in a sulphuric acid medium; this method is more satisfactory than the procedure described by Furman because the first potential break is quite marked and it is more convenient because it avoids the high temperature required for the second stage of the titration in the Furman procedure. Chromium<sup>III</sup> and iron<sup>III</sup> do not interfere in these titrations.



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

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

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

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# A CRITICAL EXAMINATION OF METHODS USED FOR THE DETERMINATION OF AVAILABLE OXYGEN IN HIGHER METAL OXIDES

D. A. PANTONY and A. SIDDIQI

Department of Metallurgy, Imperial College, London S.W.7, England

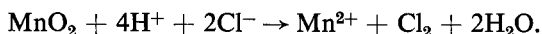
(Received 13 June 1961. Accepted 23 May 1962)

**Summary**—Careful examination of the Bunsen, oxalate, iodide and ferrous methods used in the determination of available oxygen in manganese and cobalt oxides has shown that the last three methods invariably give high results while the Bunsen method, when suitably modified, gives accurate results. It is suggested that the discrepancy between the Bunsen and other methods is caused by an adsorbed monolayer of oxygen upon the surface of the oxides examined.

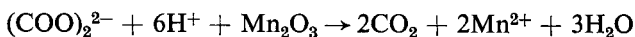
## INTRODUCTION

AVAILABLE oxygen (*i.e.* the percentage of excess oxygen above that required by the lowest stable valency state) in certain metal oxides can be determined by at least five standard methods, none of which offers simultaneously the advantages of speed, accuracy, precision, and convenience of operation:—

(1) *Bunsen's method.* The sample is heated in concentrated hydrochloric acid and the liberated chlorine collected in potassium iodide. The resulting iodine is titrated with standard thiosulphate:

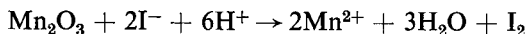


(2) *Oxalate method.* The higher oxides are digested with a dilute sulphuric acid solution of excess sodium oxalate until decomposition is complete, *e.g.*



and the excess oxalate is back titrated with standard permanganate. The method is satisfactory for most mineral manganese oxides, but fails inexplicably with some.

(3) *Direct iodide method.* This method, which is applicable only to finely-ground chemically pure oxides containing cations which do not form insoluble iodides or sulphates, is based upon reactions of the type:



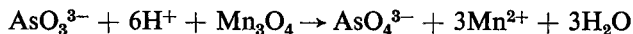
and the liberated iodine is titrated with standard thiosulphate.

(4) *Ferrous method.* The essential reaction is, for example:



followed by a back titration of excess ferrous ions with standard permanganate or, better, dichromate. The decomposition of the oxide, which must be performed at the boil under an inert atmosphere, is slow for low grade mineral oxides of manganese.

(5) *Arsenite method.* The oxide is heated with arsenite in dilute sulphuric acid solution:



and the excess arsenite back titrated with standard permanganate in the presence of iodate as catalyst.

These methods allow the determination of all higher valencies in the samples, provided that the reduction potentials are suitable. Hence, as an example, the determination of available oxygen in a pyrolusite specimen by the oxalate method gives a titre which is derived from the dioxide and any manganic or manganomanganic oxides which are almost certain to be present in the mineral. The reporting of the oxidising power, "available manganese," of manganese minerals as  $\text{MnO}_2$  is therefore open to criticism.

Of the methods tested, the oxalate reduction is the most popular because of its simplicity of manipulation and reasonable accuracy, while the ferrous reduction is open to errors from air-oxidation and, in common with the direct iodide and arsenite methods, is less versatile in the determination of lower grade pyrolusites. The Bunsen chlorine evolution method has long been regarded as the referee method for higher oxides, but because of its relatively complex manipulation has not proved popular as a routine method.

Little regard has been paid to the accuracy of the methods: the reasons for choosing Bunsen's method as the most precise and accurate for referee purposes seem lost in antiquity, while only recently<sup>1</sup> has the oxalate method been investigated in any detail. It is difficult to judge the standards upon which any estimate of accuracy is or has been made in any of the methods.

In the present work an attempt has been made to compare the accuracy of the methods, and incidentally, to compare their precision and improve the techniques. The methods investigated were (1) Bunsen's method because of its supposed referee qualities, (2) the oxalate method because of its universal usage, (3) the iodide method because of its extraordinary simplicity in the determination of chemically prepared oxides, and (4) the ferrous method because of its use of chemically reversible systems. The arsenite method was not investigated because of its lack of versatility. Although most of the work was performed on manganese oxides, some results are reported on those of cobalt.

## RESULTS AND DISCUSSION

### (1) *Bunsen's method*

In using the apparatus and technique described in standard works,<sup>2</sup> it was found that, in comparison with the oxalate method and with reasonably pure standard samples of manganese dioxide and manganomanganic oxide, the chlorine evolution method gave results which were as much as 5% low in recovery of available oxygen. The design of the distillation apparatus was improved with particular regard to quantitative distillation and quantitative collection of the chlorine: thus the vapour path was shortened and made as free of obstruction and dead-gas pockets as was practicable, and the absorption was performed through a sintered glass plate. The final design of apparatus is shown in Fig. 2, but for the earlier investigations the small distillation flask was replaced with a similar 100-ml flask. In this apparatus rarely did the witness flask show evidence of ingress of chlorine and all of the available

chlorine was displaced into the first potassium iodide absorption flask in a reasonable time at a reasonable flow rate of carbon dioxide. Additions of pure sodium bicarbonate to the absorption solution in order to prevent excessively high hydrogen ion concentrations had little effect, and results were still low. (This practice became completely unnecessary when smaller volumes of acid were used for the decomposition.) These low results were ascribed to either or both the dissolution or reaction of chlorine in the water present in the still or the formation of complex chlorides of higher valency states of the metal concerned. Both of these effects should be reduced by decreasing the recommended volume of hydrochloric acid. Results for varying volumes and two concentrations of acid are shown in Fig. 1, based upon suitable weights of specimens of oxides of approximately known composition.

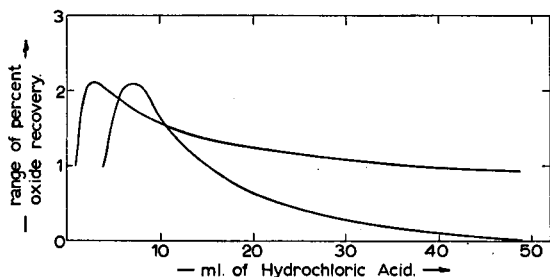


FIG. 1.—General shape of curves for the recovery of manganese and cobalt oxides with varying volumes of hydrochloric acid.

It is evident that the volume of hydrochloric acid normally recommended (25–50 ml) is much too great and that with an optimum volume of acid, maximum recovery is obtained. This maximum is obtained at a volume which is barely twice that required for chemical equivalence, and at the same time, no high concentrations of hydrogen ions are introduced into the receiver and the blank experiments give negligible titres.

In an effort to reduce still further the quantity of water in the still, experiments were performed with mixtures of anhydrous phosphoric acid (“100% orthophosphoric acid”) and dried sodium chloride instead of hydrochloric acid. However, even under optimum conditions, found to be 20 ml of phosphoric acid with 5.5 g of sodium chloride for 0.2–0.3 g of the various manganese or cobalt oxides, a maximum recovery of less than that obtained in the modified Bunsen’s method was obtained on the same bulk samples (see Table 1).

TABLE I.—ANALYTICAL RECOVERY OF MANGANESE OXIDES BY TWO MODIFICATIONS OF BUNSEN’S METHOD

Decomposition agent	Analytical recovery of manganese oxides, %		
	MnO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub>
2.5 ml of 12N HCl	98.8	99.9	99.5
20 ml of H <sub>3</sub> PO <sub>4</sub> + 5.5 g of NaCl	97.9	98.5	97.8

Considerable care was exercised in controlling the temperature of decomposition; although the maximum temperature was 160°, some dehydration of the orthophosphoric acid did occur, as evidenced by appreciable quantities of condensed water in the still head. At the same time it was noted that the residue in the still had a strong

purple colour, similar to that of the manganic-pyrophosphate complex. Complex formation of an intermediate valency, present even in small quantities, with a condensed phosphoric acid product would lead to the low results found in practice.

Similar complex formation may well account for the low results obtained with the classical Bunsen's method, in that the liquid remaining after the distillation from any volume of hydrochloric acid often had a distinct greenish-purple colour. This was particularly obvious when the optimum (2.5 ml) volume of acid was used, but could be discharged by evaporating the liquid just to dryness, when it did not reappear on dissolving the residue in water, or by adding sodium thiosulphate. In all of the cases tested no further detectable chlorine was evolved, or the quantity of 0.05*N* thiosulphate required was less than 1 drop.

The method appeared to be applicable to lead oxides, giving results for triplumbic tetroxide which were in reasonable agreement with the calculated figures and with a standard deviation similar to the results for manganese oxides. However, none of the other methods could be applied to lead oxides and comparisons were, therefore, made impossible.

### (2) *Oxalate method*

The standard technique was used, but the approximately 0.1*N* potassium permanganate was standardised against sodium oxalate solutions which had been treated in a manner identical to the determination mixtures. The method failed for lead oxides, even when other acids were used instead of sulphuric acid.

### (3) *Direct iodide method*

The sample (0.2–0.5 g) was dissolved in 50 ml of dilute (1:20 or 1:10) sulphuric acid in the presence of 4–5 g of potassium iodide while the mixture was cooled in ice. For pure oxides of manganese the reaction is fairly rapid, but much slower for those of cobalt; most minerals and lead oxides, even when finely ground, are largely insoluble.

Results for analyses by this method are highly reproducible and in remarkably good agreement with those of the oxalate method, but slightly higher than those of the modified Bunsen's method. To check whether this discrepancy was caused by the presence of oxygen in the solutions used, experiments were run in a still nitrogen atmosphere after degassing the solutions with nitrogen. In fact, degassing with nitrogen has little effect save the reduction of the blank to a negligible figure. On the assumption that Bunsen's method gives the correct results, these slightly high figures from the direct iodide method may be caused by either catalytic decomposition of iodide by the surface of the oxides, or, more likely, any adsorbed oxygen on the surface is reduced by the iodide ions and the resulting iodine titre is then ascribed to "available oxygen." This hypothesis is in accord with the fact that maximum development of the triiodo ion's colour is almost instantaneous when a sample of manganous or cobaltous oxide is added to a dilute sulphuric acid solution of potassium iodide and the more finely divided samples of the oxides gave higher available oxygen figures.

### (4) *Ferrous method*

This method has already been shown<sup>1</sup> to give results somewhat lower than those of the oxalate method. On two high grade pyrolusites the results shown in Table II by the modified Bunsen, oxalate and ferrous methods were obtained. Potassium dichromate was used as primary standard for the latter method.



TABLE II.—COMPARISON OF RESULTS BY THE BUNSEN, OXALATE AND FERROUS METHODS

Method	Available oxygen as MnO <sub>2</sub> , %	
	Sample 1	Sample 2
Oxalate	88.8	83.9
Ferrous	88.2	83.8
Bunsen	88.0	83.6

Results obtained on samples of manganese dioxide and manganomanganic oxide show that results are similarly intermediate between the Bunsen and oxalate methods.

#### *Comparison of results between methods and with standards*

Results for various samples of manganese and cobalt oxides carefully prepared according to the literature,<sup>4,5</sup> are presented in Table III.

Ignoring manganese dioxide samples 1, 2, 6, 7a and 7b, which are discussed later, it is quite clear from these data that the oxide, oxalate and ferrous methods give results which are reproducible and in close agreement. In addition, the methods digress from the modified Bunsen's method by a positive value of 0.15–0.25%, while the ferrous method tends to give intermediate results. Obviously the composition of different preparations of the oxides is so variable that it is not easy to decide, by comparison with calculated available oxygen values, which is the most accurate method. However, for routine purposes it is clear that any of the four methods would be satisfactory provided that simple ores were under investigation.

The preparation of a really good standard of a manganese or cobalt oxide presents a remarkably difficult problem. There are no standards, except electrolytic manganese metal, from which to make a compound of sufficient quality for this work. Ignition of the metal to, say approximately manganomanganic oxide, requires an excessively long time during which volatilisation losses could be serious, while dissolution of the sample, say in acid, followed by ignition to an oxide has so many possible sources of loss that it would be open to criticism. In any case, the formula of the product could not be assumed to be correct with exactitude, because workers who assigned formulae to the various oxides must have used analytical procedures which had not been subjected to the present intensive criticism and took no account of non-stoichiometry. Hence, the oxidation would have to be followed gravimetrically and all traces of manganese metal removed from the product. However, oxidation of electrolytic manganese in platinum and alumina crucibles under air at 1000° was attempted, with mean results shown in Table IV.

Although the gain of available oxygen by weight agrees more closely with Bunsen's method than with the oxalate method, more cognisance should be taken of the agreement of the Bunsen method with the calculated available oxygen content of trimanganic tetroxide. This agreement is also found in other good samples of this oxide (see Samples 1, 2, 3, 4 and 6 in Table III). Trimanganic tetroxide is said to be the "most stable" oxide of manganese and to display the least non-stoichiometry of the series.

Another approach to the problem lies in the preparation of pure manganous oxide, MnO. This oxide can be prepared<sup>3</sup> by reduction of the higher oxides with pure

TABLE III—PERCENTAGE OF AVAILABLE OXYGEN IN MANGANESE OXIDES BY FOUR METHODS

Method	Manganese dioxide (Calculated [O] = 18.40%)			Manganic oxide (Calculated [O] = 10.13%)			Trimanganic tetroxide (Calculated [O] = 6.99%)								
	Bunsen	Iodide	Oxalate	Ferrous	Bunsen	Iodide	Oxalate	Ferrous	Bunsen	Iodide	Oxalate	Ferrous			
Sample 1	18.42 <sub>6</sub> ± 0.02 <sub>1</sub>	18.20 <sub>9</sub> ± 0.01 <sub>4</sub>	18.21 <sub>1</sub> ± 0.01 <sub>4</sub>	—	9.52 <sub>5</sub>	9.62 <sub>8</sub>	9.66 <sub>8</sub>	—	6.88 <sub>8</sub>	6.99 <sub>8</sub>	7.03 <sub>3</sub>	—			
2	—	—	18.08 <sub>8</sub> ± 0.02 <sub>5</sub>	18.00 <sub>9</sub> ± 0.01 <sub>1</sub>	9.80 <sub>7</sub>	9.92 <sub>0</sub>	9.96 <sub>7</sub>	—	6.89 <sub>8</sub>	7.02 <sub>7</sub>	7.05 <sub>7</sub>	—			
3	—	—	—	—	9.89 <sub>8</sub>	10.02 <sub>7</sub>	10.05 <sub>3</sub>	—	6.91 <sub>7</sub>	7.05 <sub>0</sub>	7.07 <sub>7</sub>	—			
4	—	—	—	—	9.97 <sub>8</sub>	10.09 <sub>3</sub>	10.11 <sub>0</sub>	—	6.97 <sub>8</sub>	7.10 <sub>8</sub>	7.12 <sub>3</sub>	—			
5	—	—	—	—	—	—	—	—	—	—	—	—			
6	18.29 <sub>8</sub> ± 0.02 <sub>0</sub>	18.17 <sub>6</sub> ± 0.02 <sub>0</sub>	18.20 ± 0.02 <sub>6</sub>	18.14 <sub>0</sub> ± 0.02 <sub>8</sub>	10.09 <sub>6</sub>	10.27 <sub>8</sub>	10.31 <sub>3</sub>	10.12 <sub>0</sub>	6.96 <sub>7</sub>	7.06 <sub>5</sub>	7.29 <sub>1</sub> ± 0.02 <sub>4</sub>	7.07 <sub>4</sub> ± 0.01 <sub>1</sub>			
7(a)	18.38	18.28	18.26	18.27	—	—	—	—	—	—	7.14 <sub>4</sub>	6.97 <sub>7</sub>			
(b)	18.36	—	18.29	—	—	—	—	—	—	—	—	—			
(c)	18.22	18.26	18.27	18.23	—	—	—	—	—	—	—	—			
	Standard deviation of a single result														
	± 0.02 <sub>6</sub>			± 0.02 <sub>4</sub>			± 0.02 <sub>3</sub>			± 0.02 <sub>0</sub>			± 0.01 <sub>9</sub>		

TABLE IV.—AVAILABLE OXYGEN IN MANGANESE OXIDE OBTAINED BY AIR-OXIDATION OF ELECTROLYTIC MANGANESE

Sample	Available oxygen		
	By weight, %	By Bunsen, %	By oxalate, %
1	6.90	6.94	7.09
2	6.81	6.93	7.13
3	6.80	6.96	7.24

dry hydrogen at 1100–1600°. Of the oxides, the manganic at 1200° appeared to be the best starting material in giving the greenest product which appeared to oxidise (through a brownish-green) extremely slowly. Use of other oxides and lower temperatures gave more finely divided products which oxidised much more rapidly. Examination of the product and the similar cobaltous oxide prepared by heating cobalto-cobaltic oxide in pure dry nitrogen, by the three methods gave the results listed in Table V, in which samples 3 and 4 were the best preparations.

TABLE V.—PERCENTAGE AVAILABLE OXYGEN IN MANGANOUS AND COBALTOUS OXIDES

Method:	Manganous oxide			Cobaltous oxide		
	Bunsen	Iodide	Oxalate	Ferrous	Bunsen	Oxalate
1	Nil	0.053	0.057	—	Nil	0.20
2	Nil	0.044	0.047	—	Nil	0.16
3	Nil	0.036	0.033	0.021	Nil	0.11
4	Nil	0.028	0.026	—	Nil	0.10
5	—	—	0.076	0.041	—	—

Although the oxalate and iodide methods give results higher than those of the Bunsen method, the quantity by which they are high (0.026–0.057 and 0.10–0.20, respectively) is far less than the difference obtained on the higher oxides. Hence, if oxygen is added to the manganous oxide, the increase in weight (*i.e.* available oxygen) measured gravimetrically can be truly compared with the available oxygen determined titrimetrically.

Weighed samples of manganous and cobaltous oxide specimens were heated at 750° in a stream of pure dry oxygen for 18 hr, cooled in the gas, and the resulting black oxides, corresponding approximately to manganic oxide and cobalto-cobaltic oxide, were reweighed. The increase in weight was compared with available oxygen determinations obtained by the three titrimetric methods.

The differences between the gravimetrically measured gain and the results obtained by the Bunsen and oxalate methods obtained from a large number of determinations are shown in Table VI with the corresponding standard deviations.

TABLE VI.—DIFFERENCES BETWEEN DETERMINATIONS OF AVAILABLE OXYGEN BY WEIGHT AND BY CHEMICAL MEANS

Method	Manganese Oxide			Cobalt Oxide	
	Bunsen	Iodide	Oxalate	Bunsen	Oxalate
Mean Difference	$-0.00_4 \pm 0.03_8$	$+0.29_2 \pm 0.05_3$	$+0.23_3 \pm 0.02_3$	$-0.03_0 \pm 0.01_3$	$+0.28 \pm 0.06_5$

The differences are clearly significant and according to this test, the modified Bunsen method can be taken as accurate *and* precise whereas the oxalate and direct iodide methods, while being precise, suffer from a positive constant error of approximately 0.25%. This is in agreement with the findings of the several analyses performed on other oxide specimens; such a large discrepancy is far greater than that from any unknown quantity of available oxygen in the manganous or cobaltous oxides, this being a maximum of 0.05 and 0.15%, respectively, determined by any method.

Qualitative inspection of the oxide samples indicated that average particle sizes varied in the order manganous oxide > cobaltous oxide > manganese dioxide, manganic oxide, manganomanganic oxide, and for manganous oxide specimens (Table V), samples 4 > 3 > 2 > 1. Coupled with the observation that, in the iodide method, development of the triodo ion's colour is virtually complete in the first few moments of bringing the reagents together, this correlation between particle size, and therefore area, and discrepancy between the results of the various analytical methods indicates that the cause lies in a surface phenomenon. Consequently, experiments were conducted using the Brunauer-Emmett-Teller adsorption isotherm<sup>7</sup> in order to evaluate the surface area of some of the oxides. Results are given in Table VII, together with the area occupied by a monolayer of oxygen atoms calculated from the excess available oxygen obtained as a difference between the modified Bunsen's and oxalate methods.

TABLE VII.—SURFACE AREA OF MANGANESE OXIDES

Sample	Oxygen difference, %	Specific surface area, $\text{cm}^2\text{g}^{-1}$	
		From excess oxygen	From B.E.T. isotherm
Manganous oxide	0.030	$1.6 \times 10^3$	$1.7 \times 10^3$
Manganomanganic oxide	0.15 <sub>6</sub>	$8.3 \times 10^3$	$.8.5 \times 10^3$
Manganic oxide	0.17 <sub>7</sub>	$7.4 \times 10^3$	$7.3 \times 10^3$

Because the estimated error in all of the surface area measurements is expected to be approximately  $\pm 0.4 \times 10^3 \text{ cm}^2 \text{ g}^{-1}$ , the correlation between the results is extremely close and it is reasonable to suppose that these oxides, as prepared, have an adsorbed monolayer of oxygen atoms. Furthermore, because this oxygen is available for reduction only by certain reducing agents, the mechanism is likely to be chemical rather than physical adsorption.

Against this it may be argued that the difference between methods for any given oxide are remarkable constant while among several preparations it is unlikely that the same surface area is consistently obtained. Moreover, the agreement between the Bunsen method and the addition of oxygen measured by weight (Table VI) and the corresponding high results for the oxalate and iodide methods is not in accord with the hypothesis.

The high results obtained with the Bunsen method for manganese dioxide samples 1, 6, 7(a) and 7(b) are from the presence of an impurity, probably manganous nitrate, in these samples. A specimen (2.5 g) of manganese dioxide prepared by a published method<sup>4</sup> was examined thermogravimetrically under one atmosphere of dry oxygen: the sample began to lose weight at 425°, and at 510° reached constant weight within 5 hr. Above 520° decomposition to manganic oxide commenced. A more finely ground sample (1.4 g) behaved similarly but constant weight was reached within 1 hr

at 510°. The weight loss corresponds approximately to a 0.74% content of manganese nitrate which would account for 0.14% of available oxygen as determined by the Bunsen method, but would not interfere in any of the other methods. The presence of oxynitrogen ions was demonstrated qualitatively in the original sample, but could not be detected in samples heated in oxygen at 510° for several hr. It was also observed that after the last treatment the finely ground samples gained weight on cooling in dry oxygen, but coarser specimens did not; however, the weight changes were so small that they could not be measured with any reasonable degree of accuracy. Results of these experiments are given in Table VIII.

TABLE VIII

Sample	Available oxygen, %		Loss on heating to 510° in dry oxygen	Gain on cooling in dry oxygen
	Bunsen	Oxalate		
7(a) As prepared <sup>4</sup>	18.38	18.26	0.37% (≡0.14%[O])	Nil
7(b) After grinding and heating to 300° for 72hr	18.36	18.29	0.34% (≡0.12%[O])	~0.05%
7(c) After grinding and then heating to 510° in O <sub>2</sub>	18.22	18.27	—	—

It is clear that the earlier samples of manganese dioxide were unsuitable for comparison purposes, although the statistical data obtained from them is satisfactory.

#### CONCLUSIONS

It is evident from the results that the four methods investigated are very reproducible on the samples examined. The modified Bunsen's method appears to give the most accurate results, while those of the ferrous, oxalate and direct iodide are consistently high. The positive error is probably caused by simultaneous oxidation of the oxalate ( $E_0$ , -0.49V), ferrous ( $E_0$ , 0.77) and iodide ( $E_0$ , 0.55), which are in direct contact with the sample, by adsorbed oxygen on the surface of the oxide. The more positive standard electrode potential of chloride ( $E_0$ , 1.36) used in the Bunsen method, presumably does not allow reaction with this adsorbed oxygen. It is also possible that formation of oxalate and iodide complexes of tervalent manganese and cobalt could also contribute to the high results of the oxalate and direct iodide methods. For pure oxides, but not minerals, the results of the ferrous method, in which complex ion formation is unlikely, are barely significantly different from those of the iodide and oxalate methods but the trend is in accord with this suggestion.

For minerals the oxalate results are in positive error by the greatest quantity; besides air-decomposition of the oxalate, suggested by other workers,<sup>1</sup> it is possible that small quantities of oxalate complexes of other cations are formed or other reducible cations are included in the results nominally given for "available oxygen".

Nevertheless, for routine purposes on suitable minerals and ores, the oxalate and certainly the ferrous methods are adequate: only in referee analyses of oxides does the difference between the methods become significant. Clearly, for accurate work on oxides, considerable care must be exercised over sampling procedures in order that the proportions of all particle sizes and therefore surface areas, are represented in the weighted sample.

## EXPERIMENTAL

*Preparation of oxides*

Manganese and cobalt oxides were prepared by standard methods ( $\text{MnO}_2$ ,<sup>4</sup>  $\text{Mn}_2\text{O}_3$ ,<sup>5</sup>  $\text{Mn}_3\text{O}_4$ ,<sup>5</sup>  $\text{Co}_2\text{O}_3$ ,<sup>5</sup>  $\text{Co}_3\text{O}_4$ ,<sup>5</sup>). In addition, at the end of each preparation, each sample was finely ground, and reheated at the prescribed temperature for a further period of 4 hr. It was ultimately discovered that, because of included nitrate ions, it was necessary to heat manganese dioxide specimens in dry oxygen at 510° for several hr before a suitable sample was obtained. As much as 0.7% of impurity, presumably manganese<sup>II</sup> nitrate, is present in the dioxide prepared by published methods.

Manganous oxide<sup>3</sup> was prepared by passing a stream of oxygen-free hydrogen which had been dried over silica gel and anhydrous magnesium perchlorate over the sample of a higher oxide of manganese heated at 1200° for 8–10 hr. The oxide was cooled in hydrogen and analysed as soon after reduction as possible. The most massive and brightest green samples were obtained from manganic oxide, and these preserved their low available oxygen content for more than 3 years. Cobaltous oxide<sup>6</sup> was prepared similarly, the decomposition of the higher oxides being achieved with oxygen-free nitrogen which had been dried over silica gel and magnesium perchlorate and passed over copper turnings at 500–600°. Reduction of cobaltcobaltic oxide at 1100° gave the best products.

The intermediate oxides of manganese and cobalt were prepared by heating manganous or cobaltous oxide at 750–800° in a stream of pure dry oxygen for 18–24 hr.

*Apparatus*

*Weighings.* All weighings were performed on balances sufficiently precise to give a relative error of less than 0.05%. Calibrated weights were used throughout.

*Thermogravimetric analyses.* The thermogravimetry was performed on a Stanton Thermobalance modified to allow sensitive low temperature control and provision of controlled gas atmospheres round the sample.

*Titrations.* All titrations were carried out on the same calibrated Grade A burette and, as far as possible, all titres were arranged to fall between 45 and 50 ml. The same drainage time was employed throughout. The limits of reading the burette were an estimated 0.02 ml and titrations were performed to fractions of 1 drop.

*Methods*

*Oxalate method.* The determinations were performed in the usual manner. The samples were heated with the dilute (1:10) sulphuric acid solution of sodium oxalate at 95° and the sodium oxalate standards were treated similarly; no inert gas atmospheres were deliberately used.

*Ferrous method.* Standard procedures were adopted using dilute (1:10) sulphuric acid as solvent and a carbon dioxide atmosphere. Dried potassium dichromate was used as primary standard.

*Direct iodide method.* The samples (0.2–0.5 g) were dissolved in ice-cooled dilute (1:20 or 1:10) sulphuric acid containing 4–5 g of potassium iodide; the solutions were magnetically stirred, if necessary. For manganese oxides, decomposition was complete within 60 min. The solutions were titrated with standardised 0.1N sodium thiosulphate. Allowance was made for a blank.

*Modified Bunsen's method.* The final apparatus is shown in Fig. 2. Noteworthy points of design are its extremely small still (S), smooth vapour path (including capillary-tipped tap funnel, T) and efficient chlorine absorption system ( $R_1$  and  $R_2$ ). Lubrication of joints was with "Fluorube W" grease.

Place 50 ml of 20% potassium iodide in the first receiving flask ( $R_1$ ) and 25 ml in the second flask ( $R_2$ ) and surround  $R_1$  and  $R_2$  with ice-water. Into the oven-dried distillation flask place 0.2–0.5 g of sample and assemble the apparatus. With the aid of gentle suction introduce 2.5 ml of concentrated (36% w/w) hydrochloric acid into the still via the small tap funnel. Start the moist carbon dioxide stream at 60–80 ml/min, disconnect the suction line, and gently heat the flask over a small hooded flame until the sample has completely dissolved. Increase the flame so that the solution evaporates just to dryness. The overall heating time usually occupies 30–45 min, but continue the passage of carbon dioxide to a total of 60 min. With the gas still flowing, disconnect  $R_1$  and wash down the outside and inside of the delivery tube (D) with distilled water using gas pressure to assist the emptying of the tube. Immediately titrate the liberated iodine with standard sodium thiosulphate. The quantity of free iodine in the witness flask and in a blank run should both be less than 1 drop of titrant.

The sodium thiosulphate was standardised against weighed samples of dried potassium iodate which gave identical figures to those using pure copper. No indicator was used in the standardisation or determinations because the change from yellow to colourless at the end-point was extremely sharp. Standardisation of the thiosulphate was performed daily during this work.

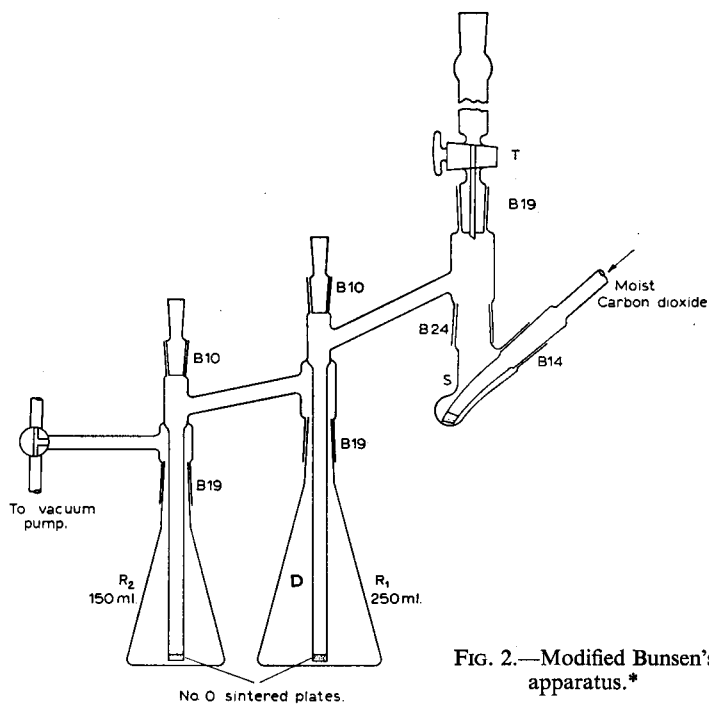


FIG. 2.—Modified Bunsen's apparatus.\*

**Acknowledgement**—Thanks are due to Dr. A. P. Prosser for facilities to perform the Brunauer-Emmett-Teller test.

**Zusammenfassung**—Folgende Methoden zur Bestimmung des aktiven Sauerstoffes in Mangan- und Cobaltoxyden wurden kritisch verglichen: Bunsen, Oxalat-Iodid- und Ferroeisenmethode. Es wurde gefunden, dass die letzteren drei Methoden zu hohe Resultate liefern, während die Ergebnisse nach Bunsen (geeignet modifiziert) korrekt sind. Der Unterschied der Ergebnisse wird auf eine monomolekulare Sauerstoffschicht an der Oberfläche des Oxydes zurückgeführt.

**Résumé**—L'examen soigné des méthodes de BUNSEN, de l'oxalate, de l'iodure et du fer ferreux utilisées dans le dosage de l'oxygène activé présent dans les oxydes de manganèse et de cobalt a montré que les trois dernières méthodes donnaient invariablement des résultats élevés, cependant que la méthode de BUNSEN, modifiée convenablement, donne des résultats précis. La différence entre la méthode de BUNSEN et les autres méthodes est attribuée à une couche monomoléculaire d'oxygène adsorbé à la surface des oxydes examinés.

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\* There is also a No. 0 sintered plate at the inner end of the CO<sub>2</sub> inlet tube.

## REACTION OF CADMIUM WITH OXINE

ROGER D. WHEALY and B. J. BLAND

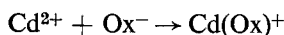
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**Summary**—The stepwise reaction of cadmium with oxine has been studied and equilibrium constants calculated by polarographic and gravimetric methods.

### INTRODUCTION

IN the course of other work it was necessary to know the specific equilibrium constant for each step of the reaction of cadmium with the oxine (8-hydroxyquinoline) anion:



and



where

$$K' = \frac{A_{\text{Cd}(\text{Ox})^+}}{A_{\text{Cd}^{2+}} A_{\text{Ox}^-}} \quad (1)^*$$

$$\text{and } K'' = \frac{1}{A_{\text{Cd}(\text{Ox})^+} A_{\text{Ox}^-}} \quad (2)^*$$

We have measured the equilibrium constants  $K'$  and  $K''$ . The measurements were carried out at an ionic strength of 1.00, temperature of 25° and initial pH of 6.

### EXPERIMENTAL

#### *Reagents*

*Oxine*: Baker reagent grade oxine was purified by two recrystallisations from alcohol solution.

*Buffer*: A potassium acid phthalate-sodium hydroxide buffer system was used as suggested by Clark and Lubs.

*Cadmium chloride*: Dissolved in de-ionised water and standardised by two methods: (1) titration with EDTA using Eriochrome Black T indicator, and (2) gravimetrically using the ethyl ester of oxine for homogeneous precipitation.

*Potassium chloride*: Reagent grade material was dried at 300° for 48 hr before weighing.

#### *Equilibrium measurements*

The solutions were prepared and allowed to stand 72 hr before measurements were made. Glass stoppered bottles were used to prevent evaporation.

Two sets of solutions were prepared, each set having four samples to be used for gravimetric determination of  $\text{Cd}(\text{Ox})_2$  and one sample for polarographic determination of  $\text{Cd}^{2+}$ . The samples were mixed as follows: 20.00 ml of buffer solution, 20.00 ml of 2.400*N* potassium chloride, 5.00 ml of 0.1010*M*  $\text{Cd}^{2+}$  and 5.00 ml of oxine in alcohol. Each set of solutions had a different ratio of  $\text{Cd}^{2+}$  to oxine initially as follows:

Set	Ratio of $[\text{Cd}^{2+}] : [\text{Oxine}]$	$[\text{Oxine}]_{\text{initially}}$
A	1 : 2	0.0200
B	1 : 1½	0.0150

\* Although equations (1), (2), (4) and (5) are expressed in activities, the calculations were actually made using concentrations, assuming concentrations to be equal to activities.



The average weight of precipitate was obtained for each set. The precipitate was weighed as  $\text{Cd}(\text{Ox})_2$  after drying to constant weight at 120–130°.

The  $\text{Cd}^{2+}$  concentration for each set was determined polarographically using a Sargent Polarograph Model XXI in connection with a Leeds Northrup dropping mercury electrode which has a constant temperature bath and air tight sample container. The pH of each solution was measured at equilibrium.

### RESULTS

The following values were obtained:

$$\begin{aligned} K' &= 5.9 \times 10^7 \pm 0.5 \times 10^7 \\ K'' &= 4.0 \times 10^{11} \pm 0.3 \times 10^{11} \\ K_{\text{sp}} &= 4.2 \times 10^{-20} \pm 0.30 \times 10^{-20}. \end{aligned}$$

### CALCULATIONS

The initial concentration of  $\text{Cd}^{2+}$  is known and the weight of  $\text{Cd}(\text{Ox})_2$  and concentration of  $\text{Cd}^{2+}$  are measured at equilibrium. Therefore the concentration of  $\text{Cd}(\text{Ox})^+$  can be calculated using the following equation:

$$[\text{Cd}(\text{Ox})^+] = [\text{Cd}^{2+}]_{\text{initially}} - \left\{ [\text{Cd}^{2+}]_{\text{equil}} + \frac{\text{Wt. ppt.} \times 20}{400.7} \right\} \quad (3)$$

This gives values for all forms of cadmium assumed to be present in the solution.\*

The  $[\text{Ox}^-]$  remains to be determined. Nasanen, Lumme and Mukula<sup>1</sup> have calculated the two ionisation constants of oxine at various ionic strengths. For a ionic strength of unity they give the following values:

$$K_1 = 6.839 \times 10^{-6} \text{ and } K_2 = 2.624 \times 10^{-10}$$

where

$$K_1 = \frac{A_{\text{H}^+} A_{\text{HOx}}}{A_{\text{H}_2\text{Ox}^+}} \quad (4)$$

and

$$K_2 = \frac{A_{\text{H}^+} A_{\text{Ox}^-}}{A_{\text{HOx}}} \quad (5)$$

Using the equation:

$$\text{Total Oxine} = [\text{Ox}^-] + [\text{HOx}] + [\text{H}_2\text{Ox}^+] \quad (6)$$

the concentration of each species can be expressed as a function of  $K_1$ ,  $K_2$  and pH, for example:

$$\frac{[\text{Ox}^-]}{\text{Total Oxine}} = \frac{K_1 K_2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2} \quad (7)$$

Fig. 1 is a plot of the percentage of each of these species from pH 3 to 12. This indicates that all three species are present in this pH range.

The equilibrium concentration of oxine can be calculated as follows:

$$[\text{Total Oxine}]_{\text{equil}} = [\text{Oxine}]_{\text{initially}} - \left\{ [\text{Cd}(\text{Ox})^+] + \frac{2 \times \text{wt. ppt.} \times 20}{400.7} \right\} \quad (8)$$

Now using  $[\text{Total Oxine}]_{\text{equil}}$  and pH of the solution at equilibrium in equation (7) gives  $[\text{Ox}^-]$ .

\* The amount of  $\text{Cd}(\text{Ox})_2$  dissolved, but un-ionised, in the solution is ignored. No method could be devised to measure this amount, but it is believed from this work and from a hydrolysis study that it is quite small.

This completes calculations for all concentrations to be used in equations (1) and (2), giving  $K'$  and  $K''$ , respectively.

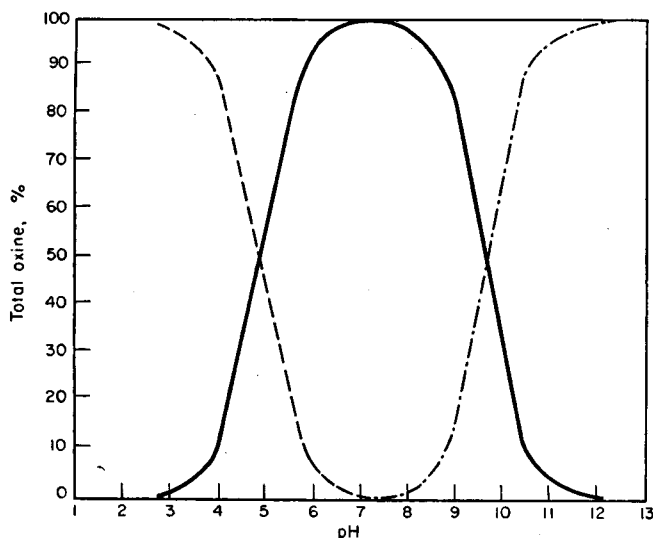


FIG. 1. ——— HOx, ---- H<sub>2</sub>Ox<sup>+</sup>, - · - · Ox<sup>-</sup>.

The various concentrations of ions and weight of Cd(Ox)<sub>2</sub> in equilibrium solutions are as follows:

TABLE I

Set	[Cd <sup>++</sup> ] × 10 <sup>3</sup>	[Cd(Ox) <sup>+</sup> ] × 10 <sup>3</sup>	pH	[Ox <sup>-</sup> ] × 10 <sup>9</sup>	Cd(Ox) <sub>2</sub> <sup>g.</sup>
A	1.30 ± 0.03	1.00 ± 0.03	4.65 ± 0.02	9.6 ± 0.1	0.1555 ± 0.0038
B	3.00 ± 0.05	0.40 ± 0.02	4.67 ± 0.02	3.55 ± 0.05	0.1343 ± 0.0006

From these data  $K_{sp}$  can also be calculated:

$$K_{sp} = \frac{1}{K'K''} = \frac{1}{(5.9 \times 10^7)(4.0 \times 10^{11})} = 4.2 \times 10^{-20} \pm 0.2 \times 10^{-20}.$$

#### DISCUSSION

This method gives a relatively simple procedure for calculating the equilibrium constants and solubility products for bivalent metal oxinates. It can be used where the methods of spectrophotometry and potentiometry might not apply.

Nasanen and Penttinen<sup>2</sup> reported a value of  $6.03 \times 10^7$  for  $K'$  which agrees very well with our value of  $5.9 \times 10^7$ . Also, our value of  $4.2 \times 10^{-20}$  for  $K_{sp}$  is in fair agreement with their value of  $3.72 \times 10^{-21}$ .

Johnston and Freiser<sup>3</sup> have studied the stability of metal oxinates and found the solubility product of Cd(Ox)<sub>2</sub> to be  $3.16 \times 10^{-9}$  in a 50% dioxane-water solution at 25°. They did not consider the stepwise reaction of oxine with the metal ions and the various species of oxine present in solution. Their data cannot be extrapolated to aqueous solutions.

**Zusammenfassung**—Die stufenweise Reaktion von Cadmium mit Oxin wurde studiert und die Gleichgewichtskonstanten mittels polarographischer und gravimetrischer Methoden ermittelt.

**Résumé**—Les auteurs ont étudié la réaction par paliers du cadmium avec l'oxine (8-hydroxyquinoléine) et calculé les constantes d'équilibre par des méthodes polarographiques et gravimétriques.

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## DETERMINATION OF ANTIMONY IN LEAD BY NEUTRON-ACTIVATION ANALYSIS

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**Summary**—Activation analysis of antimony in lead has been studied in the concentration range of 1–0.03%. Gold is used as a standard so as to avoid self-shielding problems of the antimony standard. The proposed technique is possible by making use of net photospectra and computing the antimony content directly from the ratio of the 0.40- and 0.56-gamma peaks of  $^{198}\text{Au}$  and  $^{123}\text{Sb}$ .

ACTIVATION analysis is not only a valuable tool for the determination of traces but it can also be successfully applied as a non-destructive technique for the determination of minor constituents, the accuracy of the results comparing favourably with other analytical methods.<sup>1,2,3,4</sup>

Activation analysis of traces of antimony has been studied by numerous workers as is apparent from the recent survey of Bock-Werthmann and Schulze.<sup>5</sup> The present work deals with the non-destructive determination of antimony in lead by gamma spectrometry using gold as a reference standard.

### Nuclear data

Natural antimony consists of two stable species,  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$ , which can give rise to a number of radioisotopes by neutron irradiation as given in Table I.

TABLE I.—NUCLEAR PROPERTIES OF ANTIMONY ISOTOPES

Stable isotope	Occurrence, %	Activation cross-section, barn	Isotope formed	Half life	Radiation and energy, Mev
$^{121}\text{Sb}$	57.25	3.7	$^{122}\text{Sb}$	2.8 day	$\beta^-$ 0.740; 0.900; 1.40 1.97 $\gamma$ 0.566; 0.686; 1.137; 1.256
		1.3	$^{122\text{m}}\text{Sb}$	3.5 min	I.T. $e^-$ 0.059 $\gamma$ 0.060; 0.075
$^{123}\text{Sb}$	42.75	1.1	$^{124}\text{Sb}$	61 day	$\beta^-$ 0.240; 0.610; 0.966; 1.60; 2.32 $\gamma$ 0.603; 0.641; 0.716; 1.68; 2.09
		0.013	$^{124\text{m}}\text{Sb}$	1.3 min	I.T. $e^-(\gamma)$ 0.012
		0.013	$^{124\text{m}}\text{Sb}$	21 min	I.T. $e^-(\gamma)$ 0.018

From Table I it appears that  $^{122\text{m}}\text{Sb}$ ,  $^{122}\text{Sb}$  and  $^{124}\text{Sb}$  can be used for activation purposes because they are formed in sufficiently large amounts to make accurate gamma spectrometric measurements possible. The half life of  $^{122\text{m}}\text{Sb}$  is, however,

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very short so that measurement immediately after the end of the irradiation is required, whereas  $^{124}\text{Sb}$  has a long half life and necessitates long irradiation periods to induce sufficiently large activities. Consequently,  $^{122}\text{Sb}$  was chosen for measurement. The decay scheme and gamma spectrum of  $^{122}\text{Sb}$  are given in Fig. 1.

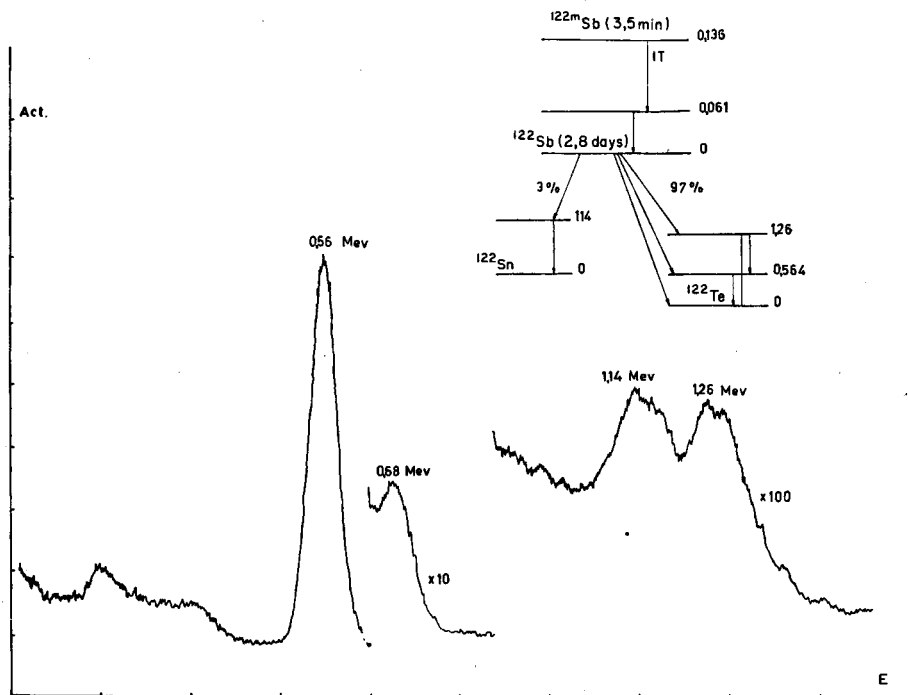


FIG. 1.—Decay scheme and gamma spectrum of  $^{122}\text{Sb}$ .

### Interfering activities

Because the activation cross-sections of the natural lead isotopes  $^{206}\text{Pb}$  and  $^{208}\text{Pb}$  are very small (0.026 and 0.0006 barn), the activity induced in the matrix is completely negligible. A number of other elements, occurring either as minor constituents or as traces, can, however, interfere with the determination of antimony as is apparent from Table II. These interferences can be minimised by restricting the measurement of  $^{122}\text{Sb}$  to the 0.56-MeV gamma peak only. In this case the interference will be limited to the 0.55-MeV gamma peak of  $^{76}\text{As}$ , the annihilation radiation of  $^{64}\text{Cu}$  and  $^{65}\text{Zn}$  and the 0.435-MeV ray of  $^{69}\text{Zn}$ . About 70 hr after the end of the irradiation the activity of  $^{64}\text{Cu}$  will be negligible. The 0.55-MeV gamma peak of  $^{76}\text{As}$  can, however, cause major difficulties, because the waiting period for complete decay of this isotope would cause a long delay; the interference is negligible for ratios of antimony:arsenic larger than 20 after a waiting period of 3 days. Simultaneous determination of both elements is also feasible by gamma spectrometry, without chemical separation, and will be described in detail elsewhere. For ratios of zinc:antimony smaller than 15 the interference is still within 1% as was the case with our samples.

TABLE II.—INTERFERING ACTIVITIES

Isotope	Occurrence, %	Activation cross-section, barn	Isotope formed	Half life	Gamma energy, MeV
<sup>75</sup> As	100	4.3	<sup>76</sup> As	26.5 hr	0.55; 0.64; 1.20 1.78; 2.10; 2.80
<sup>63</sup> Cu	69.1	3.0	<sup>64</sup> Cu	12.8 hr	0.511; 1.34
<sup>65</sup> Cu	30.9	0.65	<sup>66</sup> Cu	5.1 min	0.83; 1.04
<sup>64</sup> Zn	48.9	0.25	<sup>65</sup> Zn	245 day	0.511; 1.11
<sup>68</sup> Zn	18.56	0.02	<sup>69m</sup> Zn	13.8 hr	0.438
<sup>70</sup> Zn	0.62	4.8	<sup>71m</sup> Zn	3 hr	0.38; 0.49; 0.61
<sup>107</sup> Ag	51.53	23	<sup>108</sup> Ag	2.3 min	0.430; 0.511; 0.600; 0.630
<sup>109</sup> Ag	48.65	54	<sup>110</sup> Ag	24.2 sec	0.660; 0.720 0.810; 0.880 0.940
		1.4	<sup>110m</sup> Ag	270 day	0.656; 0.681; 0.706; 0.764; 0.884; 0.940; 1.381; 1.481
<sup>112</sup> Sn	0.95	0.013	<sup>113</sup> Sn	112 day	0.260; 0.392
<sup>116</sup> Sn	14.24	0.001	<sup>117m</sup> Sn	14 day	0.161; 0.320
<sup>122</sup> Sn	4.71	0.007	<sup>123</sup> Sn	40 min	0.153
<sup>124</sup> Sn	5.98	0.01	<sup>125m</sup> Sn	9.5 min	0.326
<sup>23</sup> Na	100	0.54	<sup>24</sup> Na	14.8 hr	1.38; 2.76

### Self-shielding effects

Plumb and Lewis<sup>6</sup> have investigated the specific activity of <sup>122</sup>Sb and <sup>124</sup>Sb as a function of sample size and concluded that self-shielding effects were very large for the former isotope even with very small samples. This is because of the fact that <sup>121</sup>Sb has a very large resonance peak of 1,300 barn at a neutron energy of 6 eV. This effect was confirmed by irradiating an antimony sphere of 0.7 cm in the reactor core of BR-1 at a flux of  $8 \times 10^{11}$  neutrons/cm<sup>2</sup>/sec. After irradiation this sphere was dissolved stepwise in hydrochloric acid–nitric acid mixtures. By weighing the antimony sphere after each step it thus became possible to determine the specific activity as a function of the radius. From Fig. 2 (curve 1) it appears that the activity of <sup>122</sup>Sb decreases exponentially in the outer 500  $\mu$  of the sphere and tends towards a constant value afterwards. <sup>124</sup>Sb shows a similar behaviour (Fig. 2, curve 2).

From this experiment it is apparent that self-shielding in an antimony standard can only be avoided by shielding with at least 0.5-mm antimony foil. Another alternative would be to dilute the standard with an inert material such as graphite. The specific activity of <sup>122</sup>Sb as a function of concentration in high purity graphite is given in Fig. 3 (curve 1). From this it appears that antimony (as Sb<sub>2</sub>O<sub>3</sub>) should be diluted with at least 50 parts of graphite before a constant specific activity is obtained.

It could, of course, also be expected that a similar problem will occur in the lead samples. From Fig. 3 (curve 2) it appears that the upper concentration of antimony in lead is about 1%.

### External gold standard

Leliaert *et al.*<sup>7,8</sup> have shown that self-shielding problems and neutron flux irregularities can be avoided by the use of an internal standard. This technique is, however,

not applicable where self-shielding is from resonance peaks which do not appear in the internal standard. To avoid these problems preference was, therefore, given to the use of a gold standard spotted on the lead samples. Gold was chosen as a standard because it offers the following advantages:

1. Gold is monoisotopic, giving rise by an  $(n, \gamma)$  reaction to  $^{198}\text{Au}$  with a large activation cross-section ( $\sigma = 98$  barns).

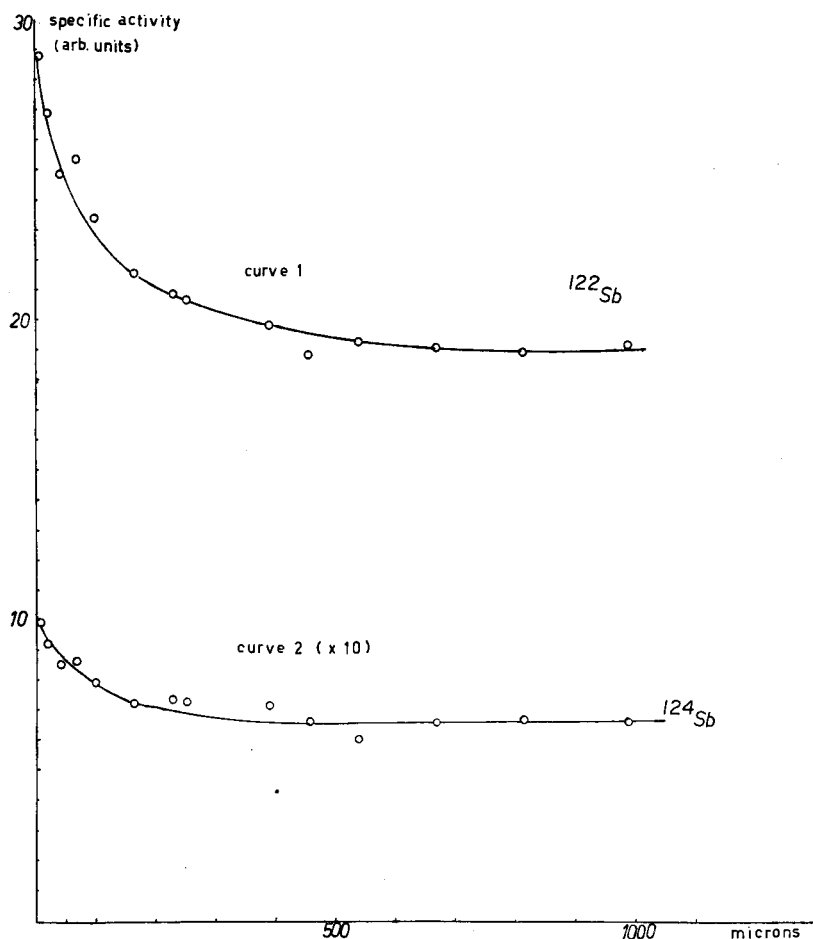


FIG. 2.—Specific activity of  $^{122}\text{Sb}$  as a function of sphere radius.

2. The half life of  $^{198}\text{Au}$  (2.69 day) is very close to the half life of  $^{122}\text{Sb}$  (2.80 day) so that the ratio of the induced activities is practically independent of the irradiation time and of the decay period after irradiation.
3.  $^{198}\text{Au}$  emits for almost 100% a gamma of 0.40 MeV which can be easily resolved from the 0.56 MeV of  $^{122}\text{Sb}$  with a NaI(Tl) detector of good resolution. The other gammas of 1.09 MeV (0.16%) and 0.68 MeV (0.82%) are very weak and do not interfere.

Consequently, when the lead samples are spotted with a standard solution of a gold salt, the antimony content can be computed from the following equation:

$$\% \text{Sb} = \frac{C_{(t)}}{s} \cdot \frac{h^{122}\text{Sb}}{h^{198}\text{Au}} \quad (1)$$

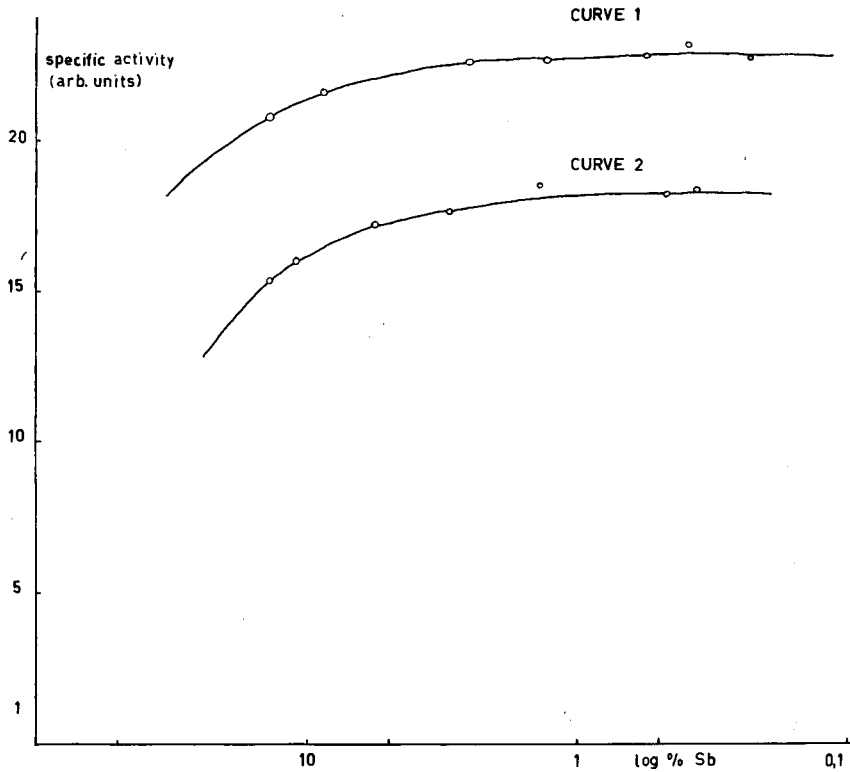


FIG. 3.—Specific activity of  $^{122}\text{Sb}$  as a function of concentration in graphite and lead.

where  $C_{(t)}$  = proportionality constant,  
 $s$  = sample weight,

$h^{122}\text{Sb}$  = height of the 0.56-MeV peak of  $^{122}\text{Sb}$ ,  
 and  $h^{198}\text{Au}$  = height of the 0.40-MeV peak of  $^{198}\text{Au}$ .

The constant  $C_{(t)}$  is dependent upon the amount of gold used and the decay period after the end of the irradiation:

$$C_{(t)} = C_0 \exp \left( -0.693 \left( \frac{1}{2.80} - \frac{1}{2.69} \right) \right) \quad (2)$$

$^{124}\text{Sb}$  is, however, simultaneously produced with  $^{122}\text{Sb}$ . The former emits a gamma of 0.60 MeV which interferes with the height measurement of the 0.56-MeV gamma of the latter. Assuming a 5 min irradiation and taking into account the respective cross-sections, half lives and decay modes, it is possible to compute the percentage interference of this isotope. From the activation cross-sections of  $^{121}\text{Sb}$  and  $^{124}\text{Sb}$  and the respective half lives, the ratio of the activities appears to be *ca.* 74 for an irradiation



period of 1 min. Taking into account that the 0.56-MeV ray of  $^{122}\text{Sb}$  occurs in 66% of the decay mode, whereas the 0.60 MeV gamma of  $^{124}\text{Sb}$  occurs for 99%, the respective peak to total ratios and the resolution as a function of energy as given by De Soete and Hoste,<sup>9</sup> it can be computed that the interference of the 0.60-MeV line in the measurement of the height of the 0.56 MeV will be, respectively, 0.61, 0.78 and 1.00% after, respectively, a 0-hr, 24-hr and 48-hr waiting period. These are in good agreement with the experimental values of 0.6, 0.75 and 0.95.

Furthermore, it is obvious that the amount of gold should be chosen so as to

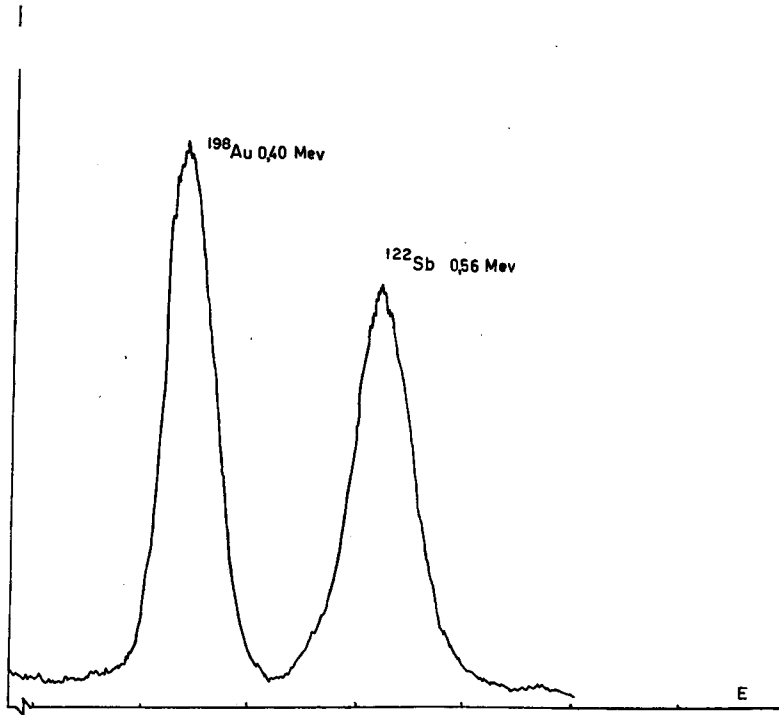


FIG. 4.—Compton compensated spectrum of  $^{122}\text{Sb}$  and  $^{198}\text{Au}$ .

obtain a peak height of the same order of magnitude as the 0.560-MeV peak of  $^{122}\text{Sb}$ . Moreover, equation (1) is valid for net photopeaks only. This can be achieved by the method described by Peirson *et al.*<sup>10,11,12</sup> According to these authors net photopeaks are obtained by subtracting the Compton continuum of the NaI(Tl) detector with a second detector equipped with an anthracene crystal, after correct equalisation for pulse height and count rate. Because equalisation of count rate with the variable switching unit recommended by Peirson appeared to be quite delicate and introduces a large dead time, a complete single channel analyser was used for each detector, the signals being fed to a differential rate meter. Correct count rate equalisation was achieved by adjusting the symmetry arrangement of the two detectors. A typical compensated spectrum of  $^{198}\text{Au} + ^{122}\text{Sb}$  is given in Fig. 4.

In all of the experiments the count rate was determined from the peak height because this procedure gives rise to a smaller error than measurement of the photopeak area. A series of net gamma spectra were recorded for  $^{198}\text{Au}$  and  $^{122}\text{Sb}$  with

increasing count rates. It appeared that up to  $5 \times 10^5$  cpm the standard deviation was *ca.* 2.5%.

Reliable results are, however, only possible with highly stable instrumentation: multiplier phototube with stable gain as a function of count rate, high quality high voltage, stabilised linear amplifier and pulse height analyser and a thermostatically controlled counting room within 0.5°. In these conditions the shift over a period of several weeks is completely negligible.

### EXPERIMENTAL

#### Apparatus

Nuclear Enterprises linear amplifier 5202 and associated pulse height analyser 5102. Tracerlab precision high voltage supply RLI-7 (common for both detector operating at *ca.* 950 V). Hilger and Watts NaI(Tl) detector with EMI 9531 A photomultiplier (integral assembly); resolution for the 0.663 line: 8.9%.

Differential count-rate meter

Philips XY recorder, type PR 2220 A.

#### Procedure

The lead samples (weight *ca.* 0.5 g, diam. 1 cm) are spotted with 100  $\mu$ l of a standardised gold chloride solution (5 mg of gold/ml). The solvent is evaporated under an infrared heater in the

TABLE III.—ACTIVATION ANALYSIS OF LEAD ALLOYS

Sb taken, %	Sample weight, g	Sb found, %	Average
0.926	0.3249	0.928	0.927
	0.3906	0.942	
LB 2	0.3750	0.920	s = 1%
	0.3566	0.919	
	0.3611	0.929	
0.854	0.3465	0.842	0.844
	0.3512	0.821	
LB 3	0.3870	0.849	s = 1.6%
	0.3741	0.859	
	0.3218	0.858	
0.231	0.4867	0.226	0.220
	0.4412	0.236	
	0.4734	0.234	s = 2%
	0.5099	0.231	
	0.5053	0.224	
0.197	0.5233	0.190	0.196
	0.5101	0.201	
	0.5309	0.196	s = 2.4%
	0.4867	0.201	
	0.4912	0.192	
0.0577	0.5155	0.0545	0.0573
	0.5143	0.0595	
	0.5433	0.0562	s = 3.7%
	0.5527	0.0593	
	0.5868	0.0570	
0.0433	0.5229	0.0440	0.0443
	0.5667	0.0427	
	0.5439	0.0433	s = 6%
	0.5970	0.0491	
	0.5672	0.0425	
0.0303	0.5765	0.0321	0.0315
	0.5751	0.0310	
	0.5430	0.0344	s = 5.4%
	0.5971	0.0298	
	0.5623	0.0307	

presence of hydrazine to avoid losses of the volatile gold chloride. The gold-plated sample is wrapped in aluminium foil, packed in a standard can and irradiated in the core of BR-1 at a flux of  $8 \times 10^{11}$  neutrons/cm<sup>2</sup>/sec for 3 min. A net photopeak spectrum is recorded after a waiting period of a few hr at a scanning speed of the bias voltage of 1 V/50 sec (time constant of rate meter: 10 sec). For antimony contents of ca. 1% a rate meter range of 25 K was chosen because this gives rise to peak heights of ca. 60 scale divisions on the paper strip. For lower antimony contents, correspondingly lower amounts of gold and longer irradiation periods of up to 1 hr were used. Using this technique a complete analysis can be performed within 0.5 hr to 1.5 hr depending on the required irradiation time.

The proportionality constant  $C_0$  was determined with Johnson Matthey Standard LB 1-LB 5 for the concentration range from 1 to 0.6% whereas the lower concentrations (down to 0.03%) were made by mixing antimony powder (200 mesh) with lead powder (100 mesh) and pressing the mixtures into pellets of ca. 0.5 g, diam. 0.5", at a pressure of 100,000 lb/sq. inch. Homogeneous mixtures of lower antimony content could not be prepared with this technique. The results of a number of analyses are given in Table III.

From Table III it is apparent that in the concentration range of 1% to 0.1% the standard deviation is within 2.5% which compares favourably with other instrumental methods, whereas down to concentrations of 0.03% the standard deviation is still only 5-6%. An antimony content of 0.03% does not, of course, represent the lower limit of the proposed technique. An irradiation of 1 hr at  $10^{12}$  neutron cm<sup>2</sup>/sec would yield 12,000 cpm per  $\mu$ g of antimony.

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**Zusammenfassung**—Eine nicht-destruktive Methode zur Bestimmung von Antimon in Blei im Konzentrationsgebiet von 1–0,03%, mit Hilfe eines Goldstandards, wird beschrieben. Peirsongammaskopie wurde angewandt und der Antimongehalt aus dem Verhältnis der 0,40 und 0,56 MeV Aktivitäten der <sup>198</sup>Au und <sup>122</sup>Sb Isotopen berechnet. Die Methode kann für kleinere Antimongehalten erweitert werden, und ist auch auf andere Aktivierungsanalytische Probleme anwendbar.

**Résumé**—Les auteurs décrivent une méthode non-destructive pour le dosage de l'antimoine dans de plomb, par analyse par activation en utilisant un étalon d'or. On peut calculer la teneur en antimoine à partir du rapport des hauteurs des pics de 0.40 MeV et 0.56 MeV de l'or et de l'antimoine. On a utilisé à cet effet un spectromètre gamma à soustraction Compton selon le procédé de Peirson. On a appliqué la méthode à des échantillons dont la concentration en antimoine variait de 0.03 à 1%, avec possibilité d'étendre la mesure à des teneurs en antimoine encore plus faibles.

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## AMMONIUM HEXANITRATOCERATE(IV) AS AN OXIDISING AGENT

### TITRATION OF OXALIC AND MANDELIC ACIDS AT ROOM TEMPERATURE

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**Summary**—The use of ammonium hexanitratocerate(IV) in oxidimetry has been very little studied, although the salt can be obtained in a high degree of purity. Conditions have now been established for the titration of oxalic and mandelic acids with this reagent at room temperature in a nitric or hydrochloric acid medium using ferroin as indicator. The procedures developed give precise results and they constitute definite improvements over those involving cerium<sup>IV</sup> sulphate.

SMITH, Sullivan and Frank<sup>1</sup> described the preparation of ammonium hexanitratocerate(IV) in a high degree of purity and studied its stability in aqueous solution acidified with nitric or sulphuric acid. Subsequently, Smith and Fly<sup>2</sup> described the preparation of ammonium hexanitratocerate(IV) in a sufficient degree of purity to be used as a primary standard. They claimed several advantages for the use of this salt: (1) high equivalent weight, (2) high degree of stability in the crystalline condition,\* and (3) the attainment of a high oxidation potential in perchloric acid (1.70–1.87v from 1–8N) or in nitric acid (1.61–1.56v from 1–8N) media. Smith, Sullivan and Frank<sup>1</sup> determined the purity of the salt by dissolving a weighed sample in sulphuric acid (1:10) and titrating with standard iron<sup>II</sup> sulphate solution, using ferroin as indicator. Smith and Fly<sup>2</sup> determined the purity of the salt by dissolving weighed samples in 70% perchloric acid and titrating with a standard solution of sodium oxalate in perchloric acid solution, using nitroferroin as indicator. This reverse titration is preferred to the usual direct titration for reasons fully discussed in their original paper.

The use of ammonium hexanitratocerate(IV) in a nitric acid medium does not appear to have been studied although Smith, Sullivan and Frank stated that "The nitrate ion had no influence upon the determination of ferrous iron, the most commonly determined element. It is not expected to interfere in most cases. The value of the proposed new standard need not be in the least minimised by such considerations. From a solution of known weight of ammonium hexanitratocerate in sulphuric acid, a solution of ceric ammonium sulphate is easily obtained free from nitric acid by the simple process of digestion. All question of the possible presence of the undesirable nitrate ion is thus eliminated."

The process of digestion with sulphuric acid to eliminate the nitrate ion is to be

\* The reagent is somewhat unstable in solution and requires frequent standardisation.

avoided for three reasons: (1) it is tedious, (2) it deprives the advantage of this complex salt as a primary standard, and (3) the conversion of the ammonium hexanitratocerate(IV) to cerium<sup>IV</sup> ammonium sulphate as proposed by Smith, Sullivan and Frank<sup>1</sup> will remove its advantages as a reagent of high oxidation potential. Further, according to Smith and Fly,<sup>2</sup> the preparation of a solution of ammonium hexanitratocerate(IV) in a sulphuric acid medium requires great care, otherwise mixed insoluble nitratosulphatocerates may be precipitated. Although a higher oxidation potential of the ammonium hexanitratocerate(IV) can be utilised by working with solutions of the salt in a perchloric acid medium, there are some difficulties associated with this reagent as discussed fully by Smith and Fly.<sup>2</sup>

A survey of the literature has shown that so far no one has extensively studied the reagent in a nitric acid medium, using ferroin as indicator. We have now made a study of this reagent both in nitric acid and hydrochloric acid media. Our results are somewhat at variance with the statement of Smith, Sullivan and Frank about the non-interference of nitric acid. We have ascertained the concentrations of nitric acid under which iron<sup>II</sup> and oxalate can be titrated accurately with the cerate solution at room temperature.

## EXPERIMENTAL

### Reagents

*Ammonium hexanitratocerate(IV) solution:* The crystalline complex salt is prepared according to the method of Smith *et al.*<sup>1</sup> A known weight of the solid thus obtained is dissolved in nitric acid and the solution made up to 1 litre with the requisite amount of dilute nitric acid so that the overall concentration of nitric acid is 1.0N. Although Smith *et al.* experienced some difficulty in the preparation of clear solutions of ammonium hexanitratocerate(IV) in 1.0N perchloric acid because of the precipitation of complex perchloratonitratocerates, no such difficulty has been experienced by us in the preparation of a nitric acid solution of this reagent. The solution is stored in an amber coloured Jena glass bottle. The solution is standardised against a solution of Mohr's salt in a sulphuric acid medium, using ferroin as indicator, the Mohr's salt solution having been previously standardised against a standard cerium<sup>IV</sup> sulphate solution which in its turn has been standardised against a standard solution of reagent grade sodium oxalate with a potentiometric end-point.

All other reagents employed in this investigation were of analytical reagent grade.

### Titration of iron<sup>II</sup>

*Titration in a sulphuric acid medium.* From 5.0–10.0 ml of an approx. 0.05N iron<sup>II</sup> solution (prepared by dissolving iron wire of AnalaR grade in sulphuric acid and adjusting the overall sulphuric acid concentration to about 1N) were taken in an Erlenmeyer flask and treated with 20 ml of 2N sulphuric acid and 20 ml of distilled water. The mixture was treated with 0.5 ml of 0.001M ferroin then titrated with the ammonium hexanitratocerate(IV) solution with constant stirring until a permanent pale blue colour persisted.

The indicator correction is negligible in titrations with 0.1–0.05N solutions of the cerate, but in titrations with 0.02–0.01N solutions a correction is necessary depending on the quantity of ferroin, added. Accordingly, it is convenient to dilute 0.01M ferroin solution 10 times and use 0.5 ml of this solution each time as indicator. The indicator correction can then be precisely applied.

*Titration in a nitric acid medium.* Iron<sup>II</sup> can be titrated in 1.0N nitric acid using ferroin as indicator, provided the iron<sup>II</sup> solution is not kept for more than 5–10 min after the addition of nitric acid. If the mixture is allowed to stand longer, the iron<sup>II</sup> is oxidised slowly by the nitric acid, leading to low titres and sluggish end-points. This difficulty is enhanced by increasing the concentration of nitric acid. A closer study of the matter revealed that difficulty concerning the indicator action is traceable to the nitrous acid formed as a result of the reaction between iron<sup>II</sup> and nitric acid. Nitrous acid is capable of slowly reducing ferroin to ferroin, this reduction occurring only when all of the iron<sup>II</sup> is oxidised. It is, therefore, desirable to add nitric acid last to an iron<sup>II</sup> solution, *i.e.* after the addition of water and the indicator solution. In no case should nitric acid of concentration greater than 2.0N be added to the iron<sup>II</sup> solution. Using these precautions it is possible to carry out accurately the titration of even a 0.01N solution of iron<sup>II</sup> with 0.01N ammonium hexanitratocerate(IV).

The reverse titration of ammonium hexanitratocerate(IV) in nitric acid with iron<sup>II</sup> sulphate solution can also be carried out without difficulty using ferroin as indicator. Evidently ferroin is

quite stable in contact with an excess of ammonium hexanitratocerate(IV) solution in 1.0*N* nitric acid without losing its reversibility as an indicator.

#### *Determination of oxalate*

Kirk and Tompkins<sup>9</sup> carried out the microtitration of oxalate with ammonium hexanitratocerate(IV) both in nitric acid and in perchloric acid media. These authors stated that the results obtained in a nitric acid medium "are somewhat misleading in that the reaction is too slow for convenience and the end-point was difficult to read with ortho-phenanthroline ferrous sulphate particularly in presence of asbestos". Consequently, the authors did not recommend this procedure but preferred the back-titration using cerium<sup>IV</sup> sulphate.

We have found that the microtitration of oxalate is fairly satisfactory if the initial concentration of nitric acid in the titration mixture is 0.1–0.2*N* and if the titrant is added slowly. If the concentration of nitric acid in the titration mixture exceeds 0.2*N* the end-point becomes difficult to recognise, the difficulty increasing with increasing concentration of the acid. Our experiments show that this difficulty in detecting the end-point arises from two factors: (1) the reduction of the light blue ferroin by oxalate to the red ferroin is slow; (2) as the titration progresses there is a gradual decrease in the intensity of the ferroin red colour, with the result that the red colour reaches only a small fraction of its original intensity near the end-point even after waiting for some time. Curiously enough this difficulty is enhanced when the speed of addition of the cerium<sup>IV</sup> salt is increased. For these reasons the transition from the very light red colour to the very light blue colour is difficult to notice in macrotitrations.

Significant observations made during attempted macrotitrations of oxalate with ammonium hexanitratocerate(IV) in a nitric acid medium are summarised as follows:

(1) During the early stages of the titration, on the addition of each portion of the cerate solution the ferroin red colour changes to the yellow colour of the cerium<sup>IV</sup> which gradually changes to red, through orange, in about 6–8 sec; the intensity of the restored red colour is somewhat less than that at the start of the titration.

(2) The intensity of the restored red colour, as stated above, becomes less and less as the equivalence point is approached.

(3) The loss in intensity of the ferroin red colour increases as the nitric acid concentration of the titration mixture is increased, so that in titrations carried out in media of nitric acid concentrations greater than 0.2*N* the colour transition at the equivalence point is difficult to discern.

(4) Macrotitrations of oxalate are not possible, even in 0.1–0.2*N* nitric acid media, because of the difficulties pointed out above.

We have made the interesting observation that the addition of a little potassium iodide or iodate (1 ml of 10<sup>-3</sup>*M* solution per 50 ml of titration mixture) eliminates these difficulties; both the micro and macrotitrations can then be accurately carried out in nitric acid media ranging from 0.1 to 0.8*N*. When potassium iodide is used in the mentioned amount, an extra consumption of cerate (0.1 ml of 0.01*N* solution) is required and a correspondingly lesser amount of cerate when potassium iodate is used. It has also been noticed that the correction is negligible when a mixture of potassium iodide and iodate to give a concentration of iodine equivalent to that of potassium iodide used above is employed. When titrations are made using any of these catalysts, the ferroin red colour remains almost the same in intensity throughout the course of the titration. Hence the transition from red to light blue can be sharply perceived at the equivalence point, both in micro and macro titrations when the nitric acid concentration lies between 0.1 and 0.8*N*. However, when the acid concentration is raised to 1.0*N* or above, the fading of the ferroin colour again makes itself felt, and the titrations become difficult even in the presence of the above mentioned catalysts. In our opinion the action of the catalyst is more concerned with the functioning of the indicator rather than with the reaction of cerate with oxalate. Further work is in progress to elucidate the mechanism of the action of the catalyst.

*Recommended procedure for the titration of oxalate in a nitric acid medium.* Take 5–10 ml of the oxalate solution in a 100-ml Erlenmeyer flask and treat with 40 ml of 0.5–0.8*N* nitric acid, 0.5 ml of 0.001*M* ferroin and 1 ml of a mixture of potassium iodide and potassium iodate (equivalent to 10<sup>-2</sup>*N* iodine). Titrate with a solution of ammonium hexanitratocerate(IV) till the ferroin red colour just changes to very pale blue. If the blue colour reverts to a pale red tinge in 10–15 sec, a fraction of a drop of the cerate solution may be added to obtain a permanent pale blue colour.

A large number of micro and macro titrations have been made according to this procedure. Some typical results are given in Table I.

*Titration of oxalate in a hydrochloric acid medium.* Oxalate can be conveniently titrated in 0.2–0.5*N* hydrochloric acid at room temperature with ammonium hexanitratocerate(IV) using ferroin as indicator. The fading of the ferroin colour noticed during titrations in a nitric acid medium is not so much in evidence here. Accurate results have been obtained both in titrations with 0.05*N* and 0.01*N*

TABLE I.—DETERMINATION OF OXALATE BY AMMONIUM HEXANITRATOCERATE(IV) IN A NITRIC ACID MEDIUM

Oxalate taken, <i>m</i> moles	Oxalate found, <i>m</i> moles	Oxalate taken, <i>m</i> moles	Oxalate found, <i>m</i> moles
2.3000	2.2900	0.1600	0.1601
1.2000	1.2010	0.1200	0.1202
0.5600	0.5610	0.0860	0.0859
0.4500	0.4508	0.0590	0.0588
0.3400	0.3401	0.0350	0.0351
0.2300	0.2295	0.0240	0.0241

cerate solutions. When the concentration of hydrochloric acid is raised to 1.0*N* or above, an increasing fading of the ferroin colour is noticed, and the titration becomes almost impossible in a 2.0*N* hydrochloric acid medium. The use of iodide-iodate mixture, however, enables the titration to be made with the usual facility, even in 2.0*N* hydrochloric acid.

The titration<sup>5</sup> of oxalic acid with cerium<sup>IV</sup> sulphate at room temperature in the presence of barium ion as a scavenger for sulphate ion is subject to the limitation that the colour of the ferroin indicator is somewhat masked by the precipitated barium sulphate. The present method, involving the use of ammonium hexanitratocerate(IV) in a nitric acid or hydrochloric acid medium, does not suffer from this disadvantage.

#### Determination of mandelic acid

Titration of mandelic acid is not possible in either nitric acid or hydrochloric acid media, even of very low concentration, without the use of the catalyst. This is because the ferroin red colour does not return about 0.2–0.3 ml before the equivalence point, even after waiting for 10–15 min.

If the catalyst is added at the stage when the ferroin colour fades very much (about 0.4–0.5 ml before the equivalence point), however, the red colour is regained in good intensity and the titration can be carried out without any further difficulty. In view of these findings, the following procedure is recommended for the titrimetric determination of mandelic acid:

Take 5–10 ml of mandelic acid solution (0.01–0.05*N*) in an Erlenmeyer flask, then add 40–45 ml of 0.2*N* nitric acid (or hydrochloric acid) and 0.5 ml of 0.001*M* ferroin. Titrate with a solution of ammonium hexanitratocerate(IV) of appropriate strength. Near the equivalence point when the ferroin red colour has faded very much, add 0.5 ml of potassium iodide-iodate mixture (equivalent to 10<sup>-3</sup>*N* iodine) and continue the titration dropwise until a permanent light blue colour is obtained.

A large number of titrations have been carried out as described above. Some typical results are given in the Table II.

TABLE II.—TITRIMETRIC DETERMINATION OF MANDELIC ACID WITH AMMONIUM HEXANITRATOCERATE(IV)

Mandelic acid, <i>m</i> moles	
Taken	Found
0.6800	0.6805
0.6000	0.5980
0.5500	0.5507
0.5300	0.5285
0.4300	0.4310
0.2300	0.2290
0.1300	0.1290
0.0965	0.0966
0.0595	0.0595

The direct titrimetric procedure now developed for the determination of mandelic acid is an improvement over the procedure of Verma and Paul,<sup>4</sup> which consists of adding an excess of cerium<sup>IV</sup> sulphate to an aliquot of the mandelic acid solution, allowing to react for 5 min, then titrating the excess cerium<sup>IV</sup> with standard iron<sup>II</sup> sulphate solution.

**Zusammenfassung**—Obwohl das Salz in hohem Reinheitsgrad erhältlich ist wurde die Anwendung von Ammonium hexanitratocerate in der Oxydimetrie nur wenig studiert. Bedingungen wurden ausgearbeitet um Oxalsäure und Mandelsäure mit dem Reagens bei Zimmertemperatur in salpeter- oder salsauem Medium zu titrieren. Ferroin wird als Indicator verwendet. Die neu entwickelte Methode gibt genaue Resultate. Die Methode hat Vorteile gegenüber der Verwendung von Cersulfat.

**Résumé**—L'utilisation d'hexanitratocérate d'ammonium en oxydimétrie a été très peu étudiée, bien que le sel puisse être obtenu avec une très grande pureté. Les conditions de titrage par ce réactif des acides oxalique et mandélique ont été établies à la température ambiante en milieu acide nitrique ou chlorhydrique en utilisant la ferroïne comme indicateur interne. Les méthodes ainsi mises au point donnent des résultats précis. Elles constituent de nettes améliorations sur les méthodes mettant en jeu le sulfate de cérium(IV) comme réactif.

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## IDENTIFICATION OF POLYATOMIC ANIONS BY INFRARED SPECTROSCOPY

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**Summary**—Mixtures of ferrocyanide, ferricyanide and cobalticyanide, and of chromate, vanadate and sulphate, may be identified by the characteristic infrared spectra of the anions. The relation between the intensity of the band and the concentration of anion enables quantitative measurements to be made on microgram amounts.

THE possibility of using the characteristic infrared absorption frequencies of inorganic salts for the identification of anions present in mixtures has been investigated. The anions selected for study have previously been separated by the authors,<sup>1</sup> using standard microanalytical techniques; each of the anions studied possesses a characteristic infrared spectrum.

Potassium ferrocyanide, ferricyanide and cobalticyanide have been studied by several workers,<sup>2-6</sup> who showed that these species absorbed in the region between 2100  $\text{cm}^{-1}$  and 2000  $\text{cm}^{-1}$ . Generally the range 2200  $\text{cm}^{-1}$  to 2000  $\text{cm}^{-1}$  could be regarded as covering all the forms in which the  $-\text{CN}$  grouping occurs in inorganic compounds. The infrared spectra of the cyanide complexes of silver, copper and gold have also been studied in aqueous solution.<sup>7-9</sup>

Potassium ferrocyanide and ferricyanide, as shown by Emschwiler,<sup>6</sup> are characterised by bands which correspond to the fundamental vibration of the  $-\text{CN}$  grouping. The absorption band is much more intense for the ferrocyanide ion than for the ferricyanide ion. Experimentally, it was proved that the cobalticyanide ion spectrum resembles the ferricyanide ion spectrum.

The infrared absorption spectra of the anions chromate, vanadate and sulphate, which are assignable to the metal-oxygen<sup>12</sup> and sulphur-oxygen stretching frequencies, have also been examined and the results of these studies and the application of the spectra to qualitative and quantitative microanalysis are discussed in this paper. Unfortunately the alkali halide salts are transparent to infrared radiation, and hence this technique cannot be used to identify mixtures of halides, the third group of anions previously studied.<sup>1</sup>

The characteristic frequencies of the various anionic groups can vary within limits of about 100–200  $\text{cm}^{-1}$ , depending on the nature of the cation and the type of bonding involved. This is particularly important in the case of complex formation, where the characteristic frequency of the anion may shift drastically from that shown by the sodium or potassium salt. Changing the cation associated with the complex anion may produce a different crystalline arrangement, resulting in a different symmetry or intensity of the electric field around a negative ion. A difference in the type or extent of hydration probably alters some of the frequencies.<sup>2</sup> Therefore, it is advisable to use the potassium salts of the anions as a standard basis for the study of the spectra. In

practice the interference from the cation may be eliminated by using ion exchange, to permit the detection by spectroscopy of the anion as the potassium salt.

## EXPERIMENTAL

### Studies on single anions

Crystals of salts containing the various anions were intimately ground with potassium bromide and pressed into a disc about 1 mm in thickness. The potassium bromide discs were prepared with a Perkin-Elmer die using an "Apex" hydraulic press with a 10-ton capacity on a ram of 2½-inch diameter. The infrared absorption spectrum of the disc was then recorded, using a Perkin-Elmer infrared spectrophotometer (Infracord, Model 137).

Most of the anions involved in the study gave clear and transparent discs with KBr. An exception was the vanadate, which showed some opacity. But with discs with low concentration of the anion, this behaviour was negligible. The spectra of pure salts and mixtures of salts were examined and the possibility of using the infrared spectra for simultaneous qualitative and quantitative analysis was investigated.

The characteristic absorption bands of the various anions are summarised in Table I.

TABLE I.—CHARACTERISTIC ABSORPTION BANDS OF ANIONS

Salt	Wave no., $cm^{-1}$	Wavelength, $\mu$	Relative intensity*	Reference	Notes
Potassium ferrocyanide, AnalaR, $K_4Fe(CN)_6 \cdot 3H_2O$	1630	6.13	s. sp.	2	<i>a</i>
	1650	6.07	m.	2	<i>a</i>
	2015	4.96	v.s.	2	<i>a</i>
	2040	4.90	v.s.	6	<i>a</i>
Potassium ferricyanide, AnalaR, $K_3Fe(CN)_6$	2100	4.77	s.	2	<i>b</i>
	2115	4.73	s.	6	<i>b</i>
Potassium cobalticyanide, B.D.H., $K_3Co(CN)_6$	2100	4.77	s.		<i>c</i>
	2115	4.73	s.		<i>c</i>
Potassium sulphate, AnalaR, $K_2SO_4$	1110	9.00	v.s.	2	<i>d</i>
Potassium chromate, AnalaR, $K_2CrO_4$	872	11.45	v.s.	2	<i>e</i>
Sodium metavanadate, Hopkin and Williams, $NaVO_3 \cdot 4H_2O$	828	12.08	s.	2	<i>f</i>
	910	11.00	v.w.	2	<i>f</i>
	935	10.70	s.	2	<i>f</i>
	957	10.45	s.	2	<i>f</i>

\* s. = strong sp. = sharp m. = medium v. = very w. = weak b. = broad.

### Notes

(a) The frequencies in  $cm^{-1}$  for maximum absorption for most of the ferrocyanide salts range between 2010 for thallium ferrocyanide to 2120 for aluminium ferrocyanide.<sup>6</sup>

(b) The frequencies in  $cm^{-1}$  for maximum absorption for most of the ferricyanide salts range between 2115 for potassium ferricyanide to 2176 for copper ferricyanide. AnalaR potassium ferricyanide showed two additional bands; the first one at  $1630\text{ cm}^{-1}$  ( $6.13\ \mu$ ) s.sp.,<sup>2</sup> and the second one at  $2015\text{ cm}^{-1}$  ( $4.96\ \mu$ ) v.s.<sup>2</sup>

If the surface of a crystal of potassium ferricyanide (which normally shows the 2040 band) is washed and dried, only one very strong band at  $2100\text{ cm}^{-1}$  ( $4.77\ \mu$ ) is obtained. This test indicates that AnalaR potassium ferricyanide actually contains ferrocyanide as an impurity. The evidence has been confirmed by examining a synthetic mixture (1:1) of ferrocyanide and ferricyanide, after mixing them with KBr, on the spectrophotometer where the same bands as those given by the AnalaR ferricyanide were given.

From the figures shown in Table I, it can be observed that the bands of ferricyanide and cobalticyanide (in the potassium salts) are superimposed on each other. Each of the above salts was, therefore, subjected individually to treatment with a concentrated neutral solution of KI. After drying the mixture of the two ions, it was found that ferricyanide was reduced completely to ferrocyanide and that the spectrum of ferrocyanide ion was the only one given. On the other hand cobalticyanide

was not affected. It can be concluded, therefore, that potassium iodide can be used as a selective reductant for the ferricyanide.

(c) The frequencies in  $\text{cm}^{-1}$  for maximum absorption for most of the sulphate salts range between 1080 for zirconium sulphate to 1135 for manganese sulphate.<sup>2</sup> Potassium sulphate shows only one very strong band at  $1110\text{ cm}^{-1}$  ( $9.0\ \mu$ ).

(d) The frequencies in  $\text{cm}^{-1}$  for maximum absorption for most of the chromate salts (except for aluminium chromate) range between 795 for zinc chromate to 890 for sodium chromate.<sup>2</sup> Potassium chromate gives the following distinct bands:  $858\text{ cm}^{-1}$  ( $11.65\ \mu$ ) w.sp.  $872\text{ cm}^{-1}$  ( $11.45\ \mu$ ) v.s.  $935\text{ cm}^{-1}$  ( $10.7\ \mu$ )s.

(e) The frequencies in  $\text{cm}^{-1}$  for maximum absorption for the two metavanadates studied<sup>2</sup> range from 828 for sodium metavanadate to 935 for ammonium metavanadate. Sodium metavanadate shows the characteristic bands<sup>2</sup> listed in Table II.

TABLE II.—ABSORPTION OF SODIUM METAVANADATE

Wave no., $\text{cm}^{-1}$	Wavelength, $\mu$	Relative intensity
693	14.4	s.b.
828	12.08	s.
910	11.0	v.w.
935	10.7	s.
957	10.45	s.
3450	2.9	w.b.

#### Studies on mixtures of anions

1. *Ferrocyanide, ferricyanide and cobalticyanide*: A synthetic mixture containing equal amounts of the three complex cyanides was prepared. A weighed portion was mixed with KBr, and the absorption spectrum of the KBr disc was recorded. Two very strong bands appeared in the  $2040\text{ cm}^{-1}$  and  $2115\text{ cm}^{-1}$  regions, indicating the presence of either two or three anions in the unknown.

Another portion, of equal weight to the first, was dissolved in the minimum amount of water and a concentrated solution of KI was added. The solution was evaporated to dryness and baked in an oven at  $105^\circ$ . The residue obtained was mixed with KBr and again the infrared spectrum was recorded. A shift of the strong band from  $2115\text{ cm}^{-1}$  to  $2040\text{ cm}^{-1}$  and the enhancement of the  $2040\text{ cm}^{-1}$  band indicates the presence of ferricyanide. No shift proves the presence of cobalticyanide. No shift of the band  $2115\text{ cm}^{-1}$  and no enhancement of the band  $2040\text{ cm}^{-1}$  indicates the absence of ferricyanide.

2. *Sulphate, chromate and metavanadate*: The infrared spectrum of a synthetic mixture of these three anions showed no interference arising from overlapping of the spectra of the corresponding individual anions, although the bands were appreciably broader than the complex cyanide bands.

3. *Six anions*: Fig. 1 shows the infrared spectrum of a KBr disc containing ferrocyanide, ferricyanide, cobalticyanide, sulphate, chromate and vanadate anions. The following points may be noted:

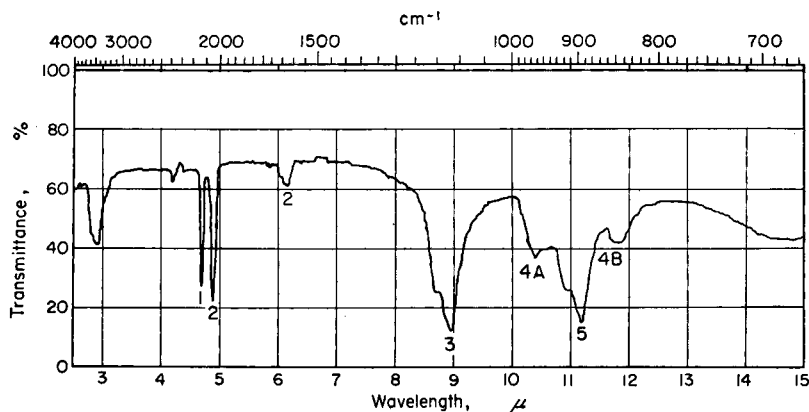


FIG. 1.—Infrared spectrum of mixture of anions.

- |                                    |             |
|------------------------------------|-------------|
| 1—ferricyanide and cobalticyanide. | 4—vanadate. |
| 2—ferrocyanide.                    | 5—chromate. |
| 3—Sulphate.                        |             |

(a) the bands of ferricyanide and cobalticyanide are superimposed on each other in the region  $2115\text{ cm}^{-1}$ . For resolution of these two spectral bands, treatment with concentrated KI solution is required;

(b) ferrocyanide gives its characteristic band at  $2040\text{ cm}^{-1}$ ;

(c) sulphate appears at  $1110\text{ cm}^{-1}$ ;

(d) chromate appears at  $872\text{ cm}^{-1}$ ;

(e) metavanadate gives two bands, one at  $957\text{ cm}^{-1}$  and one at  $828\text{ cm}^{-1}$ .

It was possible to identify the anions from their corresponding bands if they were present in the amounts shown in Table III.

TABLE III.—LIMIT OF IDENTIFICATION OF ANIONS

Anion	$\mu\text{g}$
Ferrocyanide	5
Ferricyanide	20
Cobalticyanide	20
Sulphate	20
Chromate	20
Metavanadate	80

#### Quantitative studies

*Preparation of the disc:* A portion of the salt containing 2 mg of the anion was weighed accurately on to the near edge of a watch glass. The salt was quantitatively transferred to an agate mortar containing 1000 mg of Specpure KBr. The mixture was ground for 5 min to produce a fine, thoroughly-mixed powder. Each mg of the resulting powder therefore contained  $2\text{ }\mu\text{g}$  of the anion. For other experiments  $x$  mg of the powder were mixed with 200 mg of KBr, accurately weighed, and the mixture was again ground to a fine powder. A disc was made from this combined powder and the spectrum was recorded on the Infracord. The intensity of the absorption at the characteristic bands was found to vary more or less linearly with the concentration of anion present. Using the Infracord, measurable intensities were obtained with microgram amounts of anion present.

#### DISCUSSION

It was found easier to identify microgram amounts of the selected anions by infrared spectroscopy than by the techniques described by Benedetti-Pichler<sup>10</sup> and other workers.<sup>11</sup> The infrared method is simpler and faster than the ultramicro technique. The time required to make an infrared experiment is not more than 20 minutes, while with the other technique it can take an hour or more. With the anion systems examined there was no interference between spectral bands of the individual anions, and each of the anions had a characteristic absorption band. The number of anionic species which possess such characteristic infrared absorption peaks, is, however, limited. For example, the alkali halide salts are transparent to these radiations and hence this technique cannot be used to identify mixtures of halides. On the other hand, there are other polyatomic anion species which should absorb infrared radiation. These are being examined, and work is also proceeding to extend the applications of this technique to micro-analysis.

Because there is a linear relationship between intensity of absorption and amount of anion present, it should be possible to develop further sensitive qualitative and quantitative separation procedures.

**Zusammenfassung**—Eine infrarotspektrophotometrische Methode wurde entwickelt um die folgenden Anionen in Mikrogrammengen von Mischungen zu nachweisen und zu bestimmen: Ferrocyanid, Ferricyanid, Kobalticyanid; und Chromat, Vanadate, Sulfat.

**Résumé**—Les auteurs ont mis au point une méthode de spectroscopie d'absorption infra-rouge permettant l'identification et le dosage de microgrammes des mélanges des anions suivant: ferrocyanure, ferricyanure, cobalticyanure; et chromate, vanadate, sulfate.

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# QUANTITATIVE TREATMENT OF EXCHANGE EQUILIBRIA INVOLVING COMPLEXANS—I

## POLAROGRAPHIC DETERMINATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM

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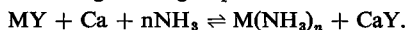
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**Summary**—In order to find optimum conditions for the indirect polarographic determination of calcium, a quantitative consideration is made of the following exchange equilibrium:

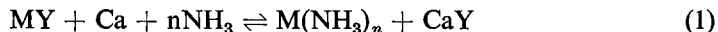


The use of Cd-EGTA is proposed for the selective determination of calcium in the presence of a large excess of magnesium.

DIFFICULTIES are encountered in the polarographic determination of such elements as calcium and magnesium which do not give a well-defined reduction wave at the dropping mercury electrode in a suitable potential range. However, the indirect polarographic determination of such elements is sometimes successful by utilising an appropriate exchange reaction. Thus, Přebil *et al.*<sup>1,2</sup> proposed a novel method in which an ammoniacal Zn-EDTA solution was added to the sample solution and the zinc-ammine complex liberated by calcium was determined polarographically. Sensitive though the method is, the sum of calcium and magnesium is determined when the two are present together. Přebil *et al.* claimed to be able to determine calcium in the presence of five times as much as magnesium, precipitating the latter as magnesium ammonium phosphate. In the present work attention was drawn to the difference in stability constants between the EGTA [ethyleneglycol-*bis*-( $\beta$ -aminoethyl ether)-N:N'-tetraacetic acid] chelates of calcium and magnesium, and a procedure was developed for the selective polarographic determination of calcium in mixtures containing a large excess of magnesium. Quantitative consideration of the exchange equilibrium involved<sup>3</sup> led to the use of Cd-EGTA instead of Zn-EGTA.

### Choice of complexan

The exchange equilibrium involving MY and calcium ion in ammoniacal media may be described (omitting charges for simplicity) as follows:



where M represents Cd or Zn (see the following section). If M is added as MY

( $[M]_t = [Y]_t$ ) and  $\text{NH}_3$  designated as A, from an equation (10) derived elsewhere:<sup>3</sup>

$$[\text{Ca}]_t = \left( [\text{MA}_4] - \frac{[\text{M}]_t - [\text{MA}_4]}{[\text{MA}_4]} \cdot K_2[\text{A}]^4 \right) \left( 1 + \frac{[\text{MA}_4]}{[\text{M}]_t - [\text{MA}_4]} \cdot \frac{1}{K_1[\text{A}]^4} \right) \quad (2)^*$$

where

$$K_1 = K_{\text{CaY}} K_{\text{MA}_4} / K_{\text{MY}} \text{ and } K_2 = K_{\text{MA}_4} \alpha_{\text{H(Y)}} / K_{\text{MY}}.$$

In (2) the term  $\frac{[\text{M}]_t - [\text{MA}_4]}{[\text{MA}_4]} \cdot K_2[\text{A}]^4$  may be neglected in comparison with  $[\text{MA}_4]$  if  $K_2[\text{A}]^4$  is sufficiently low. Thus

$$[\text{Ca}]_t = [\text{MA}_4] \left( 1 + \frac{[\text{MA}_4]}{[\text{M}]_t - [\text{MA}_4]} \cdot \frac{1}{K_1[\text{A}]^4} \right) \quad (3)$$

The second term in the parentheses of (3) may be neglected provided  $K_1[\text{A}]^4$  is sufficiently high or  $\frac{[\text{MA}_4]}{[\text{M}]_t - [\text{MA}_4]}$  is sufficiently low, and then:

$$[\text{Ca}]_t = [\text{MA}_4] \quad (4)$$

In order to apply (4) to a wider range of calcium concentration,  $K_1[\text{A}]^4$  should be sufficiently high and  $K_2[\text{A}]^4$  sufficiently low. In the range where (4) holds calcium can be successfully determined by means of polarography of  $\text{MA}_4$ .<sup>†</sup> It must be borne in mind that, the relationship  $K_1/K_2 = K'_{\text{CaY}}$  existing always,  $K'_{\text{CaY}}$  of higher than  $10^6$  is preferable for the successful indirect polarographic determination of calcium according to exchange equilibrium (1).<sup>‡</sup>

In Fig. 1  $[\text{MA}_4]/[\text{M}]_t$  is plotted against  $[\text{Ca}]_t/[\text{M}]_t$  for various values of  $K_1[\text{A}]^4$ . The higher the value of  $K_1[\text{A}]^4$  is, the wider is the range where (4) holds, *i.e.*  $[\text{Ca}]_t$  is proportional to  $[\text{MA}_4]$  to a value of  $[\text{Ca}]_t/[\text{M}]_t$  more close to unity. From Fig. 1 it is also obvious that  $K_1[\text{A}]^4$  should be more than  $10^2$  in order to apply (4) to a point  $[\text{Ca}]_t/[\text{M}]_t = 0.5$ .

The same considerations for the case of magnesium yields:

$$[\text{Mg}]_t = [\text{MA}_4] \left( 1 + \frac{[\text{MA}_4]}{[\text{M}]_t - [\text{MA}_4]} \cdot \frac{1}{K_1'[\text{A}]^4} \right) \quad (5)$$

where  $K_1' = K_{\text{MgY}} K_{\text{MA}_4} / K_{\text{MY}}$ .<sup>§</sup> In Fig. 2  $[\text{MA}_4]/[\text{M}]_t$  is plotted against  $[\text{Mg}]_t/[\text{M}]_t$  for various values of  $K_1'[\text{A}]^4$ . For sufficiently low values of  $K_1'[\text{A}]^4$  ( $< 10^{-3}$ ), the amount of  $\text{MA}_4$  liberated by magnesium is very small and can be neglected. In order to be successful in the selective determination of calcium in the presence of magnesium,  $K_1[\text{A}]^4$  should be sufficiently high and  $K_1'[\text{A}]^4$  should be sufficiently low. Because  $K_1[\text{A}]^4/K_1'[\text{A}]^4 = K_{\text{CaY}}/K_{\text{MgY}}$ , a complexan should be chosen for which the difference in stabilities between its calcium and magnesium chelates is large.

\* In the case of zinc and cadmium,  $n = 4$  when  $[\text{NH}_3] = 0.1 \sim 1M$ .

† The limiting current of  $\text{MA}_4$  may be practically regarded as diffusion-controlled and its wave-height is proportional to the concentration of  $\text{MA}_4$  in the bulk of the solution.

‡ In an ammoniacal solution ( $\text{pH} \geq 10$ ), it is not difficult to find a complexan forming a calcium chelate of apparent stability constant higher than  $10^{10}$ :  $\log K_{\text{Ca-BDTA}} = 10.7$ ,  $\log K_{\text{Ca-BGTA}} = 11.0$ , *etc.* Thus in these cases it is possible to realise a sufficiently high value of  $K_1[\text{A}]^4$  ( $> 10^2$ ) together with a sufficiently low value of  $K_2[\text{A}]^4$  ( $< 10^{-3}$ ).

§ The ammine complexes of magnesium are not very stable and their formation may be practically neglected:  $[\text{Mg}]_t/[\text{Mg}] < 3$  in  $1M$  ammonia solution.

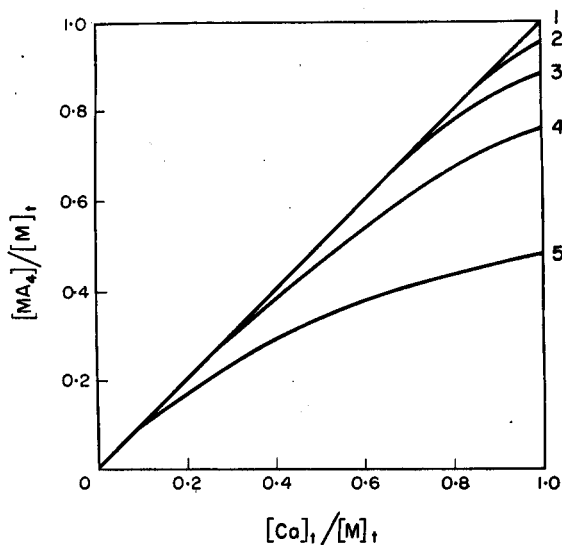


FIG. 1— $[MA_4]/[M]_t$  versus  $[Ca]_t/[M]_t$ .  
 $K_1[A]_4$ : (1)  $10^4$ , (2)  $10^3$ , (3)  $10^2$ , (4) 10, (5) 1.

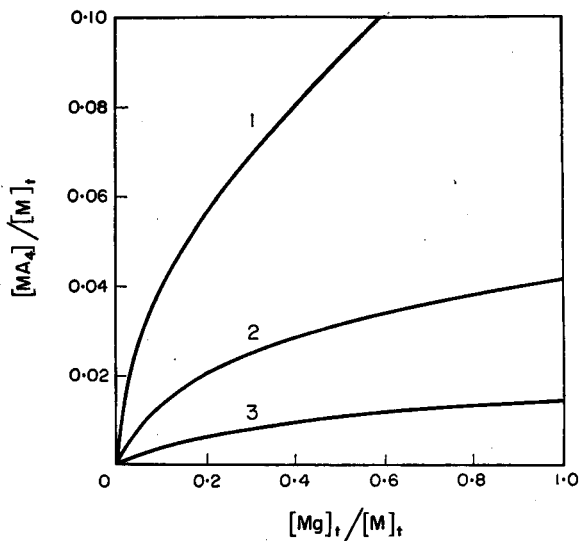


FIG. 2— $[MA_4]/[M]_t$  versus  $[Mg]_t/[M]_t$ .  
 $K_1[A]_4$ : (1)  $10^{-2}$ , (2)  $10^{-3}$ , (3)  $10^{-4}$ .



$K_{Ca-EGTA}/K_{Mg-EGTA}(10^{5.8})$  is much greater than  $K_{Ca-EDTA}/K_{Mg-EDTA}(10^{2.0})$ , and one can realise  $K_1[A]^4$  higher than  $10^2$  together with  $K_1'[A]^4$  lower than  $10^{-3}$  in an exchange equilibria in which EGTA participates.

### Choice of M

It is preferable that M gives a well-defined polarogram under the given conditions. Moreover,  $K_{MY}$ ,  $K_{MA_4}$  and the rate of exchange reaction (1) must be taken into consideration. Elements such as copper, zinc, cadmium, nickel and cobalt are known to form more or less stable ammine complexes. Among them only zinc and cadmium give a one-step reduction wave in an ammonia-ammonium chloride supporting electrolyte and their rate of exchange reaction (1) is sufficiently fast. Thus it is convenient to confine our considerations to the cases of zinc and cadmium.

The stability constants of the species concerned are:<sup>4-6</sup>

$$\begin{aligned} \log K_{Ca-EGTA} &: 11.0 & \log K_{Mg-EGTA} &: 5.2 \\ \log K_{Zn-EGTA} &: 12.8 & \log K_{Cd-EGTA} &: 16.7 \\ \log K_{Zn(NH_3)_4} &: 9.58 & \log K_{Cd(NH_3)_4} &: 7.0. \end{aligned}$$

Using these constants  $K_1[A]^4$  and  $K_1'[A]^4$  can be calculated for various concentrations of ammonia. The results are tabulated in Table I.

TABLE I—CALCULATED VALUES OF  $\log K_1[A]^4$  AND  $\log K_1'[A]^4$  FOR VARIOUS CONCENTRATIONS OF AMMONIA

$[NH_3], M$	Zn-EGTA		Cd-EGTA	
	$\log K_1[A]^4$	$\log K_1'[A]^4$	$\log K_1[A]^4$	$\log K_1'[A]^4$
2.0	8.8	3.0	2.5	-3.3
1.0	7.6	1.8	1.3	-4.5
0.5	6.4	0.6	0.1	-5.7
0.1	3.6	-2.2	-2.7	-8.5

In the case of Zn-EGTA,  $K_1[A]^4$  is so high even in 0.1M ammonia solution, that it is difficult to get a sufficiently low value of  $K_2[A]^4$  because  $K_1/K_2 = K'_{Ca-EGTA}$ . Thus (4) does not hold for a wide range of  $[Ca]_t/[Zn]_t$ . On the other hand,  $K_1'[A]^4$  cannot be sufficiently low under such conditions, as seen from the relationship  $K_1/K_1' = K_{Ca-EGTA}/K_{Mg-EGTA}$ . This is why the effect of magnesium can hardly be neglected in the case of Zn-EGTA. Though  $K_2[A]^4$  and  $K_1'[A]^4$  become fairly low in more dilute ammonia solutions ( $<0.1M$ ), it is not possible to obtain a well-defined wave of zinc ammine complex in such solutions.

In the case of Cd-EGTA, on the contrary, the circumstances are much more favourable, because  $K_{Cd-EGTA} > K_{Zn-EGTA}$  and  $K_{Cd(NH_3)_4} < K_{Zn(NH_3)_4}$ . One can thus easily realise a sufficiently high value of  $K_1[A]^4$  together with a sufficiently low value of  $K_1'[A]^4$  in 0.5-1M ammonia solution. From the practical point of view, the use of cadmium seems to be advantageous for the following reasons:

1. The cadmium ammine complex gives a reduction wave at a potential less negative than that of the zinc ammine.

2. Because of the ease of reversibility of the reduction of the cadmium ammine complex, it would be possible to realise higher sensitivity with the aid of square wave polarography.

## EXPERIMENTAL

### Reagents

$10^{-1}M$  EGTA solution: Twenty ml of 1*N* sodium hydroxide solution are added to 3.8036 g of the pure reagent (Dojin Chemical Co., Kumamoto, Japan) and the whole is diluted to 100 ml. The solution is standardised chelatometrically with cadmium standard solution using Erio T as indicator.

$1.04 \times 10^{-3}M$  Zinc solution: 0.6808 g of metallic zinc (99.99%) is dissolved in a small amount of hydrochloric acid. The excess acid is expelled by evaporation and the solution diluted to 100 ml.

$1.04 \times 10^{-3}M$  Cadmium solution: 1.169 g of metallic cadmium (99.99%) is dissolved in a small amount of hydrochloric acid. The same procedure is then followed as for the zinc solution.

*Metal-EGTA solution*: Equivolume mixtures of the preceding solutions give a  $5 \times 10^{-2}M$  metal-EGTA solution containing a slight excess of metal.

$10^{-2}M$  Calcium standard solution: 1.000 g of calcium carbonate (G.P.) is dissolved in a small amount of hydrochloric acid and carbon dioxide is expelled by boiling. The whole is diluted to 1 litre. The solution is standardised chelatometrically.

$10^{-2}$  and  $10^{-1}M$  Magnesium standard solution: Magnesium chloride (G.P.) is dissolved in water and the solution is standardised chelatometrically.

0.2% Gelatine solution: Prepare daily.

### Apparatus

Pen-recording polarograph (Yanagimoto Co. Ltd., Kyoto, Japan); Characteristics of the dropping mercury electrode:  $m = 1.42$  mg/sec,  $t = 6.4$  sec (open circuit).

### Trial procedure

Calcium and/or magnesium solution and 1.0 ml of 0.2% gelatine solution are added to a 10-ml volumetric flask containing 1 ml of  $5 \times 10^{-2}M$  metal-EGTA solution, 1–2 ml of 1.0*M* ammonium chloride solution and various amounts of 8.0*M* ammonia solution. The solution is then diluted to the mark. An aliquot of the solution is transferred to the polarographic cell. Dissolved oxygen is expelled by a stream of nitrogen passed through an ammonia solution of the same concentration as the electrolytic solution. The polarogram of zinc or cadmium ammine is finally recorded.

### Recommended Procedure

The sample solution should preferably contain 5–20 mg of magnesium and less than 1 mg of calcium in 1–2 ml. One–two ml of sample solution are added to a 10-ml volumetric flask containing 1 ml\* of  $5 \times 10^{-2}M$  Cd-EGTA solution, 1 ml of 1.0*M* ammonium chloride solution and 1 ml of 5.0*M* ammonia solution.† After 1 ml of 0.2% gelatine solution is added, the whole is diluted to the mark. Oxygen is expelled by a stream of nitrogen passed through a 0.5*M* ammonia solution. The polarogram is recorded between  $-0.5$  and  $-1.0$  V. The same procedure is followed on a solution containing 5–20 mg of magnesium and no calcium. The difference in wave-heights between the two measurements may be attributed to the cadmium ammine complex produced by calcium. Consulting a previously constructed calibration curve, one finds the amount of calcium in the sample solution.

## RESULTS AND DISCUSSION

The relationship between wave-height and calcium or magnesium concentration was examined for various concentrations of ammonia and the results are summarised in Figs. 3–6. These results verify the previous considerations. In the case of Zn-EGTA, a linear relationship is observed between  $[Ca]_t$  and the wave-height of the zinc ammine complex when the ammonia concentration is higher than 0.06*M*. However, in these solutions zinc ammine produced by magnesium cannot be neglected (see Fig. 4). Though the effect of magnesium may be neglected in more dilute ammonia solutions, zinc does not give a well-defined polarogram in these solutions.

\* The amount of Cd-EGTA should be more than twice as large as the expected amount of calcium on an equivalence basis.

† If the sample solution contains free base or acid in appreciable amount, it must be taken into consideration.

In the case of Cd-EGTA, a linear relationship holds between  $[Ca]_t$  and the wave-height of the liberated cadmium ammine complex in the following range:  $0.4 \times 10^{-3}M$  of  $[Ca]_t$ , i.d.  $0.0-0.8 [Ca]_t/[Cd]_t$ , in  $1M$  ammonia solution and  $0.3 \times 10^{-3}M$  of  $[Ca]_t$ , i.d.  $0.0-0.6 [Ca]_t/[Cd]_t$  in  $0.5M$  ammonia solution (Fig. 5). As

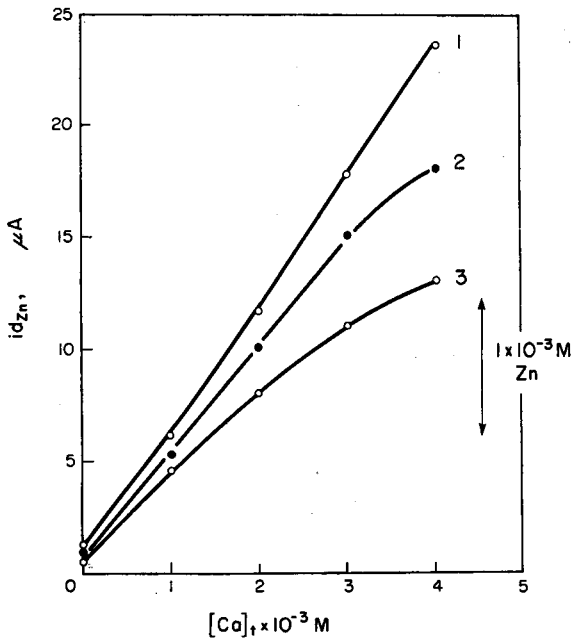


FIG. 3— $i_{dZn}$  versus  $[Ca]_t$

Total concentration of EGTA:  $4.71 \times 10^{-3}M$ ; total concentration of zinc:  $4.80 \times 10^{-3}M$ ;  $NH_4Cl$ :  $0.1M$ ; gelatine:  $0.02\%$ ;  $NH_3$  concentration: (1)  $0.06-0.08M$ , (2)  $0.03M$ , (3)  $0.02M$ .

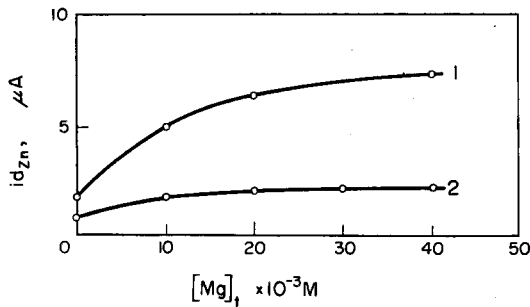


FIG. 4— $i_{dZn}$  versus  $[Mg]_t$

Total concentration of EGTA:  $4.71 \times 10^{-3}M$ ; total concentration of zinc:  $4.80 \times 10^{-3}M$ ;  $NH_4Cl$ :  $0.2M$ ; gelatine:  $0.02\%$ ;  $NH_3$  concentration: (1)  $0.08M$ , (2)  $0.04M$ .

seen from Fig. 6, in  $0.5-1.0M$  ammonia solutions very little effect from magnesium is observed. Particularly in  $0.5M$  ammonia, the effect of magnesium may be neglected even if the concentration attains  $10^{-1}M$  ( $[Mg]_t/[Cd]_t = 20$ ). Thus one may choose

any concentration of ammonia between 0.5 and 1.0M according to the expected concentration of calcium and magnesium in the sample solution.

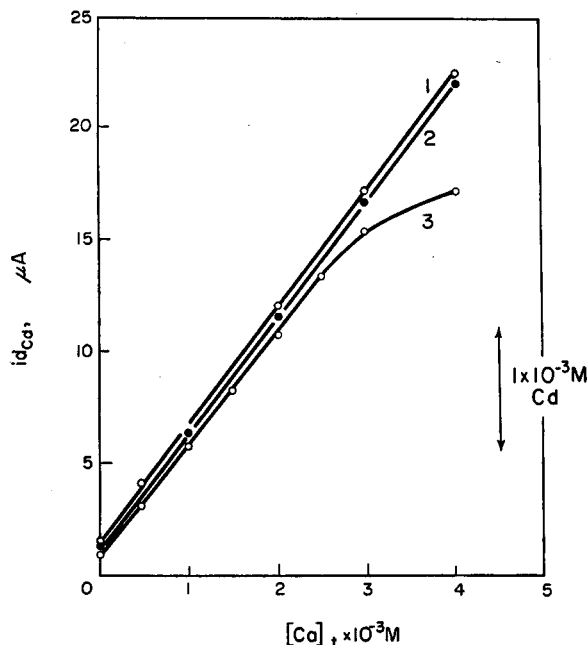


FIG. 5— $i_{dCa}$  versus  $[Ca]_t$

Total concentration of EGTA:  $4.89 \times 10^{-3}M$ ; total concentration of cadmium:  $4.98 \times 10^{-3}M$ ;  $NH_4Cl$ : 0.1M; gelatine: 0.02%;  $NH_3$  concentration: (1) 1.6M, (2) 1.0M, (3) 0.5M.

In Fig. 6 it is shown that the higher the magnesium concentration, the smaller is the value  $\Delta i_{dCd}/\Delta[Mg]_t$  (i.d.  $\Delta[Cd(NH_3)_4]/\Delta[Mg]_t$ ). Therefore, when one deals with a sample containing a large amount of magnesium, it may be convenient to minimise its effect by adding magnesium in an amount 10–20 times\* as much as

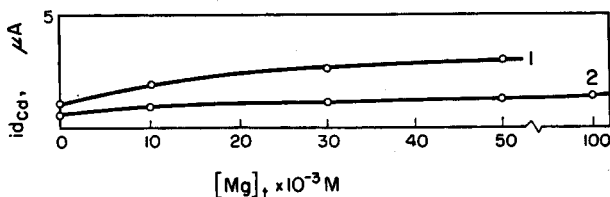


FIG. 6— $i_{dCa}$  versus  $[Mg]_t$

Total concentration of EGTA:  $4.89 \times 10^{-3}M$ ; total concentration of cadmium:  $4.98 \times 10^{-3}M$ ;  $NH_4Cl$ : 0.2M; gelatine: 0.02%;  $NH_3$  concentration: (1) 1.0M, (2) 0.5M.

calcium and subtracting the wave-height of the blank solution† from the resulting wave-height. Thus it is possible to determine calcium accurately in mixtures containing a large excess of magnesium (*cf.* Table II).

\* The effect of magnesium not being considerable, one need not necessarily add exactly the same amount of magnesium as in the sample solution (*cf.* Fig. 6).

† This solution is composed of no calcium and *about* the same amount of magnesium as in the preceding solution.

TABLE II—DETERMINATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM

Ca taken, mg	Mg taken, mg	Mg/Ca (atomic ratio)	Ca found, mg	Diff., mg
0.20	0	0	0.19	-0.01
			0.20	0
	0.25	2	0.19	-0.01
	2.5	20	0.21	+0.01
0.40	5.0	40	0.22	+0.02
	0.25	1	0.39	-0.01
	2.5	10	0.40	0
	10	40	0.42	+0.02
	10	40	0.45 <sup>a</sup>	+0.05
0.80	2.5	5	0.79	-0.01
	10	20	0.82	+0.02
1.20	2.5	3.3	1.16	-0.04
	7.5	10	1.21	+0.01
	10	13.3	1.20	0

<sup>a</sup> No magnesium was added to the blank solution.

Taking into account these considerations, the *Recommended Procedure* for the selective determination of calcium in the presence of magnesium was finally adopted.

In Fig. 7 the influence of magnesium on the determination of calcium is shown. As seen from the results given in Table II, submilligram quantities of calcium can be determined in the presence of a large amount of magnesium.

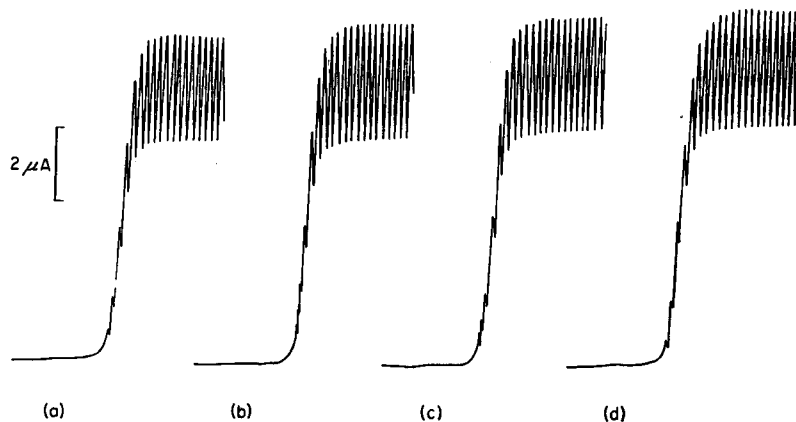


FIG. 7—Influence of magnesium on the determination of calcium.

Total concentration of EGTA:  $4.89 \times 10^{-3}M$ ; total concentration of cadmium:  $4.98 \times 10^{-3}M$ ;  $NH_4Cl$ :  $0.2M$ ;  $NH_3$ :  $0.5M$ ; gelatine:  $0.02\%$ ; calcium added:  $10^{-3}M$ ; magnesium added: (a)  $0M$ , (b)  $10^{-2}M$ , (c)  $5 \times 10^{-2}M$ , (d)  $10^{-1}M$ .

#### Stability constants of Zn-EGTA and Cd-EGTA

Because the values of  $K_{Ca-EGTA}$ ,  $K_{Mg-EGTA}$ ,  $K_{Zn(NH_3)_4}$  and  $K_{Cd(NH_3)_4}$  are known, equations (3) and (5) enable one to calculate the stability constants of Zn-EGTA and Cd-EGTA provided the concentration of zinc and cadmium amines can be determined experimentally.

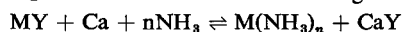
A linear relationship between the limiting current and square root of mercury head confirms that the observed waves are diffusion-controlled. Thus it may be considered that the limiting current reflects the concentration of zinc or cadmium ammine complex.

The results are tabulated in Table III. The constancy of these values confirms the validity of our earlier considerations. These values compare favourably with those obtained by previous workers.<sup>5</sup>

TABLE III—STABILITY CONSTANTS OF Zn-EGTA AND Cd-EGTA (AT  $20 \pm 1^\circ$ )

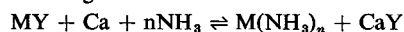
1 Zn-EGTA			
Conditions	Mg added ( $\times 10^{-3}M$ )	Zn(NH <sub>3</sub> ) <sub>4</sub> produced ( $\times 10^{-3}M$ )	log K <sub>Zn-EGTA</sub>
{ 0.5M NH <sub>3</sub> 0.2M NH <sub>4</sub> Cl 5 $\times 10^{-3}M$ in Zn-EGTA	5.0	1.20	12.5 <sub>5</sub>
	10.0	1.61	12.8 <sub>3</sub>
Conditions	Ca added ( $\times 10^{-3}M$ )	Zn(NH <sub>3</sub> ) <sub>4</sub> produced ( $\times 10^{-3}M$ )	log K <sub>Zn-EGTA</sub>
{ 0.02M NH <sub>3</sub> 0.1M NH <sub>4</sub> Cl 5 $\times 10^{-3}M$ in Zn-EGTA	2.0	1.89	12.7 <sub>3</sub>
	4.0	2.65	12.7 <sub>8</sub>
2 Cd-EGTA			
Conditions	Mg added ( $\times 10^{-3}M$ )	Cd(NH <sub>3</sub> ) <sub>4</sub> produced ( $\times 10^{-3}M$ )	log K <sub>Cd-EGTA</sub>
{ 0.5M NH <sub>3</sub> 0.2M NH <sub>4</sub> Cl 5 $\times 10^{-3}M$ in Cd-EGTA	10.0	0.05 <sub>0</sub>	15.0 <sub>2</sub>
	100.0	0.11 <sub>1</sub>	15.5 <sub>0</sub>
{ 1.0M NH <sub>3</sub> 0.2M NH <sub>4</sub> Cl 5 $\times 10^{-3}M$ in Cd-EGTA	10.0	0.12 <sub>8</sub>	15.6 <sub>9</sub>
	30.0	0.22 <sub>6</sub>	15.6 <sub>5</sub>
	50.0	0.30 <sub>8</sub>	15.6 <sub>1</sub>
Conditions	Ca added ( $\times 10^{-3}M$ )	Cd(NH <sub>3</sub> ) <sub>4</sub> produced ( $\times 10^{-3}M$ )	log K <sub>Cd-EGTA</sub>
{ 0.5M NH <sub>3</sub> 0.1M NH <sub>4</sub> Cl 5 $\times 10^{-3}M$ in Cd-EGTA	35.0	2.95	15.8 <sub>9</sub>
	40.0	3.26	15.8 <sub>4</sub>

**Zusammenfassung**—Man betrachtet das Austauschgleichgewicht:



um eine günstigen Bedingungen für die polarographischen Indirektbestimmung des Calciums zu finden. Es wird die Benutzung von Cd-ÄGTA vorschlagen für die selektiven Bestimmung des Calciums im Gegenwart eines grosses Überschusses des Magnesiums.

**Résumé**—Pour trouver une condition optima pour le dosage polarographique indirect du calcium, la considération quantitative est faite sur l'équilibre d'échange suivant:



On propose l'emploi de Cd-EGTA pour le dosage selectif du calcium en présence d'un grand excès de magnésium.

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# POTENTIOMETRIC DETERMINATION OF VANADIUM<sup>IV</sup> WITH CERIUM<sup>IV</sup> SULPHATE AT ROOM TEMPERATURE

## SIMULTANEOUS DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON<sup>II</sup> AND VANADIUM<sup>IV</sup> AT ROOM TEMPERATURE

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**Summary**—The use of orthophosphoric acid as a catalyst has enabled the potentiometric titration of vanadium<sup>IV</sup> to be carried out with cerium<sup>IV</sup> sulphate in 1.0–2.0*N* sulphuric acid medium at room temperature. Using the same catalyst a method has also been developed for the simultaneous differential potentiometric titration of iron<sup>II</sup> and vanadium<sup>IV</sup> with cerium<sup>IV</sup> sulphate in a sulphuric acid medium; this method is more satisfactory than the procedure described by Furman<sup>1</sup> because the first potential break is quite marked and it is more convenient because it avoids the high temperature required for the second stage of the titration in the Furman procedure. Chromium<sup>III</sup> and iron<sup>III</sup> do not interfere in these titrations.

FURMAN<sup>1</sup> attempted the potentiometric determination of vanadium<sup>IV</sup> in sulphuric acid medium with cerium<sup>IV</sup> sulphate. When the titration was carried out at room temperature, he observed that it required several min for the potential to become constant in the neighbourhood of the equivalence point and therefore recommended the titration to be carried out at 50–60°. He observed that the potential break at the equivalence point varied from 25 to 100 mv per 0.05 ml of 0.05*N* cerium<sup>IV</sup> solution when the initial volume of the titration mixture was varied from 200 to 25 ml. Almost simultaneously Willard and Young<sup>2</sup> reported that vanadium<sup>IV</sup> can be determined potentiometrically at 70–75° with cerium<sup>IV</sup> sulphate in sulphuric, hydrochloric or perchloric acid media.

We have observed that potentiometric titrations in 0.5 to 2.0*N* hydrochloric acid medium give much higher titres than the theoretical, the error increasing with increasing concentration of hydrochloric acid. During the earlier part of the titration the potential rises, then remains steady for a long interval until the equivalence point is passed when the potential shows a sudden jump. We<sup>3</sup> have shown that the need for a high temperature arises from the fact that the reaction between vanadium<sup>IV</sup> and cerium<sup>IV</sup> is slow in a sulphuric acid medium at room temperature. Various catalysts were tried to see if the reaction could be accelerated sufficiently well to enable the titration to be carried out at room temperature and it was found that orthophosphoric acid has a pronounced accelerating effect on the reaction. This observation has now been utilised for the potentiometric determination of vanadium<sup>IV</sup> with cerium<sup>IV</sup> sulphate at room temperature and for the differential potentiometric titration of iron<sup>II</sup> and vanadium<sup>IV</sup> in mixtures.



## EXPERIMENTAL

*Reagents*

*Iron<sup>II</sup> ammonium sulphate solution, approx. 0.05N:* Prepared by dissolving about 20 g of the substance in 1 litre of water, sufficient sulphuric acid being added before dilution to give an overall acidity of 1.0N. The solution is standardised against cerium<sup>IV</sup> sulphate solution.

The preparation of 0.05N cerium<sup>IV</sup> sulphate and 0.05N vanadium<sup>IV</sup> sulphate solutions and the source of phosphoric acid have already been described.<sup>3</sup>

*Apparatus*

The potentiometric titration assembly consisted of a Junior potentiometer and a Taut suspension galvanometer (both manufactured by W. G. Pye & Co., England), a saturated calomel electrode as reference electrode and a bright platinum rod electrode as indicator electrode. The salt bridge consisted of a U-tube (with porous end plates) filled with saturated potassium chloride solution. The titration mixture was stirred during the titration by means of a B.T.L. magnetic stirrer.

## RESULTS AND DISCUSSION

About 5.0 ml of 0.05N vanadium<sup>IV</sup> solution is taken in a 150-ml Pyrex beaker and diluted to 80 ml with 1.0N sulphuric acid. When the mixture is titrated at room temperature (28°), the potentials attain stable values quickly after each addition of the cerium<sup>IV</sup> sulphate solution in the initial stages. As the equivalence point is approached, however, the potentials show considerable drift with time, reaching steady values in about 3 min, then just before the equivalence point, it takes 4 min for the potential to reach a constant value. After the equivalence point is reached, the potentials again attain steady values quickly. This behaviour is exemplified by the results presented in Table I. The results also show that in the presence of phosphoric acid (1.0 ml of syrupy phosphoric acid for 80 ml of titration mixture) the potentials do not show any drift with time even in the neighbourhood of the equivalence point.

TABLE I.—POTENTIOMETRIC TITRATION OF VANADIUM<sup>IV</sup> WITH CERIUM<sup>IV</sup> SULPHATE AT ROOM TEMPERATURE (28°)

Volume of cerium <sup>IV</sup> sulphate added, ml	Addendum	e.m.f. (v) observed after							
		30 sec	60 sec	90 sec	120 sec	150 sec	180 sec	210 sec	240 sec
5.70	Nil	0.869	0.867	0.866	0.865	0.865	0.865	—	—
	1.0 ml of H <sub>3</sub> PO <sub>4</sub>	0.864	0.864	0.864	—	—	—	—	—
5.80	Nil	0.905	0.885	0.881	0.880	0.880	0.880	—	—
	1.0 ml of H <sub>3</sub> PO <sub>4</sub>	0.879	0.877	0.877	0.877	0.877	—	—	—
5.90	Nil	0.960	0.950	0.945	0.930	0.927	0.920	0.914	0.911
	1.0 ml of H <sub>3</sub> PO <sub>4</sub>	0.907	0.904	0.904	0.904	0.904	—	—	—
6.00	Nil	1.081	1.080	1.080	1.080	1.080	1.080	—	—
	1.0 ml of H <sub>3</sub> PO <sub>4</sub>	1.004	1.004	1.004	1.004	1.004	1.004	—	—
6.10	Nil	1.127	1.128	1.128	1.128	—	—	—	—
	1.0 ml of H <sub>3</sub> PO <sub>4</sub>	1.075	1.075	1.075	—	—	—	—	—

5.0 ml of vanadium<sup>IV</sup> solution  $\equiv$  5.98 ml of cerium<sup>IV</sup> sulphate solution.

The value of the potential break obtained in a titration carried out (in the presence of phosphoric acid) at room temperature is about 20 mv lower than the potential break obtained during a titration carried out at 60° in the absence of phosphoric acid. This is evident from the data in Table II.

Although the potential break in the presence of phosphoric acid is lower than that obtained in its absence, the potential break is still sufficiently high to enable the equivalence point to be detected easily. The potential break increases as the sulphuric

acid concentration decreases, but there is a risk of cerium phosphate being precipitated when the concentration of sulphuric acid is below 1.0*N*. Several titrations of vanadium<sup>IV</sup> have also been carried out keeping the concentration of sulphuric acid at 2.0*N*, but varying the amount of syrupy phosphoric acid from 0.5 to 2.5 ml. The results in Table III show that the potential break decreases as the phosphoric acid concentration increases. Moreover, when the amount of syrupy phosphoric acid is increased beyond 2.5 ml precipitation of cerium phosphate begins. In view of these findings, the optimum amount of syrupy phosphoric acid is fixed as

TABLE II

Conditions of titration	Potential break at the equivalence point per 0.1 ml of 0.04 <i>N</i> cerium <sup>IV</sup> sulphate, <i>mV</i>
0.5 <i>N</i> H <sub>2</sub> SO <sub>4</sub> at 60°	153
0.5 <i>N</i> H <sub>2</sub> SO <sub>4</sub> + 1.0 ml of H <sub>3</sub> PO <sub>4</sub> at 28°	129
1.0 <i>N</i> H <sub>2</sub> SO <sub>4</sub> at 60°	147
1.0 <i>N</i> H <sub>2</sub> SO <sub>4</sub> + 1.0 ml of H <sub>3</sub> PO <sub>4</sub> at 28°	108
2.0 <i>N</i> H <sub>2</sub> SO <sub>4</sub> at 60°	107
2.0 <i>N</i> H <sub>2</sub> SO <sub>4</sub> + 1.0 ml of H <sub>3</sub> PO <sub>4</sub> at 28°	96

1.0 ml for 80 ml of the titration mixture and the optimum concentration of sulphuric acid prescribed as 1.0 to 2.0*N*. When 5.0 ml of syrupy phosphoric acid is used, the titration can be made in 4.0*N* sulphuric acid medium without any risk of cerium phosphate being precipitated. The potential break under these conditions is 84 *mV* per 0.1 ml of 0.04*N* cerium<sup>IV</sup> solution as compared with the break of 96 *mV* obtained in titrations in 2.0*N* sulphuric acid (using 1.0 ml of syrupy phosphoric acid) and a break of 108 *mV* observed in titrations in 1.0*N* sulphuric acid (using 1.0 ml of syrupy phosphoric acid). These results can be understood when we take into account the facts that the vanadium<sup>V</sup>/vanadium<sup>IV</sup> potential increases with increase in the acid concentration, and that the cerium<sup>IV</sup>/cerium<sup>III</sup> potential does not change very much with an increase in the concentration of sulphuric acid.

TABLE III.—EFFECT OF PHOSPHORIC ACID ON THE POTENTIOMETRIC TITRATION OF VANADIUM<sup>IV</sup> WITH CERIUM<sup>IV</sup> SULPHATE IN 2.0*N* SULPHURIC ACID AT ROOM TEMPERATURE

Amount of phosphoric acid added, <i>ml</i>	Break in potential at the equivalence point per 0.10 ml of 0.04 <i>N</i> cerium <sup>IV</sup> sulphate, <i>mV</i>
0.50	109
1.00	96
2.50	91

*Recommended procedure for potentiometric titration of vanadium<sup>IV</sup> with cerium<sup>IV</sup> sulphate*

An aliquot volume of vanadium<sup>IV</sup> solution taken in a 150-ml Pyrex beaker is diluted to 80 ml with 1.0 to 2.0*N* sulphuric acid, then treated with 1.0 ml of syrupy phosphoric acid. The titration is carried out with 0.05*N* cerium<sup>IV</sup> sulphate solution using the electrometric titration assembly described above. The cerium<sup>IV</sup> sulphate is added while stirring the solution and the stirring is continued for about 15 sec after each addition. The stirring is then stopped and the potential noted. Towards the close of the titration, the potentials are noted 1 min after each addition of cerium<sup>IV</sup> sulphate. The break in potential at the end-point per 0.05 ml of 0.05*N* cerium<sup>IV</sup> sulphate corresponds to about 50–60 *mV*.

Some typical results are given in Table IV.

Amount of vanadium <sup>IV</sup> , millimoles	
Taken	Found
0.3030	0.3018
0.3310	0.3315
0.4417	0.4402
0.6061	0.6046
1.0200	1.0170

### Interferences

Iron<sup>III</sup> and chromium<sup>III</sup> do not interfere with the determination of vanadium<sup>IV</sup> by the proposed method. The presence of these salts does not even effect the value of the break in potential.

### Titration in a hydrochloric acid medium

Titration of vanadium<sup>IV</sup> with cerium<sup>IV</sup> sulphate in hydrochloric acid medium at room temperature using phosphoric acid as a catalyst gave slightly higher titres than the theoretical values (about 1.5% higher in 1.0N hydrochloric acid and 2.0% higher in 2.0N hydrochloric acid).

### Titration in a perchloric acid medium

In the titration of vanadium<sup>IV</sup> with cerium<sup>IV</sup> sulphate solution in 0.5 to 2N perchloric acid medium the potential jumps are higher than in a sulphuric acid medium, but the titres are still slightly higher (about 0.5 to 1.0%) than the theoretical values.

### Differential titration of iron<sup>II</sup> and vanadium<sup>IV</sup> in mixtures

Furman<sup>1</sup> reported the potentiometric titration of a mixture of iron<sup>II</sup> and vanadium<sup>IV</sup> with cerium<sup>IV</sup> sulphate in the following manner. The mixture is first titrated at room temperature, then at 50–60°. The first jump in potential corresponds to complete oxidation of iron<sup>II</sup> and the second jump corresponds to complete oxidation of vanadium<sup>IV</sup>. The method is not satisfactory because the first jump in potential is very small. The correct equivalence point corresponding to the complete oxidation of iron<sup>II</sup> can be obtained only from the curve showing the relation between  $\frac{\Delta E}{\Delta V}$  and V. The equivalence point cannot be obtained from the simple curve showing the relation between E and V. Smith and Getz<sup>4</sup> carried out the differential potentiometric titration of a mixture of iron<sup>II</sup> and vanadium<sup>IV</sup> perchlorates in 8N perchloric acid medium with ammonium nitratocerate. They found that the potential break at either of the stages is about 300 mv. Obviously this method is not of much practical interest because it would be very tedious indeed to get both of the metals in the form of perchlorates.

We have been able to carry out the simultaneous differential titration of iron<sup>II</sup> and vanadium<sup>IV</sup> in 1.0–2.0N sulphuric acid medium at room temperature using a small quantity of orthophosphoric acid as a catalyst for the oxidation of vanadium<sup>IV</sup> by cerium<sup>IV</sup>.

When a mixture of iron<sup>II</sup> and vanadium<sup>IV</sup> is titrated with cerium<sup>IV</sup> sulphate, iron<sup>II</sup> will be oxidised first and even if a little vanadium<sup>IV</sup> is oxidised, the vanadium<sup>V</sup> formed will, in turn, oxidise iron<sup>II</sup> and itself be reduced to vanadium<sup>IV</sup>, so that in effect vanadium<sup>IV</sup> will not be oxidised until iron<sup>II</sup> is completely oxidised. After all of the iron<sup>II</sup> is oxidised the slight excess of cerium<sup>IV</sup> oxidises vanadium<sup>IV</sup> to vanadium<sup>V</sup> and there will be a sudden jump in potential. This break in potential corresponds to the one obtained during the electrometric titration of iron<sup>II</sup> with vanadium<sup>V</sup>. Moreover, the presence of phosphoric acid helps to increase the value of this break in potential; under our experimental conditions the first break has been found to have a value of 60–70 mv per 0.05 ml of 0.05N cerium<sup>IV</sup> sulphate solution. The second break in potential has been observed to have a value of 55–65 mv per 0.05 ml of 0.05N cerium<sup>IV</sup> sulphate solution.

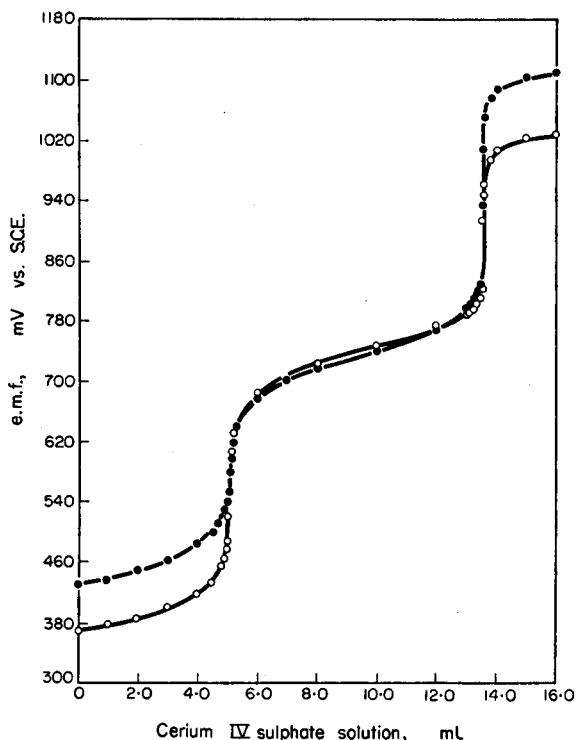


FIG. 1.—Electrometric titration of a mixture of iron<sup>II</sup> and vanadium<sup>IV</sup> with cerium<sup>IV</sup> sulphate:  
 ●—1.0N sulphuric acid, according to Furman's procedure  
 ○—1.0N sulphuric acid in the presence of 1 ml of phosphoric acid, at room temp.

*Recommended procedure for potentiometric titration of a mixture of iron<sup>II</sup> and vanadium<sup>IV</sup> with cerium<sup>IV</sup> sulphate*

The mixture of iron<sup>II</sup> and vanadium<sup>IV</sup> taken in a 150-ml Pyrex beaker is diluted with 1.0–2.0N sulphuric acid to 50 ml and 1.0 ml of syrupy phosphoric acid is added. It is then titrated with cerium<sup>IV</sup> sulphate solution at room temperature using the potentiometric equipment already described.

Some typical results are presented in Table V.

Fig. 1 gives a typical curve showing the relation between the observed e.m.f. and the volume of cerium<sup>IV</sup> sulphate solution added. The results show that the method now

developed is precise and more convenient than those of previous investigators. The method is likely to prove of great value in the analysis of vanadium steels and chrome vanadium steels.

We have attempted to use ferroin in the phosphoric acid catalysed system. If the titration is made in a 1.0*N* sulphuric acid medium the indicator shows the colour change when both iron<sup>II</sup> and vanadium<sup>IV</sup> are oxidised, but the colour transition is not sharp on account of the diminishing intensity of the ferroin red colour as the end-point is approached. This determination can be made very satisfactorily by carrying out

TABLE V

Amount of iron <sup>II</sup> , millimoles		Amount of vanadium <sup>IV</sup> , millimoles	
Taken	Found	Taken	Found
0.2939	0.2947	0.3988	0.3988
0.3000	0.2996	0.5000	0.4983
0.3515	0.3530	0.3843	0.3843
0.4000	0.3985	0.4000	0.3985
0.6000	0.5991	0.4000	0.3992

the titration in a 1.5–2.5*N* sulphuric acid medium using Rhodamine 6G as a fluorescence indicator, in the presence of 1.0–1.5 ml of syrupy phosphoric acid per 50 ml of the titration mixture. Iron<sup>II</sup> alone can be determined by carrying out the titration with cerium<sup>IV</sup> sulphate in 10–12*N* sulphuric acid, because any vanadium<sup>V</sup> formed by oxidation of vanadium<sup>IV</sup> will oxidise ferroin in 10–12*N* sulphuric acid.

**Zusammenfassung**—Die Verwendung von Phosphorsäure als Katalysator ermöglicht die potentiometrische Titration von Vanadin(IV) mit Cer(IV) in 1–2 *n* Schwefelsäure bei Zimmertemperatur. Mit dem gleichen Katalysator wurde ein Methode entwickelt zur simultanen, differential-potentiometrischen Titration von Eisen(II) und Vanadin(IV) mit Cer(IV) in schwefelsaurem Medium. Diese Methode arbeitet besser als die von Furman, da der erste Potentialsprung besser ausgeprägt ist. Ein weitere Vorteil ist, dass für den zweiten Teil der Titration keine erhöhte Temperatur benötigt wird. Chrom(III) und Eisen(III) stören nicht.

**Résumé**—L'utilisation de l'acide orthophosphorique comme catalyseur permet le titrage potentiométrique du vanadium(IV) par le sulfate de cérium(IV) en milieu acide sulfurique 1,0 à 2,0 *N*, à la température ordinaire. En utilisant le même catalyseur, une méthode est proposée pour le titrage simultané par potentiométrie différentielle du fer(II) et du vanadium(IV) par le sulfate de cérium(IV) en milieu acide sulfurique; cette méthode est meilleure que celle de Furman pour deux raisons: le premier saut de potentiel est plus marqué et, de plus, la méthode est d'une mise en oeuvre plus commode en n'imposant pas d'opérer à haute température pour la deuxième partie du titrage. Le chrome(III) et le fer(III) ne gênent pas dans ces dosages.

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## BOOK REVIEWS

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**Instrumental Methods for the Analysis of Food Additives.** WILLIAM H. BUTZ and HENRY J. NOEBELS. Interscience Publishers, New York, 1961. pp. viii + 288. \$11.

THIS volume is the published proceedings of a Symposium held in Michigan State University during March, 1960. The Symposium, which was attended by Food Chemists and Biologists from a wide field, was initiated following the invoking of the new U.S. food laws. Under these laws the burden of proving the safety of additives rests with the food processor. The editors of the book (both employees of Beckman Instruments Inc.) claim that it comprises "a comprehensive review of low level analysis including specific, fast and reliable procedures both new and old."

The first part of the book is devoted to the significance of the new food laws and the way in which they operate in practice. It describes the petition that the manufacturer must make to the F.D.A. and the safeguards required by that organisation before an additive is likely to be considered as acceptable. It also describes the recourse which the petitioner has should his proposal be rejected. It is pointed out that it is a matter of opinion as to whether the biological knowledge of today is totally adequate to support legislation designed to provide complete safety in the use of these chemicals, and that the case for allowing finite amounts of specified chemicals in certain foodstuffs becomes unassailable if the populations of the world are to be fed in adequate quantities.

The second part of the book deals with analytical evaluation of additives in food. It reviews methods of sampling and the cleanup procedures advocated prior to final determination. Specifically referred to are the methods to be applied when determining DDT residues in many differing types of foodstuffs, and also of different residues which might be found in packaging materials.

The third part is concerned with identification and it is here that instrumentation is discussed in any detail. Amongst the instruments and techniques cited are those for (a) colorimetry, (b) ultra-violet spectrophotometry, (c) infrared spectroscopy, (d) isotope dilution technique, and (e) micro coulometric gas chromatography.

Part four is entitled "Analytical Procedures" and includes how to set up a food additives laboratory and what equipment is required. It includes certain specific methods, *e.g.*, quinine in tonic water, maleic hydrazide in potatoes, methylcellulose in mayonnaise, oleandomycin in animal feeds, Tween in ice cream, and gibberellic acid in beer.

The volume is of undoubted interest to food analysts everywhere, but my opinion is that the technique side of the problems is treated rather superficially and that the many snags which arise in applying methods to biological material are not given sufficient emphasis. The problems are more difficult than the authors here imply.

R. F. MILTON

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**Treatise on analytical chemistry. A comprehensive account in three parts.** Edited by I. M. KOLTHOFF and PHILIP J. ELVING, with the assistance of ERNEST B. SANDELL. **Part II. Analytical chemistry of the elements. Section A. Systematic analytical chemistry of the elements. Volume I. Inorganic nomenclature. General concepts. Hydrogen. Water. Inert gases. Alkali metals.** Authors of Volume I: H. F. BEEGHLY, GERHARD A. COOK, W. CONARD FERNELIUS, JAMES I. HOFFMAN, SILVE KALLMAN, JOHN MITCHELL, JR. Interscience Publishers Inc., New York, Interscience Publishers Ltd., London, 1961. Pp. xxi + 471, \$16.00 (Subscription price \$14.00).

THE aim of the textbook is to give a critical review of the methods of analytical chemistry rather than to be an encyclopædic work containing all methods of analysis. General analytical methods, both classical and instrumental, have already been treated in Part I. Part II is being edited in three Sections; Section A deals with the analytical chemistry of the various elements, when present in inorganic substances; Section B will present the analysis of elements in organic substances; and Section C will deal with qualitative analysis, both inorganic and organic.

The first part of this volume, *Principles of Inorganic Nomenclature* (W. Conard Fernelius), gives detailed information on this subject, on the basis of the most recent international agreements. Nomenclature is extensively illustrated by formulae and structural figures; in particular, a great number of

complexes are dealt with. It may be hoped that on this basis the nomenclature of complexes can be made uniform, since this field is at present somewhat of a jungle, because of the variety of names and concepts of nomenclature to be found in the literature.

In the short second part, *Determination of the Elements: General Concepts*, James I. Hoffman first presents an historical account of the tasks of analytical chemists, and then describes the difficulties and problems of analysts today and in the future.

The systematic treatment of elements then begins. In all subsequent parts the material is arranged according to the following system: First a short summary is given of the occurrence of the element, of industrial processes involving it, and of its toxicology. This introduction is followed by a description of analytically important physical and chemical properties of the element; distinctive features in the sampling of materials containing the element; an outline of its separation and isolation; systematic discussion of the current situation in respect of the detection and quantitative determination of the element and the analysis of its most important compounds; selected references for the determination of the element in specific materials; critically selected general laboratory procedures. The elements are in general arranged according to the Periodic Table.

The first systematically treated element is hydrogen (H. F. Beeghly). Among methods of determination, the combustion method, the vacuum fusion method and the hot extraction method are detailed separately, while miscellaneous methods are mentioned briefly, with the corresponding references (11) in the bibliography.

Water is discussed in a separate section (John Mitchell, Jr.). For the detection of water four methods, and for its determination a wide range of methods, are described. Among chemical methods, the Karl Fischer titration is discussed in detail, but the acetyl chloride, acetic anhydride, calcium carbide, calcium hydride, magnesium nitride and other methods are also described. After discussion of gravimetric methods, and the separation of water, instrumental methods are described, including photometric and spectrometric, neutron-scattering, and other physical, thermal and electrical methods. The determinations of deuterium oxide and tritium oxide are presented in separate chapters. Recommended laboratory processes are summarised separately. An extensive bibliography, comprising 356 references, concludes this part.

The next part deals with the analytical chemistry of inert gases (Gerhard A. Cook). Their isolation, and mass spectrometric methods, gas chromatography, emission spectroscopy, desorption methods and neutron-activation analysis are detailed. Analyses of binary mixtures by various physical methods are described. In addition to 129 original papers, a number of general references, including textbooks and monographs, are listed.

The last part, dealing with the alkali metals (Silve Kallman) is arranged not according to the single elements, but according to methods; within these small chapters the methods for the determination of the alkali metals are detailed separately. Problems of sampling and qualitative tests are described thoroughly, and methods for the quantitative determination are presented in the following order: chemical methods, optical methods including flame photometry, polarographic procedures, radiochemical methods, stable isotope-dilution techniques. A separate chapter deals with the analysis of alkali metal alloys and compounds; selected laboratory processes are presented. The Section concludes with 471 references.

A subject index is given at the end of the volume. The contents are presented at the beginning of the book, and in addition before each section the contents of the chapters which it includes are reprinted. This makes the book more easy to use.

Although the book is written by a number of authors, each with experience in the appropriate field of analytical chemistry, the various parts are arranged fairly uniformly. Thus, the user of the book can easily familiarise himself with the text. When future volumes have been published, and the whole work is completed, analytical chemists will have an excellent guide in their work. We await subsequent volumes with great interest.

GYULA SVEHLA

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**Treatise on Analytical Chemistry.** Edited by I. M. Kolthoff and Philip J. Elving, with the assistance of Ernest B. Sandell. **Part II. Analytical Chemistry of The Elements, Vol. 7.** Interscience Publishers, Inc., 1961, New York and London. Pp. xxiii + 567. Price \$20.75; Subscription Price \$18.50.

SECTION A of Part II of this treatise is concerned with the Systematic Analytical Chemistry of the Elements. The elements discussed in Volume 7 are sulphur (121 pp.) by B. J. Heinrich, M. D. Grimes, and J. E. Puckett; selenium and tellurium (63 pp.) by Thomas E. Green and Max Turley; fluorine (105 pp.) by Charles A. Horton; chlorine, bromine, and iodine (80 pp.) by G. W. Armstrong, H. H. Gill, and R. F. Rolf; manganese (70 pp.) by M. D. Cooper and Paul K. Winter; and rhenium (27 pp.) by Charles L. Rulfs. The chapters are organised according to the following outline: a brief discussion

of the occurrence of the element, industrial processes, toxicology, a description of the important physical and chemical properties of the element, sampling procedures, separation and isolation techniques, qualitative and quantitative analyses, discussion of selected methods for the determination of the element(s), and a few detailed laboratory procedures. In common with previous volumes in this series, there is a considerable variation in the presentations, as might be supposed from the number of pages indicated above.

In general, the treatment of the elements in this volume is much more comprehensive than in earlier volumes. For example, the discussion of the analytical chemistry of sulphur is followed by 438 references. The material presented should surely be of interest and utility to all analysts. The chapter devoted to selenium and tellurium features a knowledgeable discussion of the acidic character of these two elements and indicates a considerable amount of personal experience. There are no detailed laboratory procedures for these two elements, in the usual sense—an omission to be regretted in view of their unusual behaviour.

The chapter on fluorine is written by one who has been working in this field since his post-graduate days. As might be expected, the presentation of the material is both scholarly and comprehensive, and succeeded by 24 pages of references. Whereas most of the chapters are obviously reviews, the material on fluorine is based extensively on Dr. Horton's personal experience and evaluation.

The chapter devoted to the halogens is, in general, well presented, and is worthy of note by the analyst. It is marred, however, by several unusual and/or ambiguous statements, for example, "Since the most stable metal-to-halogen bonds are those that are most nearly covalent, the stability tends to shift preferentially to a reverse-order stability".

I found the chapter on manganese quite interesting and one of the most "readable" chapters in the series. The discussion of industrial processes involving manganese reveals a rather unusual personal knowledge of this facet.

Finally, the chapter on rhenium is very brief (as is also the material to be covered) but contains the essential information.

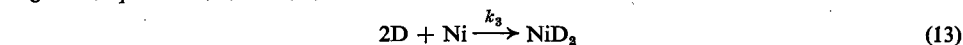
In conclusion, there is no doubt that this volume represents a noticeable improvement over earlier volumes in the series.

J. O. HIBBITS

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## ERRATA—VOLUME 9

Page 706, equations (13) and (15) should read:





## NOTICES

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

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### CZECHOSLOVAKIA

November 1962: Autumn Meeting: Association for Spectral Analysis. Prague.

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The East Bohemia Section for Analytical Chemistry of ČSVTS announces the **First International Exhibition of Photography in Microchemistry and Chemistry in Microphotography**. The purpose of the exhibition is to popularise micro methods in all branches of chemistry, preparative and analytical, and to make the public acquainted with the excellent work in this field. Everyone is welcome to participate in the exhibition with 4 black-and-white photographs (40 × 30 cm) and with 4 colour photographs (40 × 30 or 30 × 24 cm). On the reverse side of all photographs should be indicated the name of the author, his address and, if possible, the address of his employer and the description of the subject of the photograph. Material sent from abroad should be indicated by the following notice: Photographs for exhibition—Unsaleable—Free of Duty. Photographs will be accepted prior to 1 December, 1962.

The exhibition will take place at Pardubice. The authors of the five best photographs will receive a Presentation Award Certificate. When the exhibition finishes, photographs will be returned to authors, although the organisers of the exhibition reserve for propagation the right to publish the photographs. Photographs should be sent by registered post to Dr. M. VEČEŘA, výzkumný ústav organických syntéz, Pardubice, Rybitví, Czechoslovakia.

### DEUTSCHE DEMOKRATISCHE REPUBLIK

Die *Hauptjahrestagung 1962 der Chemischen Gesellschaft in der Deutschen Demokratischen Republik* findet in der Zeit von *Mittwoch, dem 21. November 1962, bis Sonnabend, dem 24. November 1962*, in Leipzig statt.

Hauptthema: **Methoden und Ergebnisse der Strukturchemie.**

### SWEDEN

April 1964: **Third International Measurement Conference (IMEKO) and Sixth Instruments and Measurement Conference (I & M)**. Stockholm.

As previously, the main purpose of the IMEKO Conference is to discuss the latest scientific achievements within fundamental and applied research from important branches of measurement and instrumentation. The papers should deal with theory or practice of measurement and instrumentation of interest to the research scientist as well as to specialists engaged in the design and manufacture of instruments.

The Sections of the Conference, into which papers will be classified, are as follows:

210. Fundamental problems of metrology.
211. Theory and practice of instrument design.
212. Technology and organisation in instrument manufacture.
213. General electronics as applied to measurements and instruments.
214. Border-questions of measurement and automation.
221. Instruments and methods for measuring geometrical and mechanical quantities, including geodetic measurements.
223. Instruments and methods for measuring thermal quantities.
224. Instruments and methods for physico-chemical measurements.
225. Instruments and methods for measuring electrical and magnetic properties.
226. Instruments and methods for measurements in radio engineering.
227. Instruments and methods for measuring radioactive radiation.

Submitted papers should contain *unpublished original material* in the field of fundamental or applied research. It is permitted, however, to send in papers which have previously been published in a technical journal having a limited circulation, but a copy of this publication should be attached to the abstract in this case.

Summaries of 150–250 words, presented in at least one of the conference languages (English, French, German or Russian), should be forwarded before 15 November, 1962, to the Member Organisation in Bulgaria, Chinese People's Republic, Czechoslovakia, German Democratic Republic, Hungary, Italy, Japan, Poland, Rumania, Soviet Union, Sweden, United Kingdom and United States of America.

While representatives of technical societies in Austria, Belgium, Denmark, France, German Federal Republic and Yugoslavia also participate in the work of the IMEKO as observers, correspondence from these and other countries not represented by Member Organisations, concerning papers to be presented at the conference, should be directed to the IMEKO Secretariat, Budapest 5, P.O. Box 3, Hungary.

#### SWITZERLAND

*Tuesday 27 August–Saturday 7 September 1963: Second International Congress of the International Federation of Automatic Control and First International Exhibition of Industrial Electronics.* Basle.

Further details of the IFAC Congress may be obtained from the Secretary's Office of the IFAC Congress 1963, Kinkelstrasse 10, Postfach 289, Zurich 35, Switzerland, and of the INEL Electronics Exhibition from the Press Department of Swiss Industries Fair, Postfach, Basle 21, Switzerland.

#### UNITED KINGDOM

*Thursday 25 October 1962: Statistical Approach to Analysis:* Dr. D. A. PANTONY: *Society for Analytical Chemistry, Midlands Section.* Technical College, Nottingham.

*Thursday 8 November 1962: Solvent Extraction:* Mr. T. B. PIERCE: *Society for Analytical Chemistry, Midlands Section.* Technical College, Coventry.

*Friday 9 November 1962: Some Organic Applications of Polarography:* *Polarographic Society.* College of Advanced Technology, Loughborough.

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The collection of spectra—infrared, ultraviolet and other types—to form a central **Spectra Index** from which scientists in this country and abroad will be able to obtain information, has begun at the Scientific Documentation Centre, Dunfermline, Scotland. The Centre was started on a full-time basis one year ago. Close liaison is being maintained by the Centre with studies in other parts of the world, especially with U.S.A., into the particular information retrieval problems found when handling spectra and several publications on the subject have been made by this unit.

During the past year, help from industrial and governmental sources has enabled the work to progress, and micro filming, dark-room and workshop facilities have been installed which have made it possible for the collection of spectra to begin.

#### UNITED STATES OF AMERICA

*Thursday–Saturday 1–3 November 1962: Annual Southeastern Regional Meeting of American Chemical Society: American Chemical Society, East Tennessee Section and Oak Ridge National Laboratory.* Gatlinburg, Tennessee (see *Talanta*, 1962, 9, 628).

*Wednesday–Friday 14–16 November 1962: 1962 Eastern Analytical Symposium and Instrument Exhibit: Analytical Chemistry Groups of American Chemical Society of New York and North Jersey Sections, and New York, Delaware Valley, New England and Baltimore–Washington Sections of Society for Applied Spectroscopy, and Metropolitan Microchemical Society.* Statler Hilton Hotel (see *Talanta*, 1962, 9, 751).

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*Monday–Thursday 20–23 May 1962: Fourteenth Annual Mid-American Spectroscopy Symposium: Society for Applied Spectroscopy, Chicago Section.* Sheraton-Chicago Hotel, Chicago.

Original papers are invited from the fields of mass, emission, X-ray, general absorption, infrared, NMR, EPR, Raman and flame spectroscopy, as well as gas chromatography. Absolute deadline for receipt to title and abstracts is 15 January, 1963.

As in the past, the meeting will feature seminars, problem clinics and an instrument exhibit by leading manufacturers in the fields of spectroscopy and gas chromatography. Further information can be obtained from JOHN E. FORRETTE, Roy C. Ingersoll Research Center, Borg-Warner Corporation, Wolf and Algonquin Roads, Des Plaines, Illinois, U.S.A.

## PAPERS RECEIVED

- Copper<sup>II</sup> catalysis of 8-acetoxyquinoline hydrolysis: C. R. WASMUTH and HENRY FREISER. (30 July 1962).
- Sodium peroxide as a flux in refractory and mineral analysis: C. B. BELCHER. (30 July 1962).
- N,N,N',N'*-Tetramethyl-*o*-tolidin (tetron) als reagen zur bestimmung geringer mengen von oxydationsmitteln (Au (III), Ce (IV), BrO<sub>3</sub><sup>-</sup> u.a.): N. JORDANOV and CH. DAIEV. (2 August 1962).
- A new reductometric reagent—iron<sup>II</sup> in a strong phosphoric acid medium—II: Titration of molybdenum<sup>VI</sup> with iron<sup>II</sup> at room temperature: G. GOPALA RAO and SEETARAMA RAJU SAGI. (2 August 1962).
- Indirect spectrophotometric determination of the sulphate ion: VLADIMIR PALATY. (2 August 1962).
- Photometric determination of boron in aqueous medium with phthalein violet: VENCESLAV PATROVSKY. (2 August 1962).
- Use of Me<sup>3+</sup>TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>.cH<sub>2</sub>O type compounds in analytical chemistry—I: The determination of potassium in barium titanate: H. AREND and J. NOVAK. (2 August 1962).
- The determination of thiomalic acid: G. ARAVAMUDAN and C. RAMA RAO. (2 August 1962).
- Polarography of Ce<sup>IV</sup> in acetate buffer: O. P. AGRWAL and R. C. KAPOOR. (6 August 1962).
- Theory of the indicator transition in chelatometry with special reference to the effect of a second metal: GENKICHI NAKAGAWA and MOTOHARU TANAKA. (6 August 1962).
- The use of oxycellulose for the collection of traces of metal—I: Qualitative investigations: E. SCHULEK, Zs. REMPERT-HORVATH and A. LASZTITY. (15 August 1962).
- Thermal neutron-activation analysis of titanium using 5.8-minute titanium-51 and rapid radiochemical separations: CHONG KUK KIM and W. WAYNE MEINKE. (16 August 1962).
- The determination of boron in zirconium and Zircaloy: EUGENE N. POLLOCK and LAWRENCE P. ZOPATTI. (16 August 1962).
- The analysis of beryllium and beryllium oxide—VII. The determination of nickel: JAMES O. HIBBITS. (16 August 1962).
- Cation-exchange separation of bivalent metal ions from rare earths: JAMES S. FRITZ and BARBARA B. GARRALDA. (16 August 1962).
- Determination of sodium in aqueous salt solutions by a glass electrode: JOHN R. GLASS and O. I. MILNER. (16 August 1962).
- In commemoration of the Hungarian scientist L. W. Winkler, on the centenary of his birth: E. SCHULEK. (14 August 1962).
- History of Hungarian analytical chemistry: F. SZABADVÁRY. (14 August 1962).
- Ascorbinometric determination of hypochlorite and hypobromite based on thallium<sup>III</sup> titration: L. ERDEY and K. VIGH. (14 August 1962).
- Investigations on the accuracy of zinc determinations by atomic absorption methods: L. ERDEY, G. SVEHLA and L. KOLTAI. (14 August 1962).
- 2-Hydroxy-4-amino-4'-methoxydiphenylamine, a new redox indication: L. ERDEY, I. KÁSA, T. MEISEL. (14 August 1962).
- Microdetermination of cyanide ions with radioactive precipitate exchange: E. BÁNYAI, F. SZABADVÁRY and L. ERDEY. (14 August 1962).
- Titration of thallium<sup>I</sup> ions using chemiluminescent end-point detection: I. BUZÁS and L. ERDEY. (14 August 1962).
- Derivatographic determination of calcite content of bauxites: F. PAULIK, G. LIPTAY and S. GÁL. (14 August 1962).
- Application of the flask method for the analysis of high-halogenated organic substances: L. MÁZOR, K. M. PÁPAY and P. KLATSMÁNYI. (14 August 1962).
- The use of a plate electrode for spectrochemical analysis of solutions: T. KÁNTOR. (14 August 1962).
- The role of rate of atomisation in flame photometry: E. PUNGOR and M. MAHR. (14 August 1962).
- Inorganic chromatographic investigations in a glacial acetic acid medium: I. KRAUSZ, I. R. TAKÁCS and A. E. HAVAS. (14 August 1962).
- Titrations in non-aqueous medium with a standard solution of amidazophene (dimethylamino-phenyl pyrazolone)—I: Determination of carboxylic chlorid and their decomposition products: L. BARCZA. (14 August 1962).

- Analytical control methods for polyvitamin preparations:** K. BURGER. (14 August 1962).
- New methods for the determination of *p*-aminosalicylic acid (PAS):** E. SCHULEK, L. MAROS and I. MOLNÁR. (14 August 1962).
- Investigation of changes in the oxidation state of cerium in hot sulphuric acid solutions:** I. PAIS, E. SCHULEK and M. RÓZSAHEGYI. (14 August 1962).
- Determination of *p*-aminobenzoic acid-*N,N*-diethyl leucynol ester methane sulphonate and its decomposition with 0.05 *N* tetrabutylammonium methoxide:** I. GYENES and A. LÁSZLÓ. (14 August 1962).
- A general paper chromatographic method for orientative qualitative analysis:** A. SCHNEER-ERDEY. (14 August 1962).
- Untersuchungen über das Kakothelin als Redox-Indicator:** P. SZARVAS and J. LANTOS. (14 August 1962)
- Argon ionisation detector in gas-liquid chromatography of organic silicon compounds:** G. GÁRZÓ and F. TILL. (14 August 1962).
- Photometrische Molybdänbestimmung mit Phenylhydrazin I. Neue Untersuchungen über den Phenylhydrazin-Molybdänkomplex:** I. BOZSAI. (14 August 1962).
- Indikatorsysteme auf Vanadiumkomplexonatis:** I. SAJÓ. (14 August 1962).
- Auf den Schwärzungsunterschieden der Manganlinien beruhende neue qualitative Auswertungsmethode, zur Bestimmung des Mangengehaltes der Aluminiumlegierungen—I:** L. PÉTER. (14 August 1962).
- Spectrographic investigations of Hungarian archeological finds from the copper and bronze age:** Z. L. SZABÓ, O. SZAKÁCS and K. ZIMMER. (14 August 1962).
- Spectrographical determination of copper contents of 0.1–1.0% in aluminium alloys:** T. TÖRÖK and A. PETHÖ. (14 August 1962).
- Induced reactions in the peroxy compounds:** L. J. CSÁNYI, S. KASZAI and I. MOLNÁR. (14 August 1962).
- Photometric titration of alkyl aluminium compounds:** COE W. WADELIN. (16 August 1962).
- Precipitation from mixed solvents—II: Nickel 8-hydroxyquinolate:** LESTER C. HOWICK and JERRY L. JONES. (16 August 1962).
- Separation of silver from lead and mercury by ion-exchange chromatography:** ANIL K. DE and SANTOSH K. MAJUMDAR. (21 August 1962).
- Zerstörungsfreie spektrochemische Analyse archäologischer Bronzefunde:** K. DOERFFEL and R. WAGNER. (21 August 1962).
- Vergleichende Untersuchung zur Bestimmung von Phosphor und Bor in Halbleitersilicium:** K. H. BERTHEL, H. G. DOGE, G. EHRLICH, A. KOTHE und A. SCHMIDT. (21 August 1962).
- Separation of titanium from iron and aluminium:** RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (21 August 1962).
- Precipitation from mixed solvents—III: Magnesium 8-hydroxyquinolate:** L. C. HOWICK, N. L. FORD and J. L. JONES. (23 August 1962).
- Precipitation from mixed solvents—IV: Copper 8-hydroxyquinolate:** L. C. HOWICK and J. L. JONES. (23 August 1962).
- Liquid scintillation counting of plutonium-239 from biological samples:** T. Y. TORIBARA, D. A. MORKEN and C. PREDMORE. (24 August 1962).
- The separation and determination of plutonium in diverse biological samples:** T. Y. TORIBARA, C. PREDMORE and P. A. HARGRAVE. (24 August 1962).
- Contributions to the basic problems of complexometry—XI: The determination of iron and titanium in the presence of aluminium:** RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (27 August 1962).
- Sorption of ferroin on silica and its analytical use:** FRANTISEK VYDRA and VERA MARKOVÁ. (27 August 1962).

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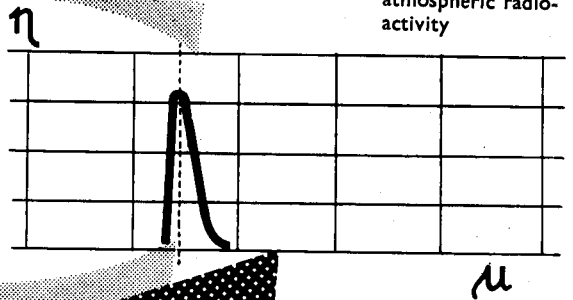
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