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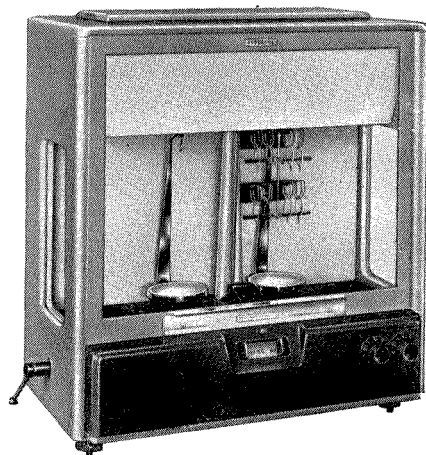
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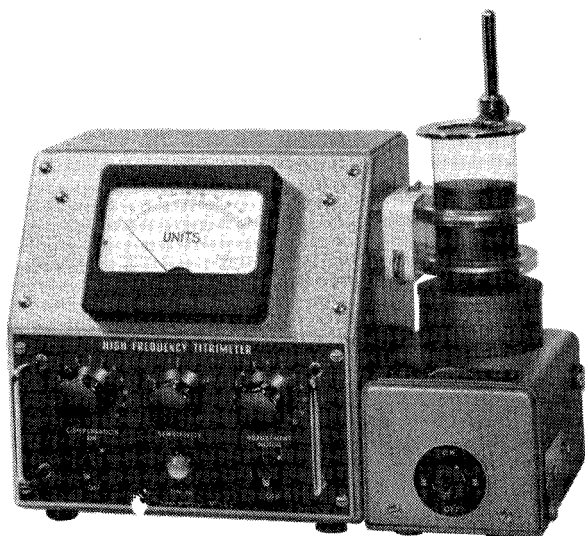


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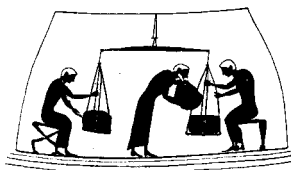
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¹ J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

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

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

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

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COULOMETRIC TITRATION OF HYDROXYLAMINE AND HYDROGEN PEROXIDE BY ELECTROGENERATED CERIC ION

TAKEO TAKAHASHI and HIROSHI SAKURAI
Institute of Industrial Science, University of Tokyo, Japan

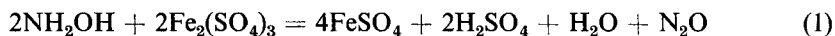
(Received 20 March 1961. Accepted 30 September 1961)

Summary—Since hydroxylamine reduces Fe^{III} quantitatively to Fe^{II} , the coulometric determination of hydroxylamine may be carried out by coulometric titration of Fe^{II} with electrogenerated Ce^{IV} . Using 0.01*N* cerous sulphate-ferric sulphate and 1*N* sulphuric acid, and a constant current of 10 mA, the error of the method is found to be within about 1%. Hydrogen peroxide reacts instantaneously and quantitatively with Ce^{IV} , and can be determined with an accuracy of about 1 to 2%, provided that 0.01*N* cerous sulphate-1*N* sulphuric acid is used as an electrolytic solution and the electrolytic oxidation is carried out at a constant current of about 10 mA.

INTRODUCTION

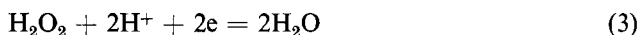
THE first coulometric method was elaborated by Furman, Cooke and Reilly,¹ who titrated ferrous ion with electrogenerated ceric ion. This coulometric cerimetry has been applied to the determinations of $[\text{Fe}(\text{CN})_6]^{4-}$,² Ti^{III} ,³ As^{III} ,⁴ I^- ,⁵ metol⁶ and hydroquinone.⁶ The authors⁷ have already reported the direct coulometric cerimetry of hydroquinone and *p*-aminophenol, as well as the indirect determination of oxalic acid, β -naphthylamine and aniline.

In the present study coulometric cerimetry has been successfully applied to the determination of hydroxylamine and hydrogen peroxide. According to Szebellédy and Somogyi,⁸ hydroxylamine has not previously been determined coulometrically with reagents other than bromine. The present investigation is based on the reaction between hydroxylamine and ferric ion:

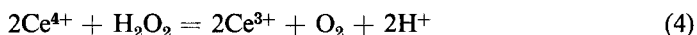


The ferrous ion is then coulometrically titrated with electrogenerated ceric ion.

In acidic medium, hydrogen peroxide may react in two ways, *i.e.*, as an oxidising or a reducing agent, thus:



Ceric ion reacts with hydrogen peroxide in a similar way to potassium permanganate, according to the equation:



This reaction proceeds instantaneously and quantitatively, with the evolution of oxygen. In the present investigation the reaction (4) was successfully applied using electrogenerated ceric ion.

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EXPERIMENTAL

Apparatus

The titration cell, the constant current source, the stirrer and the time measuring apparatus have already been described.⁷ The generating anode was a platinum electrode, 20 mm × 20 mm, and an electronic automatic balancing voltage recorder was used for measuring the potential for detection of the end-point.

Reagents

The reagents were of specially purified grade.

Water: Purified by ion-exchange.

Electrolytic solution for the determination of hydroxylamine: Dissolve ceric sulphate in 1*N* sulphuric acid until the solution is almost saturated, and to this add ferrous ammonium sulphate-sulphuric acid, 1*N*, to reduce ceric ion to cerous ion (a greater excess of ferrous ion than one equivalent must not be added). Dilute the solution with sulphuric acid (1*N*) so as to produce 0.01*N* concentrations of cerium and iron ions.

Electrolytic solution for the determination of hydrogen peroxide: Dissolve ceric sulphate in sulphuric acid (1*N*) and to this add gradually 0.01 equivalent of hydrogen peroxide to reduce ceric ion to cerous

TABLE I. THE COULOMETRIC TITRATION OF HYDROXYLAMINE

Hydroxylamine sampled, × 10 ⁻² meq	Electrolytic time, sec	Amount found, × 10 ⁻² meq	Error, %
3.810	365.8	3.738	-1.9
3.810	376.6*	3.848	+1.0
3.810	381.2*	3.895	+2.2
3.810	379.5*	3.874	+1.8
		av. 3.840	+0.8
		st. dev. 0.061	
7.619	742.8	7.590	-0.4
7.619	741.8	7.580	-0.5
7.619	749.3*	7.656	+0.5
7.619	757.1*	7.736	+1.5
		av. 7.641	+0.3
		st. dev. 0.062	
11.429	1117.3	11.416	-0.1
11.429	1112.4	11.366	-0.6
11.429	1114.9*	11.392	-0.3
11.429	1129.9*	11.545	+1.0
		av. 11.430	0.0
		st. dev. 0.072	
19.048	1869.0	19.097	+0.3
19.048	1869.8	19.105	+0.3
19.048	1874.3	19.151	+0.5
19.048	1873.8	19.146	+0.5
		av. 19.125	+0.4
		st. dev. 0.024	

ion (a greater excess of hydrogen peroxide than one equivalent must not be added). Boil the decolorised solution in order to destroy the remaining hydrogen peroxide and then dilute the cooled solution with sulphuric acid, 1*N*, to a volume of 1 litre. The solution is equivalent to 0.01*N* cerous sulphate—1*N* sulphuric acid.

Cathodic solution: Dissolve 15 g of ammonium sulphate in 85 g of water.

*Hydroxylamine solution, 0.01*M*:* Use hydroxylamine hydrochloride and purified water.

*Hydrogen peroxide solution, 0.01*M*:* Dilute concentrated hydrogen peroxide (30%) with purified water and standardise with standard potassium permanganate solution.

Experimental procedure

The detection of the end-point was carried out potentiometrically, using a platinum plate 5 mm × 5 mm as indicating electrode and a calomel electrode as reference electrode.

Determination of hydroxylamine: Take 100 ml of electrolytic solution and make its potential 0.7 V *vs.* S.C.E. If the potential is lower than 0.7 V *vs.* S.E.C., the generating electrode is used as anode and electrolytic oxidation is carried out until the potential reaches 0.7 V. If the potential is higher than 0.7 V *vs.* S.C.E., electrolytic reduction is carried out. Transfer this prepared solution into an Erlenmeyer flask (200-ml) to which the sample solution (hydroxylamine solution) is added, boil gently for 5–6 min, and return the cooled solution to the titration cell. Ferrous ion produced in the above solution is oxidised by ceric ion which is coulometrically generated at a constant current, until the potential indicates 0.7 ± 0.01 V *vs.* S.C.E. The amount of hydroxylamine can be calculated as a product of the constant current (A) and electrolytic time (sec).

Regeneration of the used electrolytic solution is carried out by adding sodium hydroxide to the used solution to make it alkaline, in order to precipitate cerium and iron as the hydroxides. These hydroxides are dissolved in sulphuric acid after filtering and washing. During this operation a small amount of cerous ion may be oxidised by oxygen in the air, so that it must be reduced electrolytically or by adding ferrous ion before its re-use. The experiments employing used electrolytic solution are shown marked with an asterisk in Table I.

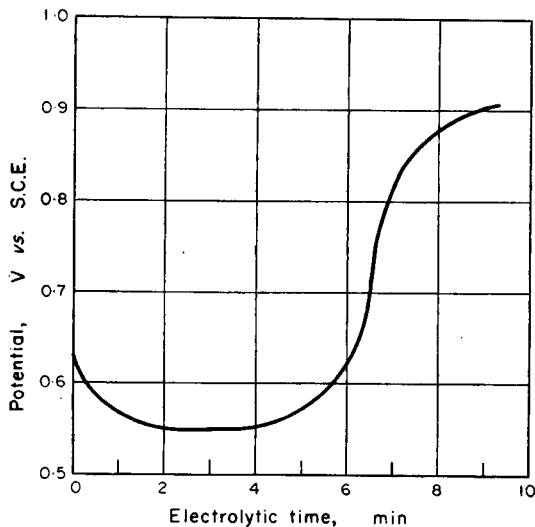


Fig. 1.—Coulometric titration curve of hydrogen peroxide

Determination of hydrogen peroxide: Take 100 ml of electrolytic solution in the titration cell, oxidise electrolytically for 1–2 sec, confirming the absence of reducing substances in the electrolytic solution by observing the indicating potential. Add the sample solution (hydrogen peroxide solution), carry out electrolytic oxidation until the potential shows 0.70 V *vs.* S.C.E., and measure the amount of hydrogen peroxide as the product of the constant current and the electrolytic time. The electrolytic solution may in this case be used without regeneration for a series of successive titrations.

RESULTS

Table I shows the results for the coulometric titration of 2–10 ml of 0.01M hydroxylamine solution at a constant current of 9.86 mA during the electrolytic oxidation. The results show that coulometric cerimetry can be applied to the determination of hydroxylamine with an accuracy of 1%. The same electrolytic solution cannot, however, be repeatedly employed because comparatively large errors are obtained (see Table I).

The coulometric titration curve of hydrogen peroxide with ceric ion is shown in Fig I. The potential decreases by ~ 50 mV from the initial potential during the titration (for 90 \sim 120 sec of the electrolytic time). This phenomenon may result from the indicated potential lag. However, the potential change shows about 300 mV at the end-point, indicating a typical type of titration curve. The reproducibility of the indicated potential before each titration shows a fluctuation of ± 50 mV. This may possibly be caused by variations in absorbed oxygen on the indicating platinum

TABLE II. THE COULOMETRIC TITRATION OF HYDROGEN PEROXIDE

Hydrogen peroxide sampled, $\times 10^{-2}$ meq	Electrolytic time, sec	Amount found, $\times 10^{-2}$ meq	Error, %
4	380	3.883	-2.9
4	389	3.975	-0.6
4	385	3.934	-1.7
4	385	3.934	-1.7
4	387	3.954	-1.3
		av. 3.934 st. dev. 0.034	-1.7
8	777	7.939	-0.8
8	776	7.929	-0.9
8	776	7.929	-0.9
8	777	7.939	-0.8
8	778	7.950	-0.6
		av. 7.939 st. dev. 0.009	-0.8
12	1166	11.914	-0.7
12	1170	11.955	-0.4
12	1173	11.986	-0.1
12	1171	11.965	-0.3
		av. 11.955 st. dev. 0.026	-0.4
20	1915	19.567	-0.2
20	1920	19.618	-0.2
20	1923	19.649	-0.2
		av. 19.608 st. dev. 0.026	-0.2

electrode. But the end-point shows an approximately constant value, namely about 0.7 V *vs.* S.C.E.

Table II shows the results of the coulometric titration of 2 ~ 10 ml of 0.01M hydrogen peroxide solution at a constant electrolytic current of 9.86 mA.

According to Table II, amounts of hydrogen peroxide larger than 10^{-4} equiv. can be determined with an error of $\pm 0.5\%$ and the error increases to about 2% in the determination of about 5×10^{-5} equiv. of hydrogen peroxide.

The repeated use of the same electrolytic solution not only saves reagents, but decreases the interval between successive titrations. Table III gives the results of experiments in which there has been repeated use of the electrolytic solution. In

TABLE III. REPEATED USE OF THE SAME ELECTROLYTIC SOLUTION

No. of times repeated	Exp. 1, sec	Exp. 2, sec
1	380	388
2	383	388
3	383	388
4	390	386
5	382	386
6	382	388
7	388	386
8	387	390
9	389	391
10	390	391
av.	385.4	388.2
st. dev.	3.6	1.7

these experiments 2 ml of 0.01M hydrogen peroxide are used each time and the electrolytic oxidation (electrogeneration of ceric ion) is carried out at a constant current of 9.85 mA. As soon as one titration is complete, the next sample solution is introduced, and the next titration takes place immediately.

Zusammenfassung—Hydroxylamin reduziert einen äquivalenten Betrag von Ferri-ionen. Es ist daher möglich Hydroxylamin durch eine coulometrische Titration des gebildeten Ferroeisens mit elektrolytisch gebildeten Cerionen zu bestimmen. Bei Verwendung einer 0.01 N Cerosulfat-Ferrisulfat Lösung, 1 N Schwefelsäure und eines konstanten Stromes von 10 mA beträgt der Fehler 1%.

Résumé—L'hydroxylamine réduit une quantité équivalente de Fe (III) en Fe(II); son dosage a donc été réalisé par titrage coulométrique de Fe(II) par Ce(IV) préparé par électrolyse. En utilisant une solution contenant du sulfate céreux et du sulfate ferrique 0,01 N et de l'acide sulfurique N, et un courant constant de 10 mA, l'erreur est d'environ 1%.

L'eau oxygénée réagit instantanément et quantitativement avec Ce(IV), de sorte qu'elle peut être dosée à 1 ou 2 pour cent près à condition d'utiliser comme électrolyte une solution contenant du sulfate céreux 0,01 N et de l'acide sulfurique N, et de réaliser l'oxydation électrolytique avec un courant constant d'environ 10 mA.

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CONTINUOUS COULOMETRIC TITRATION OF MICRO-QUANTITIES OF IRON IN WATER

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Summary—Continuous determination of micro-quantities of iron dissolved in water has been investigated by means of coulometric titration with electro-generated bromine. The test solution was allowed to flow continuously through a Jones' reductor, where all of the iron in the solution was reduced to iron^{II} and was subsequently determined coulometrically with bromine. The electrolytic solution contained potassium bromide in a buffer solution of acetic acid-sodium acetate, and the end-point was detected potentiometrically with platinum-calomel electrodes. Employing the coulometric method under suitable conditions, the relationship between the amount of iron present and electrolytic current was proportional to within about 15%.

INTRODUCTION

RECENTLY it became an urgent problem to determine continuously the minute quantity of metals in feed water for high pressure boilers in power generating stations. Iron is the most common metal dissolved in the water; moreover, its continuous determination is now considered to be important in many industrial fields. The authors¹ have already reported the coulometric titration for the determination of iron^{II} by electrogenerated bromine. In practice the dissolved iron occurs in both the bi- and tervalent states. In the present study, the first part deals with the continuous coulometric titration of iron^{II} by electrogenerated bromine, and the latter part with the continuous coulometric titration of total iron, after iron^{III} has been reduced to iron^{II} by zinc amalgam.

EXPERIMENTAL

The apparatus for continuous coulometric titration has already been reported.¹ The continuous coulometric titrator (see Fig. 1) used in the present experiments incorporates an automatic titrator. The electrolyte solution (potassium bromide solution) is introduced into the electrolytic cell at a

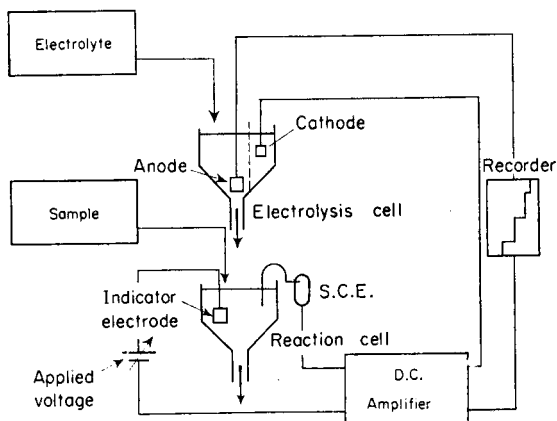


FIG. 1.—Schematic diagram of automatic continuous coulometric titrator.

definite rate, in which bromine is electrolytically generated on the generating anode surface, then reaches the titration cell where it is mixed with the stream of the sample solution. The titration cell is provided with a platinum indicating electrode for end-point detection and a saturated calomel electrode between which is applied a d.c. constant voltage a little above the potential of the end-point. The solution in the titration cell is always automatically controlled to contain a small excess of free bromine. The electrolytically generated bromine reacts with the reacting substance in the sample solution and the remaining bromine changes the potential between the indicating electrodes; the potential difference between the indicator and the reference potentials is fed into a d.c. amplifier (with a.c. convertor) and its output is supplied as electrolytic current for the electrogeneration of bromine.

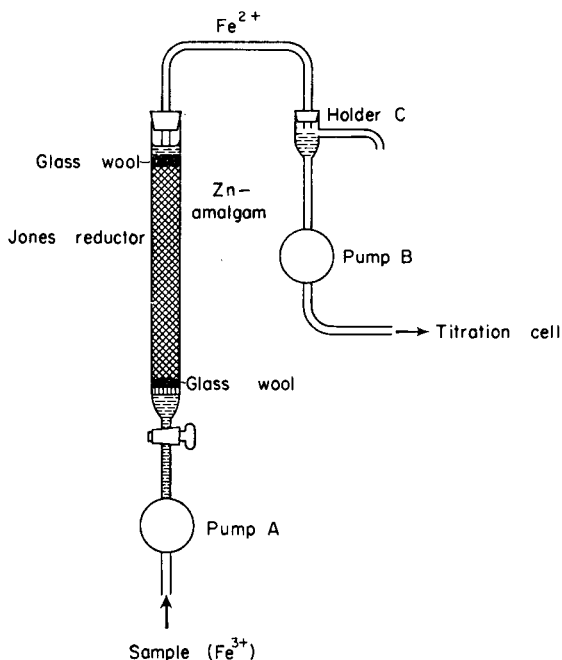


FIG. 2.—Reductor for reduction of iron^{III} ion.

The sample solution is prepared by diluting 0.01*N* ferrous or ferric ammonium sulphate-0.1*N* sulphuric acid solution with purified water. The electrolytic solution is composed of 0.1*M* potassium bromide, 1*M* acetic acid, 0.2*N* sodium hydroxide and gives a pH of about 4.2. All the reagents are of commercially pure grade and the purified water is prepared with ion-exchange resins. The solid zinc amalgam used for the reduction of iron^{III} ion is prepared by suspending 100 g of zinc granules (10 ~ 30 mesh) in 200 ml of mercuric chloride solution (2%) containing 2 ml of HNO₃ (conc.) and washing the amalgamated zinc granules very well with the purified water. The reduction is carried out by using the Jones' reductor shown in Fig. 2, the glass tube being filled with the amalgamated zinc granules. At the bottom of the glass tube (15 mm i.d. and 300 mm long) is placed a polyethylene sieve support. The amalgamated zinc granules (220 ~ 230 mm high) are supported on glass wool placed above the polyethylene sieve support. The prepared reductor is, of course, always filled with water or, alternatively, with the solution used previously, when not in use. The sample solution is fed to the bottom of the reductor at constant flow rate, using the pump A (a small pump of diaphragm type made by Denkishiki Kagakukeiki Co., Tokyo) and the reduced sample solution leaves the top of the reductor, enters the small holder C, and thence passes to the titration cell at a rate of 0.16 ml/sec. The pump B is a small geared one, driven with a synchronous motor.

Dynamic working titration curve

The continuous titration curve is not necessarily the same as the single titration curve because the rate of the reaction and attainment of equilibrium has to be taken into account. A previous paper¹ disclosed the fairly large lag near the end-point in the reaction between iron^{II} ion and bromine, which varied particularly markedly with the composition of the solution. The dynamic titration curves of

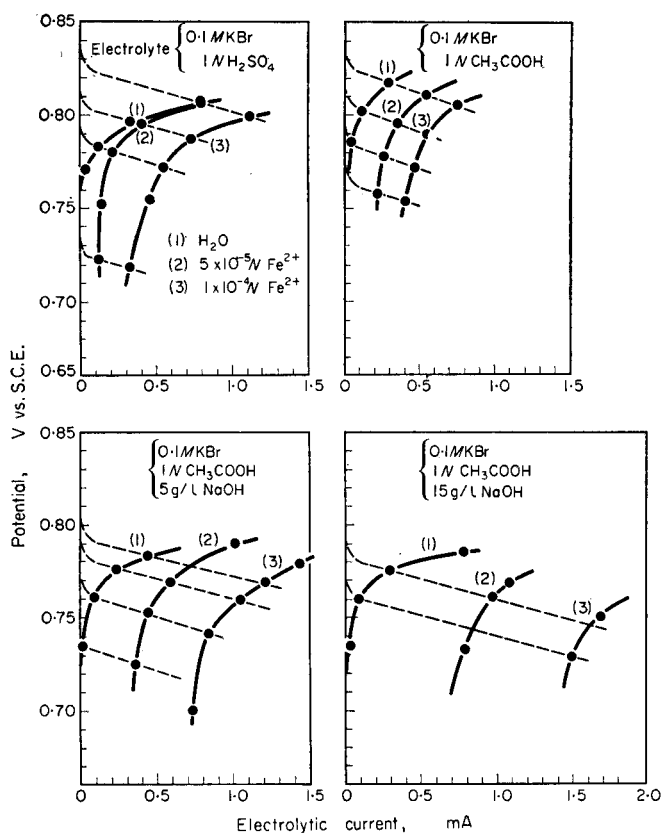


FIG. 3.—Dynamic titration curves.

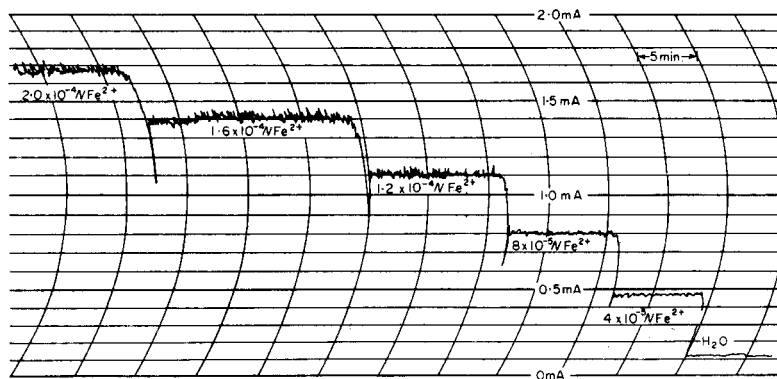


FIG. 4.—Recorded chart of the electrolysis current under various concentrations of the iron^{II} ion.

$5 \times 10^{-6}N$ and $1 \times 10^{-4}N$ iron^{II} ion in four electrolytic solutions are shown in Fig. 3. The method of preparation of these curves has been given in a previous paper.³ The theoretical values of the electrolytic current are, respectively, about 1.5 mA and 0.75 mA in the cases of $5 \times 10^{-6}N$ and $1 \times 10^{-6}N$ iron solution.

Fig. 3 shows that the relationship between the concentration of iron^I and electrolytic current is more linear in acetic acid solution than in sulphuric acid solution, and approaches more nearly to the theoretical one in higher concentrations of sodium hydroxide.

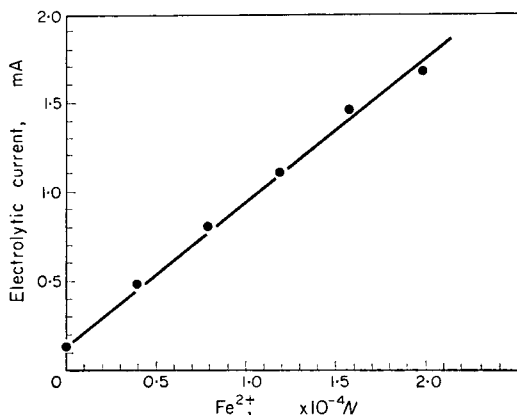


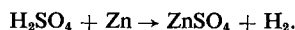
FIG. 5.—Relationship between concentration of iron^{II} ion in water and electrolysis curve.

Continuous coulometric titration of iron^{II}

Fig. 4 is the graph obtained for experiments in which iron^{II} ions were titrated in solutions composed of 0.1M potassium bromide, 0.1N sodium hydroxide and 1M acetic acid. The relationship between the iron concentration and electrolytic current calculated from the graph is given in Fig. 5. The results depicted in Figs. 4 and 5 show that the procedure is satisfactory for routine analysis.

Operating conditions for Jones' reductor

It was necessary to find the optimum concentration of sulphuric acid for the reduction of iron^{III} in the Jones' reductor, without interfering with the acetic acid-acetate supporting electrolyte used in the coulometric titration. At high concentrations of sulphuric acid, zinc amalgam reacts with sulphuric acid as follows:



and the evolved hydrogen gas is absorbed on the indicating platinum electrode, causing an erroneous indication of the potential. On the other hand, at small concentrations of sulphuric acid, iron precipitates as hydroxide so that the results are incorrect. In view of the importance of the sulphuric acid concentration, it was necessary to examine its effect on the reduction of the iron^{III} ion. The

TABLE I. EFFECT OF THE CONCENTRATION OF SULPHURIC ACID IN THE REDUCTION IN THE JONES' REDUCTOR.

H ₂ SO ₄ , N	0.01N KMnO ₄ solution, ml			
	I-fraction	II-fraction	III-fraction	av.
0.1	9.90	9.95	9.90	9.92
0.03	9.90	9.90	9.95	9.92
0.01	9.90	9.95	9.95	9.93
0.003	9.90	9.95	10.03	9.96
0.001	9.60	9.60	9.60	9.60
0.001*	3.45	3.50	3.45	3.47
H ₂ O	7.50	7.50	7.45	7.48
H ₂ O*	3.35	3.30	3.30	3.32

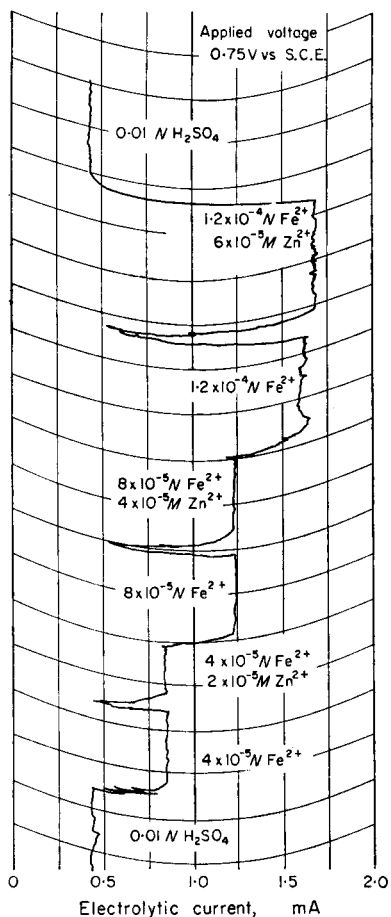


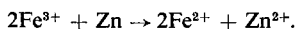
FIG. 6.—Record of continuous coulometric titrations of iron^{II} ion and iron^{III} ion plus zinc ion.

sample solution containing 0.001M iron^{III} ammonium sulphate and sulphuric acid of various concentrations was fed at a rate of about 20 ml per min to the bottom of the reductor. Fifty-ml fractions of the reduced solution were titrated with 0.01N potassium permanganate solution after adding 2 g of sulphuric acid. The results are given in Table I.

The reduction appears to be ideal when carried out in 0.1 ~ 0.003N sulphuric acid, but is poor in sulphuric acid when it is less than 0.001N. In these experiments freshly prepared solutions were used and it was noticed that the solution containing less than 0.001N sulphuric acid gradually formed a reddish-brown precipitate and accumulated in the reductor tube, resulting in a lowering of the concentration of iron^{II} ion in the reduced solution. In 0.1N sulphuric acid the evolution of hydrogen gas was observed. Sulphuric acid which was 0.01N seemed to be the most favourable concentration in the sample solution, because it did not markedly vary the pH of the acetic-acetate solution and the reduction of iron^{III} to iron^{II} was satisfactory.

Effect of zinc ion

Iron^{III} ion in the sample solution is reduced in the Jones' reductor according to the following reaction:



Since it was important to know whether the presence of zinc ions interfered with the reaction of iron^{II} ions with bromine, the following experiment was carried out.

Sample solutions composed of 0.1M potassium bromide, 1M acetic acid and 0.2N sodium hydroxide, contained iron^{II} ammonium sulphate and zinc sulphate at various concentrations. Those solutions were passed through the Jones' reductor and the electrolytic currents for electro-generation of bromine were recorded in the chart seen in Fig. 6. The results show that zinc ions in the sample solution have no effect on the coulometric titration with bromine.

TABLE II.—CONTINUOUS COULOMETRIC DETERMINATIONS OF IRON IN WATER

Sample solution used	Electrolytic current, mA										Av.	$\text{mA}/5 \times 10^{-5} \text{ eq. Fe}$	
$\text{Fe}_2(\text{SO}_4)_3$	$5 \times 10^{-5} M$	0.50	0.42	0.43	0.49	0.34	0.35	0.34	0.38			0.40 ₆	0.203
	1×10^{-4}	0.98	0.94	0.96	0.88	0.78	0.91	1.08	0.87	0.91	0.92*	0.93 ₂	0.233
	1.5×10^{-4}	1.46	1.41	1.41	1.38							1.41 ₅	0.236
	2.0×10^{-4}	1.87	1.84	1.90	1.80*	1.82*						1.84 ₆	0.231
	3.0×10^{-4}	2.60*											0.217
FeSO_4	5×10^{-5}	0.18	0.18	0.19	0.21							0.19 ₀	0.190
	1×10^{-4}	0.44	0.57	0.44	0.50	0.50*	0.40*	0.41*				0.46 ₆	0.233
	2×10^{-4}	0.96*	0.78*	0.80*								0.84 ₇	0.212
	3×10^{-4}	1.15*	1.19*									1.17	0.195
	4×10^{-4}	1.50*											0.188
$\text{Fe}_2(\text{SO}_4)_3$	FeSO_4												
	$5 \times 10^{-5} M$	0.53	0.55										0.180
	1×10^{-4}	1.13	1.29	1.46	1.30	1.52*	1.52*					1.37	0.253
	1×10^{-4}	2.01*	2.27*									2.14	0.267
	2×10^{-4}	2.50*	2.72*									2.61	0.261
2×10^{-4}	2.92*												

The applied voltage is 0.73 V but 0.75 V in the cases marked *

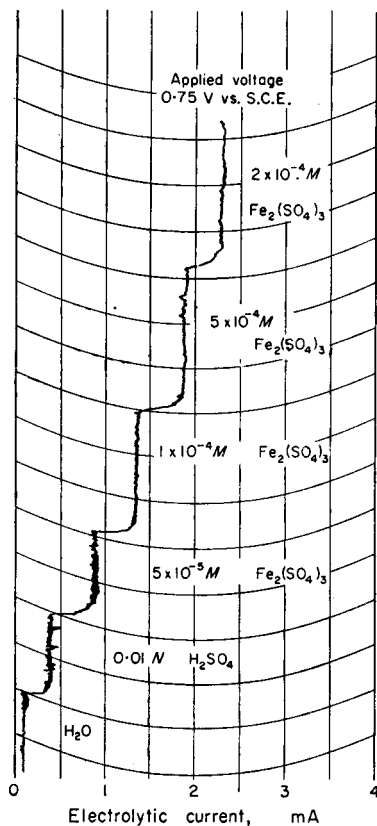


FIG. 7.—Record of continuous coulometric titrations of iron^{III} ion.

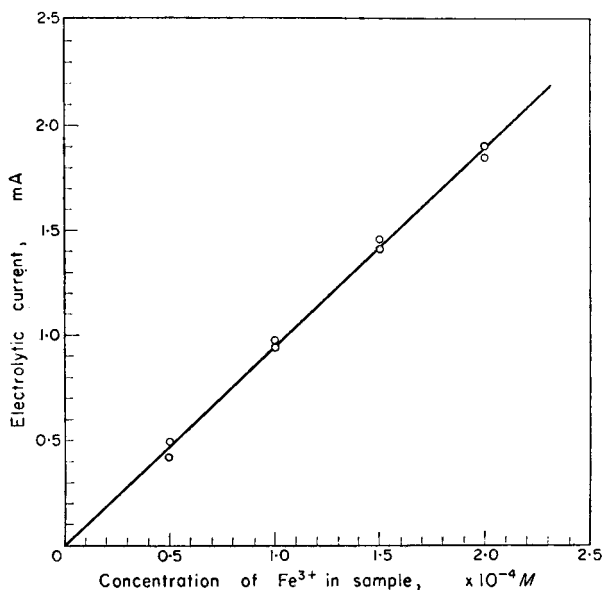


FIG. 8.—Relationship between concentration of iron^{III} ion in sample solution and electrolytic current.

Continuous coulometric titration of iron^{III}

The operation consists of two stages; the first is the reduction of iron^{III} in the sample solution by passage through the Jones' reductor (0.2 ml per sec) and the other is the continuous coulometric titration of the reduced solution flowing at 0.16 ml per sec from the small tank, C, shown in Fig. 2. The tank provides a constant head for the solution being titrated; unused solution is removed by suction. The electrolytic solution for electrogeneration of bromine flows at 0.1 ~ 0.2 ml per sec and an applied voltage of 0.73 ~ 0.75 V vs. S.C.E. is used. The electrolytic current is recorded on the chart of the recording milliammeter. An example of a run obtained is given in Fig. 7. At the change of a run of the sample solution, the recording gives a response lag of about 1 min, but the continuous method seems to be satisfactory for the analysis of the minute amounts of iron in water. The linear relationship between the concentration of iron^{III} and electrolytic current is shown in Fig. 8.

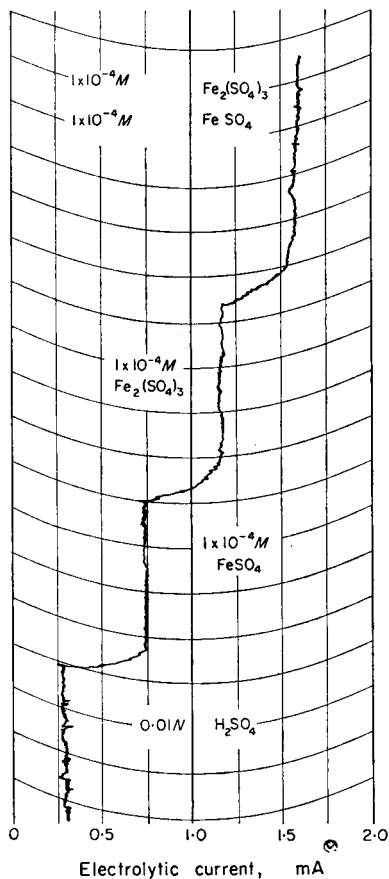


FIG. 9.—Record of continuous coulometric titrations of iron^{II} ion, iron^{III} ion and iron^{II} ion-iron^{III} ion.

Continuous coulometric titration of iron^{III} and iron^{II}

If the solution containing iron^{III} and iron^{II} is passed through the Jones' reductor, the total iron will be determined from the reduced solution. Fig. 9 shows an example of the charts recording the three kinds of sample solutions, containing respectively only iron^{II}, only iron^{III}, or both iron^{III} and iron^{II} ions. Table II summarises results obtained on the different sample solutions when they were allowed to flow for 10 min at 0.16 ml per sec with the applied voltage at 0.73 ~ 0.75 V vs. S.C.E. The experiment was continued for about 10 days, the electrolytic current values given in Table II being obtained by subtracting the background current which varied from day to day.

The variations seen in Table II might be caused by a number of factors such as differences in stirring, variations in sensitivity of the indicator electrode as well as the relative slowness of the reaction velocity between bromine and iron^{II}. The authors believe that if the experiments could be carried out without any breaks, even during the night, the results would be less prone to fluctuations.

Zusammenfassung—Es wird die kontinuierliche Bestimmung von Mikro-mengen von Eisen in wässriger Lösung mittels coulometrischen Titration mit Brom untersucht. Die Probe-lösung strömt kontinuierlich durch eine Jones' sche Reduktor darin Eisen zu Eisen^{II} reduziert wird, und coulometrisch mit Brom bestimmt wird. Die elektrolytische Lösung erhält Kalium-bromid in einer Puffer-lösung von Essigsäure-Natrium-acetat. Der End-punkt wird potentiometrisch ermittelt. Die Beziehung zwischen Eisen-mengen und elektrolytischen Ström ist zu etwa 15% proportional.

Résumé—Les auteurs ont mis au point le dosage en continu de microquantités de fer dans l'eau par titrage coulométrique avec du brome préparé par électrolyse. On fait circuler de manière continue la solution à travers un réducteur de Jones, le fer est transformé en fer ferreux et dosé par coulométrie par du brome. La solution électrolytique contenait du bromure de potassium tamponné avec le mélange acide acétique-acétate de sodium, le point équivalent était déterminé par potentiométrie avec des électrodes platine-calomel. Dans des conditions convenables, il existe une relation de proportionnalité valable à 10% près entre le courant et la quantité de fer.

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A POLAROGRAPHIC STUDY OF DISSOLVED OXYGEN—I

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Summary—A polarographic study of dissolved oxygen has been carried out. Results obtained for reduction at the dropping mercury electrode indicate a disproportionation of one of the reaction products. The diffusion coefficient of oxygen in potassium chloride solution is calculated from the polarographic data.

FROM a consideration of the fundamental postulates of the theory of current-voltage curves at a polarisable electrode it has been shown by Ilkovic¹ that, for a process at the dropping mercury electrode which is truly diffusion controlled, a linear relation between the concentration of depolariser and of the limiting current produced by its reduction is to be expected. This has been confirmed for many substances over a wide concentration range. When it is established that a given reduction at the dropping mercury electrode is diffusion controlled, then other data concerning the reaction can be deduced from the curves obtained.

Thus, it is of importance to determine the ratio of depolariser concentration to limiting diffusion current over the concentration range of interest and this was, therefore, one of the first investigations undertaken.

Measurement of the diffusion current of the two oxygen waves was made over a range of dissolved oxygen concentration from 0.1 to 10 ppm. The base electrolyte used was 0.1*N* potassium chloride solution, the drop time was usually 3.6 sec and the potential sweep was from 0.0 to -0.5 V or from 0.0 to -1.7 V *vs.* the saturated calomel electrode.

Measurements of the diffusion current were made with due allowance for the residual current in each case. With nearly all series of measurements a check was made of the actual residual current (as distinct from the extrapolated one) by blowing out the oxygen in solution, then rescanning the same voltage range.

Using these techniques it was established that a linear relationship existed between oxygen concentration and limiting diffusion current over the range studied.

Measurements were carried out on both reduction waves. Since both reductions are two-electron processes, it would be expected that, as has been stated by many authors,^{2,3,11} the two waves would be of equal height. It was noticed in this work, however, that although both the first and second reduction waves gave linear plots of limiting diffusion current against dissolved oxygen concentration the slopes were unequal, that for the first wave being equivalent to 0.229 $\mu\text{A/ppm}$ while that for the

second was only $0.200 \mu\text{A/ppm}$ (Figs. 1 and 2). This difference in slope means that while the currents of the two waves are almost equal at low oxygen concentrations, at values near oxygen saturation the first wave is about 40% greater than the second.

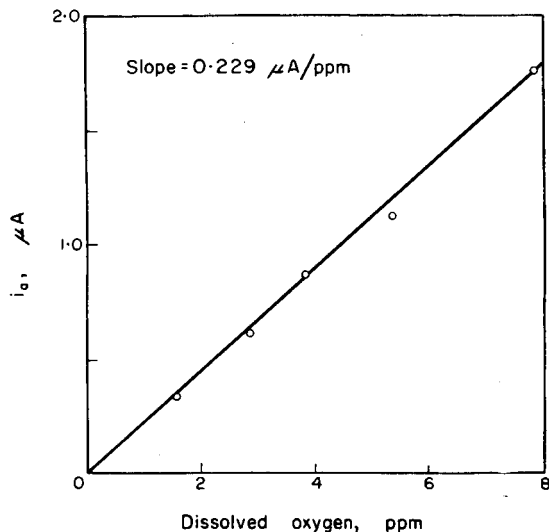


FIG. 1.—Plot of diffusion current against dissolved oxygen concentration for the first reduction wave of oxygen.

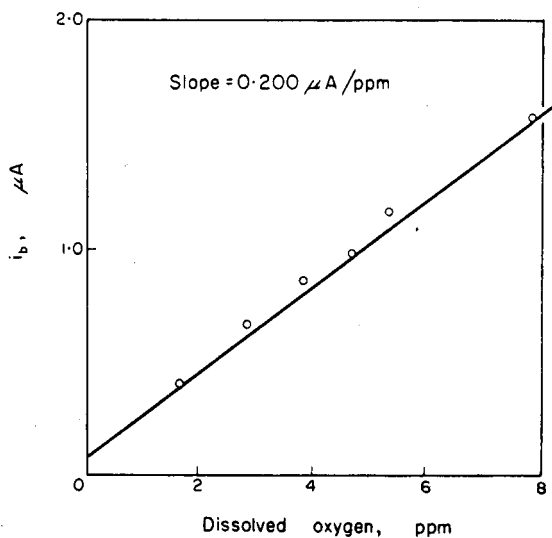


FIG. 2.—Plot of diffusion current against dissolved oxygen concentration for the second reduction wave of oxygen.

Since the second wave, from the reduction of hydrogen peroxide,^{2,3} always appears smaller than the first one, a possible explanation which suggests itself is that of catalytic decomposition of the peroxide at the mercury surface before the reduction to water or hydroxyl ion takes place. This would seem to be in agreement with the increased difference between the waves at higher dissolved oxygen values. It would appear unlikely, however, that such a catalytic effect would be very reproducible,

especially if several different batches of mercury are used, as happened during the course of this work, nor would it be expected that a plot of total current of both waves against dissolved oxygen would be linear, although this is found in practice (Fig 3).

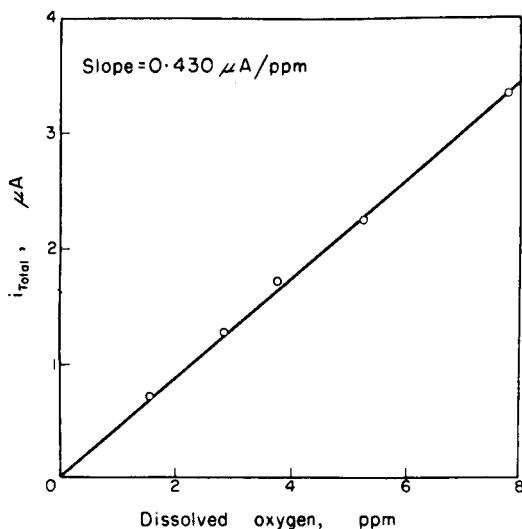


FIG. 3.—Plot of total limiting diffusion current against dissolved oxygen concentration.

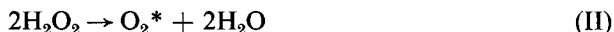
A more probable reason for the changing ratio between the wave heights lies in a disproportionation reaction of the hydrogen peroxide. This type of reaction has been observed at very high concentrations (comparatively) of hydrogen peroxide by Giguere and Jaillet⁴ who, however, state that this only occurs to any appreciable extent in solutions of hydrogen peroxide above 45 mM, while the concentrations involved in the present work are between one tenth and one hundredth of this.

If, however, we consider the first stage reduction of oxygen at the dropping mercury electrode:



then the limiting diffusion current i_A is proportional to the concentration of dissolved oxygen (O_2) [Found experimentally (Fig. 1) and agrees with the Ilkovic equation].

If a disproportionation reaction occurs:



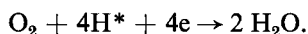
then this oxygen O_2^* will also give rise to a reduction current i_A^*

Thus the total first stage diffusion current i_a will be the sum of these two:

$$i_a = i_A + i_A^*$$

Since i_A^* is proportional to O_2^* and by (I) and (II) to the original concentration (O_2) then the gain in diffusion current (i_A^*) above that expected (i_A) at any given oxygen concentration should increase as the magnitude of this concentration increases. This is in agreement with the experimental facts quoted previously.

Now consider the overall reduction of oxygen to water at the dropping mercury electrode:



For this reaction the total diffusion current i_T should, by the Ilkovic equation, be proportional to the oxygen concentration O_2 . This is found to be the case (Fig. 3).

At any concentration of dissolved oxygen, however, we have:

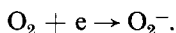
$$i_T = i_a + i_b$$

(where i_b corresponds to $H_2O_2 + 2e + 2H^* \rightarrow 2H_2O$)

Thus if i_a increases above that directly equivalent to (O_2) for the first stage reduction, then i_b should decrease.

This is just what is found experimentally, and hence it would appear that a probable explanation for the non-equality of the two reduction currents lies in the occurrence of a disproportionation reaction.

It is of interest to compare this suggested reaction with a mechanism proposed by Kolthoff and Jordan⁵ for the reduction of hydrogen peroxide at a gold electrode. These authors suggest that the reduction of an oxygen molecule occurs according to:



Further reduction then takes place with the final formation of hydrogen peroxide

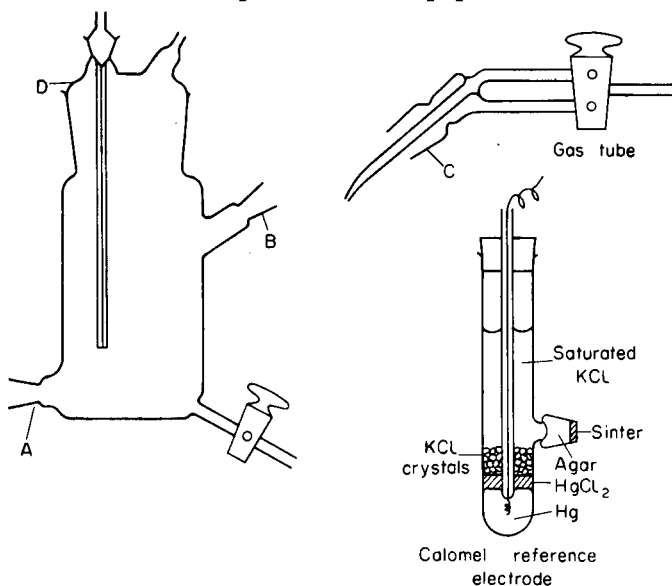
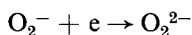


FIG. 4.—Cell used in preliminary experiments.

The O_2^- ion then reacts with a molecule of hydrogen peroxide:



Longmuir⁶, however, has suggested that his coulometric studies show that the overall reaction is not stoichiometric and that the number of Faradays passed per gram-molecule of oxygen reduced might vary with the initial oxygen concentration and thus that the relation between diffusion current and oxygen concentration would not produce a linear plot.

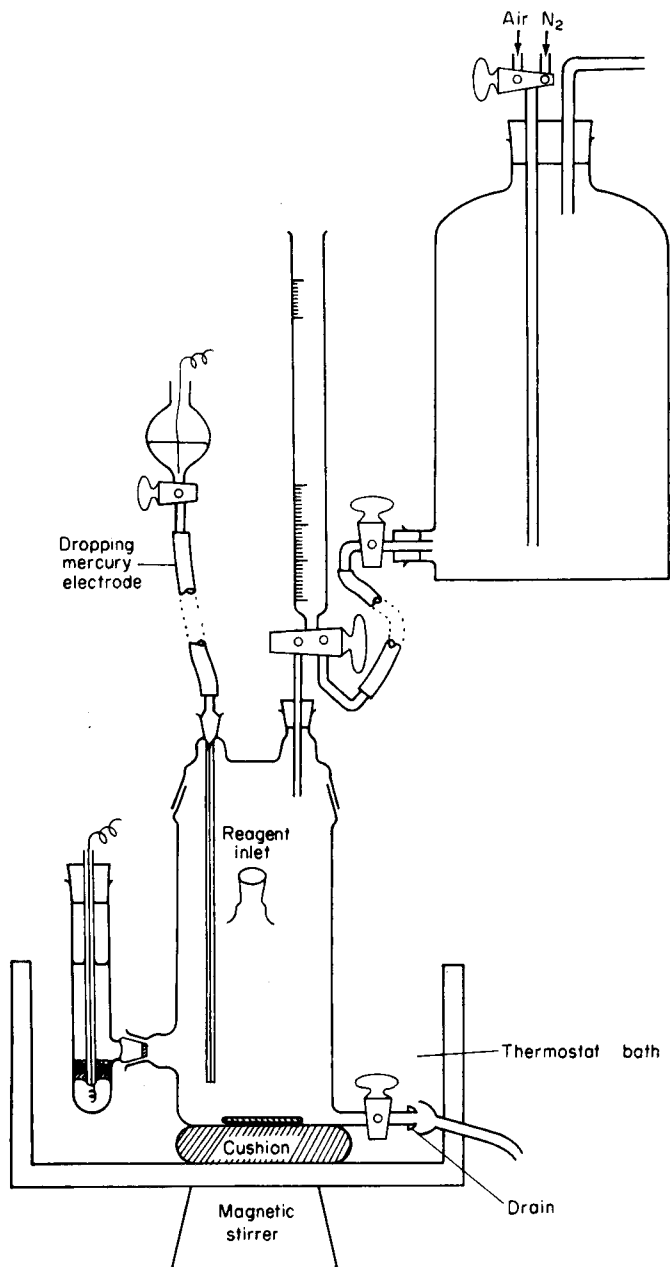


FIG. 5.—Cell used in more exact work with provision for preparation of solutions containing oxygen.

Since these present studies show, however, that the reduction at the dropping mercury electrode does give a linear plot, it is possible to calculate a value for the diffusion coefficient of oxygen (D) in 0.1*N* potassium chloride solution.

Taking the overall reduction of oxygen to water:



and using the value of $0.430 \mu\text{A/ppm}$ for the total current (corresponding to i) from Fig. 3, we obtain a value for D at 20° of $1.609 \times 10^{-5} \text{ cm}^2/\text{sec}$.

Few figures for the value of D in potassium chloride appear to be available in the literature, the value $1.86 \times 10^{-5} \text{ cm}^2/\text{sec}$ in pure water at 16° is given by Carlson and $1.98 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 18° by Moelwyn-Hughes (both quoted by Wanner⁷), while *International Critical Tables* give a value of $8.1 \times 10^{-5} \text{ sq ft/hr}$ (i.e. $2.09 \times 10^{-5} \text{ cm}^2/\text{sec}$) for pure water at 20° . Figures for the diffusion coefficient of oxygen in various buffers are given by Foffani and Vecchi⁸ ($1.92 \times 10^{-5} \text{ cm}^2/\text{sec}$), Kern⁹ ($1.71 \times 10^{-5} \text{ cm}^2/\text{sec}$ for hydrogen peroxide) and Kolthoff and Laitinen¹⁰ ($2.38 \times 10^{-5} \text{ cm}^2/\text{sec}$). The latter value was obtained at 25° using a platinum wire electrode. Foffani and Vecchi (*loc. cit*) also give a value of $2.02 \times 10^{-5} \text{ cm}^2/\text{sec}$ for the diffusion coefficient in potassium nitrate solution. This base electrolyte has also been used by Kolthoff and Miller¹¹ who obtain the high value of $2.6 \times 10^{-5} \text{ cm}^2/\text{sec}$. Arnold¹² gives a value of $2.00 \text{ cm}^2/\text{sec}$ and quotes other references giving values from $1.54 - 2.2 \text{ cm}^2/\text{sec}$ for the diffusion coefficient in water.

EXPERIMENTAL

During the preliminary experiments on this work the cell shown in Fig. 4 was used. This had a capacity of about 30 ml of solution and was fitted with a B16 standard socket A to take the reference electrode shown, a side arm B to take the gas tube and a B34 cone supporting a gas outlet and the dropping mercury electrode D.

By means of the gas tube a stream of nitrogen could be passed either through the solution for de-aeration or over its surface while measurements were being taken.

For the more exact work a cell was designed and made which could more easily be thermostatted and had provision for stirring. This latter was essential for the method used for the production of water containing a known amount of oxygen.

The method of obtaining standardised solutions of oxygen in the polarographic cell was to place a known volume of solution in the cell, de-aerate this and add a known volume of the same solution saturated with oxygen (Fig. 5). Since a reasonably large volume of air saturated solution could be prepared this could readily be standardised by the Winkler method as modified by Griffiths and Jackman¹³ and Jackman.¹⁴

The polarograph used was a Tinsley Mark 15 D.C. Polarograph and the dropping mercury electrode used with a saturated calomel electrode as reference. All reagents were of AnalaR quality.

Zusammenfassung—Gelöster Sauerstoff wird studiert und es wird gefunden, dass eine Disproportionierungsreaktion stattfindet. Der Diffusionskoeffizient von Sauerstoff in Kaliumchloridlösung wird aus polarographischen Daten berechnet.

Résumé—Les auteurs ont fait une étude de l'oxygène dissous. Les résultats indiquent une réaction de dismutation. Le coefficient de diffusion de l'oxygène en solution de chlorure de potassium est calculé d'après les résultats polarographiques.

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ACTIVATION ANALYSIS OF MOLYBDENUM IN PLANT MATERIAL

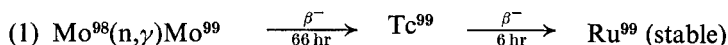
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Summary—The determination of molybdenum in plant material by means of activation analysis is described. Both activation to Mo⁹⁹ ($t_{1/2} = 66$ hr) and to Mo¹⁰¹ ($t_{1/2} = 14.6$ min) is used. With the latter method the whole analysis takes about 1 hr. The extraction of molybdenum is carried out from a sulphuric acid medium using tri-*n*-octylamine in kerosene. The analysis has been performed on clover (*trifolium sp.*) and the results are in good agreement with those obtained by colorimetry using the thiocyanate method.

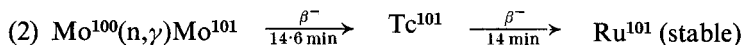
INTRODUCTION

MOLYBDENUM can be determined by neutron-activation analysis in two ways:



$$\sigma = 0.45 \text{ barns}$$

$$\theta = 23.8\%$$



$$\sigma = 0.20 \text{ barns}$$

$$\theta = 9.5\%$$

The decay-scheme of Mo⁹⁹ is reported in the literature.¹

Bowen,^{2,3} using the first method, irradiated biological samples for 3 days, followed by cooling periods of 6–72 hr. The molybdenum, separated by extraction with ether from 6*N* hydrochloric acid, was purified by precipitation of molybdenum α -benzoin-oximate. The separation took about 4 hr for 8 samples and the yield was 50 to 70%. A modified procedure, based on precipitation with α -benzoinoxime, was investigated by Decat and Roderbourg.⁹

A more rapid method, according to reaction (2), is described by Maddock and Meinke⁴ who separated the Tc¹⁰¹ daughter product of Mo¹⁰¹, by extraction with tetraphenylarsonium chloride. The irradiation takes 15 min and the analysis 1 hr.

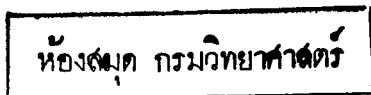
The present work deals with the selective extraction of molybdenum from destroyed plant material, in a sulphuric acid medium, with tri-*n*-octylamine in kerosene, as first described by Brown *et al.*⁵ Because the molybdenum content of the samples was of the order of 1 ppm, it was possible to check the results, obtained by activation analysis, by spectrophotometry according to a procedure described by Sandell.⁶

ACTIVATION AND MEASUREMENTS

Calculations show that reaction (1) gives 48.4 disintegrations/sec of Mo⁹⁹ after irradiation of 1 μg of molybdenum for 5 hr in a slow neutron flux of 1.4×10^{12} n.cm⁻².sec⁻¹, the maximum flux in BR 1, whereas reaction (2) gives rise to 101

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† The untimely death of Mr. Leliaert occurred during the course of this study.



disintegrations/sec of Mo^{101} at the end of an irradiation of $1 \mu\text{g}$ of molybdenum for 20 min at this flux. When the time needed for the chemical separation is about 30 min, the activity of Mo^{101} decreases to 25 disintegrations/sec. Although the sensitivity for the molybdenum determination is higher when one activates to Mo^{99} , the time needed for the whole experiment is much longer. The measurements were made by means of a TMC* 256 channel analyzer connected to a $3'' \times 3''$ NaI(Tl) well-type detector. Mo^{99} is measured at the 140 keV line and Mo^{101} at the 191 keV line.

Preliminary experimental results showed that technetium is not extracted with tri-*n*-octylamine. Nevertheless Mo^{101} can also be determined using the 307 keV line of the Tc^{101} daughter activity after it has grown in the extract. Because Tc^{101} is in transient equilibrium with Mo^{101} , it is recommended in this case to wait about 15 min after separation in order to get maximum growth of Tc^{101} . If one measures between 15 and 30 min after extraction, the Tc^{101} activity is about constant and nearly the same as the Mo^{101} activity immediately after separation.

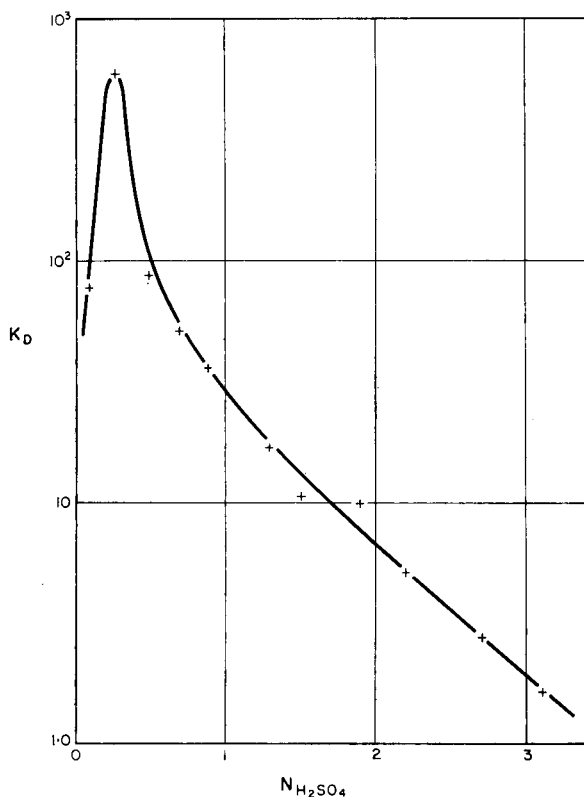


FIG. 1.—Distribution constant versus normality of sulphuric acid for molybdenum after extraction with a solution containing 2.5 v/v% of TOA in kerosene.

However, because the Tc^{101} activity is a rather complex function of time, it is practically impossible to check the half life of Tc^{101} and to correct for time differences between measurements. Although Tc^{101} measurement gives better statistics than the Mo^{101} measurement, it was preferred in view of the above mentioned reasons and the

* Technical Measurement Corporation, North Haven, Conn.

fact that in the case of Te^{101} measurement it is necessary to treat sample and standard in the same way, to determine the Mo^{101} activity on the 191 keV line. Further, the whole analysis can now be carried out by one person, because the standard does not have to be extracted.

EXPERIMENTAL

*Extraction of Molybdenum with Tri-*n*-octylamine in Kerosene*

In this study the extraction of molybdenum^{VI} from a sulphuric acid medium with tri-*n*-octylamine in kerosene was examined.⁵ To 10 ml of sulphuric acid solution in a separatory funnel was added 1 ml of molybdenum solution containing 3 mg of molybdenum/ml as Na_2MoO_4 and 1 ml of Mo^{99} -tracer solution. After shaking for 1 min with 5 ml of a 2.5 v/v% solution of tri-*n*-octylamine in petroleum ether (b.p. 100–120°), the layers were allowed to separate and aliquots of both phases were taken for counting. Fig. 1 shows the results: distribution constant (K_D) versus normality of the sulphuric acid.

The normality of the sulphuric acid solution after extraction was determined by titration of an aliquot of the aqueous layer with 0.1*N* sodium hydroxide solution. From Fig. 1 it can be calculated that $96 \pm 3\%$ of the molybdenum is extracted for

$$0.1N < N_{\text{H}_2\text{SO}_4} < 1.0N.$$

Activation Analysis

Reagents

Sample: Approximately 0.5 g of clover (air-dried).

Standard: About 4 μg of molybdenum in a sealed quartz tube.

Carrier: Molybdenum trioxide.

Destructive agent: Perchloric acid (70%) and nitric acid (sp. gr. 1.4) mixed in equal volumes.

TOA solution: 2.5 v/v% solution of tri-*n*-octylamine in petroleum ether (b.p. 100–120°).

Lymphan indicator paper L 650: pH 0.4–1.4.

Conc. sulphuric acid

Sodium hydroxide: 4*N* and 2*N* solutions.

Mo¹⁰¹

In a Plexiglass can, a sample and a standard are irradiated simultaneously for 20 min at a thermal flux of 1.4×10^{12} n.cm⁻².sec⁻¹. Immediately after irradiation, about 15 mg of carrier is added to the sample and this is heated with 4 ml of conc. sulphuric acid until fumes of sulphuric acid escape. The organic material is destroyed by adding dropwise about 5 ml of destructive agent. The resulting yellowish solution is heated again to expel the nitric and perchloric acids. After cooling for 2 min, 20 ml of water are added. When the solution is neutralised with 4*N* sodium hydroxide solution to pH 0.7–0.9 (about 0.7*N*), a slight precipitation of calcium sulphate occurs. After filtration through glass wool, the solution (approx. 40 ml) is extracted with 25.0 ml of TOA solution by mixing for 1 min. The phases are allowed to separate for 3 min and 20.0 ml of the organic layer are pipetted for measurement. When small volumes are concerned, the filtration step may be omitted.

Meanwhile the standard is dissolved in 25.0 ml of 2*N* sodium hydroxide solution and exactly 20.0 ml are counted.

The whole chemical separation takes about 15 min. About 10 min after irradiation, the standard is measured, then the sample and again the standard. Countings are made during a period of 10–13 min. Corrections are made for the decay of Mo^{101} in the sample versus the standard.

Mo⁹⁹

These analyses are made in nearly the same way. After neutron irradiation for 5 hr and a cooling period of 20 hr, the chemical separation is carried out.

Colorimetric Determination

This is carried out on samples of 2 g of clover according to the procedure described by Sandell.⁶ The plant material is destroyed with sulphuric–nitric–perchloric acid. After destruction, all perchloric acid is expelled by heating to fumes of sulphuric acid. The solution is cooled, then boiled with 5 ml

of water to destroy any nitrosyl sulphuric acid. The sulphuric acid is neutralised with ammonia solution and 5 ml of 6*N* hydrochloric acid is added, followed by 2 ml of 5% sodium fluoride solution and 1 ml of 0.1% iron^{II} sulphate solution.

After filtration into a separatory funnel, the solution is diluted to 30 ml, then 4 ml of 20% potassium thiocyanate solution and 2 ml of 40% tin^{II} chloride solution in 1.5*N* hydrochloric acid are added with mixing. The molybdenum is extracted with 5 ml of a mixture of amyl alcohol and carbon tetrachloride (1:1 by volume). The phases are allowed to separate for 10 min and, after filtration of the organic layer through cotton, the absorption of the clear extract is measured at 465 m μ against water or another suitable blank (measurements were made on a Beckman spectrophotometer model B, in our case).

RESULTS

The above-mentioned procedures were applied to clover (*trifolium sp.*) and the results are summarised in Table I.

TABLE I—SUMMARY OF RESULTS

Method	Sample No.	Sample weight, mg	Mo found, μ g	$N_{H_2SO_4}$ in aq. layer	Mo content, ppm	Devn. of the mean, %
Mo ⁹⁹	1	759	0.744	0.74	0.98	1
	2	538	0.527	0.78	0.98	
	3	491	0.471	0.91	0.96	
Mo ¹⁰¹	4	442	0.427	0.77	0.97	4
	5	550	0.476	0.77	0.87	
	6	585	0.564	1.00	0.97	
	7	531	0.510	0.68	0.96	
	8	658	0.578	0.78	0.88	
	9	491	0.454	0.81	0.93	
Colorimetry	10	2000	1.87	—	0.93	2
	11	1998	1.96	—	0.98	
	12	1999	1.96	—	0.98	

As can be seen from Table I, the results obtained by different methods are in fairly good agreement. The method of Covell⁷ was used for data evaluation of the gamma-ray spectra of Mo⁹⁹ and Mo¹⁰¹. In the case of Mo¹⁰¹, the coefficient of variation, by this method, was 4%. Other evaluation methods of the gamma-ray spectral data gave coefficients of variation between 8% and 20%, although the same mean value was obtained. The main error is introduced by the subtraction of the Compton contribution of the 307 keV line of Tc¹⁰¹ from the Mo¹⁰¹ 191 keV line (see Fig. 2).

Under the experimental conditions used, the detection limit for the Mo¹⁰¹ method seems to be 0.1 μ g, with a standard error of 35%. The recovery of molybdenum has been deduced by measurement of the acidity of the aqueous phase after extraction and by reference to the graph of distribution constant *vs.* normality of sulphuric acid (Fig. 1). The aqueous layer was always lower than 1*N* in sulphuric acid. From column 5 in Table I, it is seen that the pH adjustment can be made fairly well by the use of Lymphan indicator paper L 650.

Errors caused by Ru^{104(n, α)Mo¹⁰¹ and Ru^{102(n, α)Mo⁹⁹ are not important, because of the low abundance of ruthenium in the samples and the low cross-sections for these}}

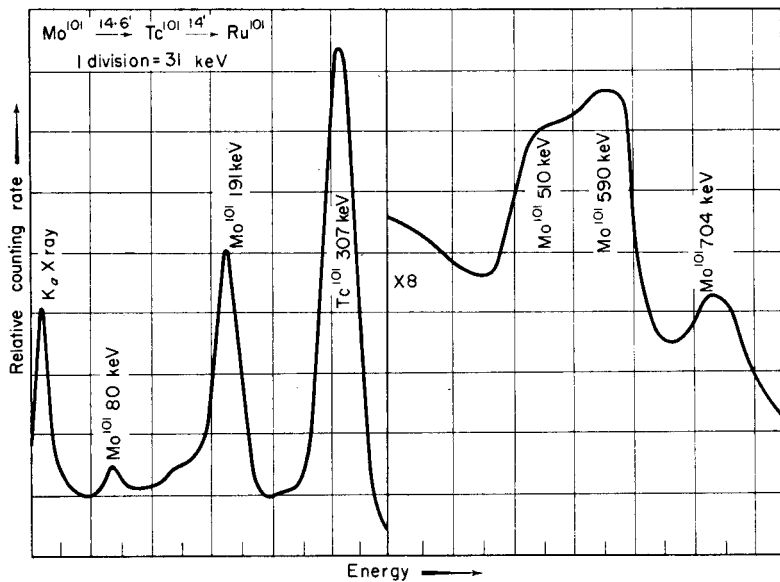


FIG. 2.— γ -Spectrum of a molybdenum standard obtained with a TMC 256 channel analyzer in a $3'' \times 3''$ NaI(Tl) well-type crystal (measurement made 10 min after irradiation for 10 min).

reactions. In the chemical treatment of the sample, uranium is co-extracted. Because the uranium content was lower than 50 ppb, no interference was introduced by the fission reaction $U^{235}(n,f)Mo^{101}$, Mo^{99} . The 74 keV line of U^{239} ($t_{1/2}$: 23.5 min) has no effect on the measurement of Mo^{101} .

A description of the determination of uranium based on the same extraction procedure will be published soon.⁸

Zusammenfassung—Die Bestimmung von Mo im Pflanzenmaterial mittels Aktivierungsanalyse wird beschrieben. Mo^{99} ($t_{1/2} = 66$ h) und Mo^{101} ($t_{1/2} = 14,6$ min) wurden herangezogen. Mit der letzteren Methode benötigt die gesamte Analyse ungefähr eine Stunde. Die Extraktion des Mo wird aus schwefelsäurer Lösung mit Tri-n-octylamin in Kerosin bewerkstelligt. Die Analyse wurde auf Klee (*Trifolium* sp.) angewandt und die erhaltenen Resultate stehen in gutem Einklang mit denen auf kolorimetrischem Wege (Thiocyanatmethode) erzielten.

Résumé—La détermination du molybdène dans les matériaux végétaux au moyen d'analyse par activation a été mise au point. L'activation au Mo^{99} ($t_{1/2}$: 66 h) aussi bien qu'au Mo^{101} ($t_{1/2}$: 14,6 m) a été employée. La durée de l'analyse totale par la dernière méthode est d'environ une heure. Le molybdène est extrait à partir d'un milieu acide sulfurique par la tri-n-octylamine. La détermination a été effectuée sur du trèfle, et les résultats sont en bon accord avec ceux obtenus par colorimétrie.

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A SCHEME FOR THE RAPID ANALYSIS OF URANIUM-ORE ACID LEACH SOLUTIONS

DETERMINATION OF ALUMINIUM, ARSENIC, CALCIUM, CADMIUM, COBALT, COPPER, MAGNESIUM, NICKEL, AND ZINC IN PRESENCE OF EXCESS IRON AND MANGANESE

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Summary—A scheme for the rapid quantitative analysis of uranium-ore acid leach solutions or solutions of similar composition is described. As, Cd, Co, Cu, Ni and Zn are determined polarographically, solutions of similar composition is described. As, Cd, Cu, Co, Ni and Zn are determined polarographically, for the separation of Al, Cd, Ca, Co, Mg and Zn from Fe and Mn and from each other by anion-exchange chromatography and solvent extraction of oxinates.

IN the course of work on effluents from uranium mines a need arose for quantitative determination of aluminium, arsenic, calcium, cadmium, cobalt, copper, iron, magnesium, manganese, nickel and zinc in "pregnant" solutions (relatively rich in uranium, ready to be processed on ion-exchange columns) and in "barren" solutions (column effluents, which are practically devoid of uranium).

Both solutions contain a few elements, such as iron and manganese, in considerable amounts, and a number of other elements in trace or near trace quantities. Interferences in analysis for these trace elements are, therefore, to be expected, and elaborate and time-consuming separations would normally be required in order to determine them. The literature search for an integrated scheme of analysis for the above elements in solutions of similar composition proved unfruitful. The aim of this work was to evolve such a scheme, the emphasis being on rapidity and simplicity. In addition to the selection and adaption of suitable methods of analysis, this involved the development of a method for the separation of Al, Ca, Cd, Co, Mg and Zn from iron and manganese and from each other by anion-exchange chromatography and solvent extraction of oxinates.

Iron and manganese were determined directly, without prior separation. Iron was determined colorimetrically with 1,10-phenanthroline.¹⁷ Although barren and pregnant solutions contained interfering ions,^{13,17} their ratio to that of iron was so small that they constituted no source of error. This method is more convenient than the titrimetric potassium dichromate method^{2,10} and results are comparable (Table II). Manganese was also determined colorimetrically,¹⁴ measuring at 525 m μ in the spectrophotometer the permanganate colour developed with potassium periodate. If the sample was well boiled with nitric acid to remove any easily oxidisable matter present, preliminary fuming with sulphuric acid and oxidation with ammonium persulphate were unnecessary.⁹

Copper and nickel were determined simultaneously by polarography, using pyridine-

hydrochloride as the base electrolyte.¹¹ This base electrolyte precipitated interfering elements, which were removed by filtration. Hitchin⁶ used this method for determination of Cu, Ni and Co in cobalt concentrates and in solutions containing uranium. However, South African barren and pregnant solutions contain zinc, which has a polarographic wave which coalesces with that of cobalt, and therefore preliminary separation of these two metals was necessary.

Arsenic was separated from interfering elements by a simple distillation,⁵ and subsequently determined polarographically.⁴

A preliminary separation was necessary in the case of Al, Ca, Cd, Co, Mg, and Zn, and it was found that this separation could be very conveniently achieved by means of ion-exchange chromatography. Kraus and Nelson⁷ studied the behaviour of many metals in hydrochloric acid solutions on strongly basic ion-exchange columns. It was clear from their work that a certain number of ions, such as those of Al, Ca, Mg, Ni and some other metals were not absorbed by the resin under selected conditions, and therefore could be collected as a separate fraction. Other ions were retained by the resin to a greater or lesser extent, and could be eluted separately and successively by changing the concentration or nature¹⁶ of the eluting solvent. In this way it was possible to separate metals present in barren and pregnant solutions into four fractions containing (a) aluminium, calcium, magnesium, manganese and nickel; (b) cobalt; (c) most of the iron; (d) cadmium and zinc. The conditions for this separation are given in the experimental section of this paper, where it will be seen that the recovery of metals was quite satisfactory. Recently similar separations were reported by Wilkins^{19,20} and Carson.¹

Cobalt was then easily determined polarographically using the same base electrolyte as in the case of copper and nickel.⁷ Zinc and cadmium were also determined by polarography, with ammonia-ammonium chloride as supporting electrolyte.¹² The concentration of zinc in these solutions was usually much higher than that of cadmium, and the particular fraction had to be diluted with base electrolyte before the polarogram for zinc could be recorded.

Although most of the interfering ions were removed by anion-exchange chromatography, nickel and manganese were still present in the fraction containing aluminium, calcium and magnesium. Aluminium was separated by extraction of its 8-hydroxyquinoline complex at pH 5 with chloroform, and determined by measuring spectrophotometrically at 395 m μ the intensity of the yellow colour formed.¹⁵ In this procedure nickel oxinate is also extracted into chloroform and interferes. It was found however, that in the case of S. African barren and pregnant solutions, where the concentration of nickel is at least ten times smaller than that of aluminium, the interference was negligible (Table III). The colour intensity should be measured without delay, in order to avoid decrease of absorbance from photochemical decomposition of the complex.⁸

Further extraction of the aqueous layer with 8-hydroxyquinoline in chloroform at pH 8 removed most of the manganese,¹⁵ and calcium and magnesium were determined together by titration with ethylenediaminetetra-acetic acid in the presence of triethanolamine with Eriochrome Black T as indicator.^{3,18}

The scheme of analysis showing the sequence of operations is given in Fig. 1. It will be seen from the analysis of a synthetic mixture (Table IV) that the accuracy and sensitivity of the methods used were satisfactory for the purposes of this work,

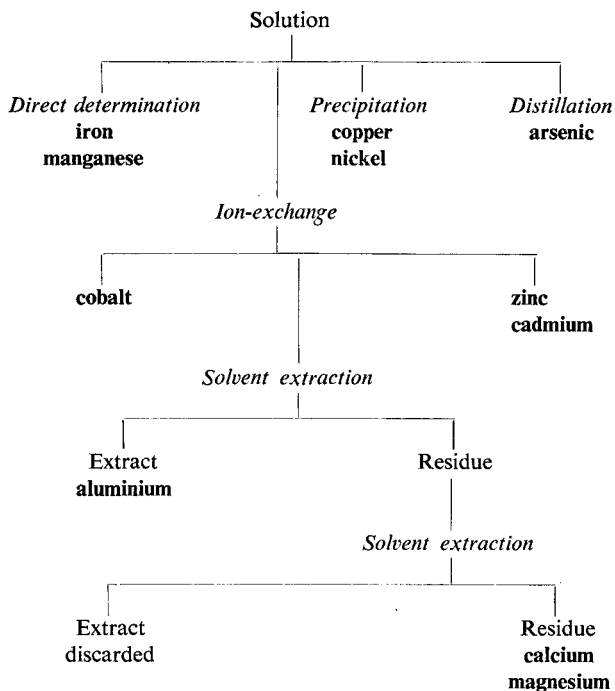


FIG. 1.—The scheme of analysis.

in which the emphasis was on speed and simplicity. There is no doubt that most of the methods of this scheme could be used in much more critical work, and the scheme itself applied to solutions other than those encountered in the uranium industry.

TABLE 1.—ANALYSIS OF URANIUM PREGNANT AND BARREN SOLUTIONS

Solution	Fe	Cu	Ni	Mn	As	Co	Cd	Zn	Al	Ca + Mg (as CaCO ₃)
(A) Pregnant	3,260	20	28	3,250	41	16	0.24	77	508	2,730
Barren	3,220	16	26	3,500	40.5	17	0.29	44	504	2,850
(B) Pregnant	3,220	16	108	4,600	410	53	0.70	148	408	3,120
Barren	2,840	13	96	4,300	339	42	0.61	133	422	2,800
(C) Pregnant	5,360	29	32	3,400	76	33	0.83	86	1,284	4,070
Barren	5,240	24	30	3,280	69	36	0.90	73	1,336	5,250
(D) Pregnant	4,880	4.0	100	260	107	66	0.43	107	861	4,750
Barren	5,120	3.6	88	275	107	71	0.57	115	1,120	6,050
(E) Pregnant	3,180	12	50	8,050	107.5	34	0.49	110	690	4,200
Barren	2,910	12	46	7,700	100	28	0.26	68	740	2,950
(F) Pregnant	4,120	14	34	5,150	54.5	20	0.33	60	1,140	4,650
Barren	3,060	6	19	2,200	32.6	16	Trace	34	444	1,550

The results are expressed as mg/litre of metal.

In order to show the range of concentrations of different metals usually encountered in S. African barren and pregnant solutions, the results of analysis of solutions from six different uranium-producing mines are reproduced in Table I. In each case the solutions were analysed according to the described scheme.

EXPERIMENTAL

Apparatus and reagents

A K-1000 Cathode Ray Polarograph, Southern Instruments, Ltd., with a polarographic cell modified in such a way that it could accommodate a saturated calomel reference electrode (S.C.E.), and a Zeiss Spectrophotometer, Model PMQ II, were used. Analytical grade reagents were used.

Iron

A 10-ml aliquot of the sample solution is diluted to 1000 ml in a volumetric flask, adding 1 ml of hydrochloric acid to keep iron in solution, if necessary. A 5-ml portion of this solution is transferred into a 100-ml flask, 1 ml of hydroxylamine hydrochloride, 10 ml of 1,10-phenanthroline solution and 1 ml of sodium acetate buffer, prepared as in reference 17, are added, and the solution is made up to the mark with distilled water. The colour intensity is read against a reagent blank, at 508 m μ in the spectrophotometer, using a 1-cm cell.

The concentrations are read from a calibration curve.

The results obtained by this method are compared in Table II with those obtained by titration of iron with potassium dichromate.

TABLE II. COMPARISON OF IRON DETERMINATIONS BY 1,10-PHENANTHROLINE AND POTASSIUM DICHROMATE METHODS

Solution	1,10-phenanthroline, <i>ppm</i>	Potassium dichromate, <i>ppm</i>
Pregnant C	5360	5200
Pregnant E	3180	3120
Pregnant F	4120	4140
Barren C	5240	5150
Barren E	2910	2840
Barren F	3060	2950

Manganese

An aliquot (1–10 ml) of the solution is pipetted into a 500-ml squat beaker. To this 30 ml of conc. nitric acid are added and the solution is boiled for 10 min, then diluted to 200 ml with water and about 1 g of potassium periodate is added. The solution is boiled for 2–3 min, then kept warm for 30 min, to allow the colour to develop fully. After cooling, it is transferred to a 500-ml volumetric flask and made up to the mark. The colour intensity is read in a 1-cm cell against a distilled water blank at 525 m μ in the spectrophotometer.

The concentrations are read from a calibration curve.

Copper and nickel

To 25 ml of the solution in a 250-ml beaker, 3 ml of 12M hydrochloric acid and 5 ml of 16M nitric acid are added. The solution is boiled for 5 min, then evaporated to incipient dryness on a water-bath, and, after moistening with hydrochloric acid, evaporated to dryness to destroy the nitric acid. The residue is dissolved in 2 ml of 12M hydrochloric acid, transferred to a 100-ml volumetric flask, 5 ml of pyridine are added, and the solution is made up to the mark with distilled water. The precipitate is filtered off on Whatman No. 42 paper, an aliquot of the filtrate is transferred to the polarographic cell, and the polarogram is recorded at -0.39 V and -0.9 V *vs.* S.C.E. for copper and nickel, respectively.

The concentrations are read from calibration graphs.

Arsenic

A long-neck distillation flask of 200-ml capacity, fitted with a thermometer, a gas inlet tube for nitrogen dipping to the bottom of the flask, and an efficient condenser, are used for arsenic distillation. The distillate is collected in a ground-glass Friedrich gas-washing bottle of 100-ml capacity, cooled in an ice bath.

A 10-ml aliquot of the sample, 5 ml of reduction mixture (10% hydrazine hydrochloride and 7% potassium bromide), 5 ml of phosphoric acid and 70 ml of 12*M* hydrochloric acid are placed in the distillation flask, and 10 ml of distilled water in the receiving flask. The apparatus is assembled, a moderate stream of N₂, which prevents bumping and sucking back, is started, and about 70 ml of the distillate are collected in the cooled receiving flask (stop distillation when temperature reaches 115°). The distillate is washed into a 600-ml squat beaker, and about 30 ml of potassium hydroxide solution (60 g dissolved in 100 ml) are added with constant cooling, till the pH is between 0.15 and 0.20 units (pH meter). This solution is transferred to a 500-ml (if necessary 250-ml) volumetric flask and made up to the mark with distilled water. An aliquot of the solution is transferred to a polarographic cell, and the polarogram recorded at -0.47 V *vs.* S.C.E.

The arsenic concentration is obtained from a calibration graph.

Separation of Ca, Mg, Al, Co, Zn and Cd by ion-exchange chromatography

A strong base anion-exchange resin, Amberlite CG-400 Type 1, 100-200 mesh, chloride form, is used. The resin is packed as a slurry in distilled water, into a 1 × 40-cm glass column provided with a tap, to the height of 30 cm. The bed volume of such a column is 20-25 ml. After washing with 50 ml of 9*M* hydrochloric acid, the column is ready for use.

A 10 ml portion of barren or pregnant solution, to which 1 ml of 100-vol. H₂O₂ is added, is evaporated to dryness on a water-bath. The residue is dissolved in a minimum amount of 9*M* hydrochloric acid, and applied to the column in the usual way. The mixture of metal complexes is then eluted, at a flow rate of about 80 ml/hr, with:

- (a) 50 ml of 9*M* HCl (two bed-volumes)
- (b) 50 ml of 4*M* HCl
- (c) 50 ml of 0.5*M* HCl
- (d) 60 ml of 1*M* HNO₃

to give fractions (a), (b), (c) and (d), respectively, which are collected separately. Fraction (c) is discarded.

After washing with 50 ml of water and 50 ml of 9*M* hydrochloric acid, the column is again ready for use. Since strong HCl attacks the resin to a certain extent, the column is normally treated with 9*M* hydrochloric acid just before it is used.

Aluminium

Fraction (a) (from the separation by ion-exchange chromatography) is made up to 100 ml with distilled water, and a 10-ml aliquot is evaporated to dryness on a water-bath. The residue is dissolved in 1 ml of 1:4 hydrochloric acid, transferred to a 100-ml separating funnel, 10 ml of 10% sodium acetate solution are added, and the whole is diluted to about 40 ml with distilled water. (The pH of the solution must be 5). A 10-ml portion of 5% 8-hydroxyquinoline in chloroform is added, and the funnel is immediately stoppered and shaken for 1 min. After separation of the phases, the chloroform layer is run off into a dry 100-ml volumetric flask. This extraction is repeated twice more using 5 ml of 5% 8-hydroxyquinoline solution mixed with 5 ml of chloroform, and finally with 10 ml of pure chloroform. All extracts are combined. The extracted aqueous layer is kept for the determination of calcium and magnesium.

The chloroform extract is made up to 100 ml with pure chloroform, about 2 g of anhydrous sodium sulphate are added, and the flask is well shaken. An aliquot is decanted into a 1-cm cell, and the absorption against a blank of 1% 8-hydroxyquinoline in chloroform is read at 395 m μ in the spectrophotometer.

The aluminium concentration is obtained from a calibration graph.

The results of the determination of aluminium by the above method in the presence of manganese, calcium, magnesium and nickel are given in Table III, from which it will be noted that nickel does not interfere significantly when present in small amounts.

TABLE III.—DETERMINATION OF Al IN THE PRESENCE OF Mn, Ni, Ca AND Mg

Taken, μg					Found, μg
Al	Mn	Ni	Ca	Mg	Al
9	10	2.5	5	2	10.5
27	30	7.5	15	6	28.6
9		2.5			11.2
27		7.5			29.8
9	10		5	2	9.0
27	30		15	6	26.9
9		10			12.0
27		30			31.8
9		1			9.2
27		3			26.7

Calcium and magnesium

After extraction of aluminium, as described above, the extracted aqueous layer is transferred to a 200-ml beaker, and the pH of the solution is adjusted to 7.5–8.0 with 5% sodium hydroxide (pH meter). The solution is then transferred back to the separating funnel and extracted with 5% 8-hydroxyquinoline in chloroform, as directed for aluminium, but the chloroform layer is discarded. The extraction is repeated with 5 ml of 8-hydroxyquinoline and 5 ml of chloroform at least three times, or until the chloroform layer becomes colourless, and finally with 10 ml of pure chloroform.

The extracted aqueous layer is transferred into a 100-ml porcelain dish, and 30 ml of 30% triethanolamine solution, 1 ml of ammonia buffer solution and a few drops of Eriochrome Black T indicator are added. The solution is titrated with standard 0.02M EDTA solution to a blue end-point. The results are expressed as ppm of CaCO_3 .

Cobalt

Fraction (b) (from the separation by ion-exchange chromatography) is evaporated to dryness on a water-bath, and the residue is dissolved in 2 ml of 12M hydrochloric acid. The solution is then transferred to a 100-ml volumetric flask, 5 ml of pyridine are added, and the whole is made up to the mark. An aliquot is transferred to the polarographic cell and the polarogram is recorded at $-1.15 \text{ V vs. S.C.E.}$

The concentration is read from a calibration graph.

TABLE IV.—ANALYSIS OF A SYNTHETIC MIXTURE

Metal	Taken, ppm	Found, ppm		
Fe	2000	1980, 2060		
Mn	2170	2180, 2200		
Cu	36	36, 37		
Ni	60	60, 60		
As	103	99, 103		
		Column 1	Column 2	Column 3
Zn	95	96	97	99
Cd	2.4	2.4	2.4	2.4
Co	25	24	24	27
Al	450	440	440	450
Ca + Mg (as CaCO_3)	3650	3600	3690	3630

Zinc and cadmium

Fraction (d) (from the separation by ion-exchange chromatography) is evaporated to dryness on a water-bath. The residue is dissolved in 2 ml of 1:1 hydrochloric acid, transferred carefully to a 10-ml volumetric flask and neutralised with ammonia. To it 0.5 g of ammonium chloride is added and the solution is made up to the mark with distilled water. An aliquot is transferred to the polarographic cell and the polarogram is recorded at -0.75 V and -1.30 V vs. S.C.E. for cadmium and zinc respectively.

The concentrations are read from calibration graphs.

Analysis of a synthetic mixture

A synthetic mixture, containing aluminium, arsenic, calcium, cadmium, cobalt, copper, iron, magnesium, manganese, nickel and zinc was analysed according to this scheme. The results are reproduced in Table IV.

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Zusammenfassung—Ein Schema zur raschen, quantitativen Analyse von sauren Auslaugungen von Uranerzen und ähnlichen Lösungen wird beschrieben. As, Cd, Co, Cu, Ni und Zn werden polarographisch erfasst, Al, Fe und Mn colorimetrisch und Ca und Mg durch ÄDTE-Titration. Eine Trennung von Al, Cd, Ca, Co, Mg und Zn von Fe und Mn sowie voneinander mittels Ionenaustauschchromatographie und Solvent-extraktion unter Verwednung von Oxin wird beschrieben.

Résumé—Les auteurs décrivent un schéma d'analyse quantitative rapide de solutions acides de mineral d'uranium ou de solutions de composition semblable. As, Cd, Co, Cu, Ni et Zn sont dosés par polarographie, Al, Fe et Mn par colorimétrie et Ca et Mg par titrage par l'EDTA. Le schéma comprend une méthode de séparation de Al, Cd, Ca, Co, Mg et Zn d'une part, et de Fe et Mn d'autre part, par chromatographie d'échange d'ions et extraction d'oxinates par un solvant.

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ANALYSIS OF GASES AND VAPOURS BY SPECTROSCOPIC TECHNIQUES—II*

REVIEW OF THE ABSORPTION SPECTRA OF GASES AND VAPOURS

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Summary—The electronic molecular absorption of gases and vapours has been reviewed, particular emphasis being given to the spectra obtained from organic molecules.

THERE exists an exceedingly large volume of information on the electronic absorption spectra of organic compounds. The relationship between the nature of the absorption spectrum and the chemical constitution of organic compounds has been reviewed by Ferguson,¹ and the many aspects of electronic absorption spectroscopy are covered in the book by Gillam and Stern.²

Most absorption results have been obtained using a liquid phase, and this practice introduces a complex variable which may be called the "solvent effect". Comparison of the absorption properties of a substance in the vapour phase and in solution shows that dissolution damps down the molecular rotation and thus produces broad absorption bands where fine structure peaks can be observed in the spectra of the vapour phase. A similar transformation is noticeable when solutions of substances in non-polar and polar solvents are compared. A change of solvent can also induce changes in the intensity of an absorption band, and can cause a displacement of bands along the wavelength scale.

Apart from these physical "solvent" effects, a change of solvent may bring about a radical change in the nature of the absorption of a substance. This change can be caused by chemical interaction with the solvent; or by complex formation; or by dissociation; or by equilibration of two tautomers in solution.

The absorption spectra obtained using the vapour phase should theoretically be free of the many disadvantages introduced by "solvent effects" but little use appears to have been made of this approach. Admittedly the experimental technique for handling gases or vapours is more cumbersome than that required for work using solutions; but as a preliminary to surveying the analytical possibilities of this approach a review has been made of existing publications on the absorption of visible and ultra-violet radiation by gases and vapours.

THEORY OF ELECTRONIC ABSORPTION SPECTROSCOPY

It is proposed to adopt here the same procedure as that used in Part I of this series, *i.e.*, to give an outline of the theoretical principles directly concerned with analytical applications, and not to delve deeply into basic theory, which is covered by existing text books.^{3,4}

* Part I: *Talanta*, 1961, 8, 892.

Atomic line spectra

The atomic line spectrum of an element can be obtained in absorption if a sufficient concentration of free atoms can be maintained in the vapour phase in a given path length. For metals this necessitates vaporisation in a flame or an electric arc, and although it would seem in this case preferable and simpler to use the emission spectrum, recent work on atomic line absorption, using flame photometric techniques, has shown that the method possesses valuable analytical possibilities.⁵

Within the scope of this review, the only gases giving rise to such line spectra are those of Group 0 in the Periodic Table, *i.e.*, the inert gas group. As stated in Part I, the emission spectra of these gases lies principally in the visible and near ultraviolet and can be used for qualitative and quantitative analysis. Their absorption spectra however lie in the extreme vacuum ultraviolet, a region not readily accessible to routine spectroscopic equipment.

Since the emission spectrum of an inert gas is in the visible region, it would appear reasonable that the absorption spectrum should lie in the same region. This is not necessarily so, however. If we take neon as a typical example, it has six $2p$ electrons and the L_1 and L_2 shells are completely filled; this means that the ground electronic state is 1^1S_0 . An excited state will result when an electron is moved from the L_2 shell to a higher orbital, but for neon, as for all inert gases, the energy required to do this is very large, because it involves a change in the principal quantum number. When only one electron is excited, we have the first excited state, which is also an S state, since the quantum number for orbital angular momentum, l , is zero. We now have two unpaired electrons, giving a total spin of 1 which means that this first excited state is 2^3S . (The multiplicity, *i.e.*, the superscript to the term symbol is given by twice the total spin + 1.) The next excited state, when two electrons are excited and paired together with opposed spins in orbit 2, will by similar reasoning be 2^1S , since the total spin is now zero. Neither of these states will combine with the ground state, because $2^3S \rightarrow 1^1S_0$ would involve a change of multiplicity, which is forbidden, and for $2^1S \rightarrow 1^1S_0$ the selection rule $\Delta l = \pm 1$ is broken. Such metastable states cannot, therefore, be reached by absorption of radiation. The first excited state which does combine with the ground state is 2^1P , and the transition $2^1P \rightarrow 1^1S_0$ gives rise to absorption in the far ultraviolet between 584 and 504 Å.

From the preceding discussion it is evident that the technique of absorption spectroscopy has no real value for the analytical determination of the inert gases, and it is fortunate that in this case emission spectroscopy provides a good means of analysis.

Molecular band spectra

The absorption spectrum of a diatomic molecule in many cases is found to be in the same spectral region as its emission spectrum. The two types of spectra need not necessarily be in the same region, however. Absorption or emission of radiation by a molecule must conform to the Franck-Condon principle, which states, in effect, that an electronic transition takes place in a time which is very short in comparison with that required for movement of the atomic nuclei. This means that transitions from any particular vibrational level on one potential curve (describing the variation of potential energy with changing internuclear distance), to some vibrational level on the second curve, are represented by vertical lines drawn from the extremities

of the vibrational level, to intersect the second curve. The vibrational levels closest to the points of intersection on this curve are then the preferred final levels for the transition. In the case of emission, the molecule is excited from the ground electronic state to a higher state after acquiring the necessary excitation energy in some processes such as collision with an energetic electron or molecule. Over a period of time, many different vibrational levels of the upper state will be populated, and there will be a corresponding large number of transitions from these levels to the various levels in the ground state allowed by the Franck-Condon principle, giving rise to a large number of bands. In the case of absorption by a gas, however, we have a very different state of affairs. Most experiments in absorption are carried out at room temperature; or at any rate at temperatures lower than about 50° . This means that the gas molecules are in the zero vibrational level of the ground electronic state, with a small number in the first vibrational level. Absorption of radiation will therefore lead to transitions between the 0 level of the ground state and the allowed levels of the upper state, with much weaker bands, if any at all, originating from the first vibrational level. This means that there will be fewer bands, in general, in an absorption spectrum of a gas than in the emission spectrum, the latter having more bands, extending to longer and shorter wavelengths than the former. Another point arising from the Franck-Condon principle, which will affect the positions of the two types of spectra, is the change in internuclear distance on going from one potential curve to the other. If there is very little difference in the internuclear distances in both electronic states, the verticals drawn from a vibrational level in one will intersect the other curve around the same place, and absorption and emission spectra will lie in approximately the same wavelength region. If there is a large change in the internuclear distance, however, this will not be so. The verticals from a vibrational level on one curve will intersect the other at a different level, leading to a difference in the positions of emission and absorption spectra.

The appearance of an absorption spectrum is further simplified in comparison with the corresponding emission spectrum, by virtue of the much simpler rotational structure in the former case. This again results from the fact that most absorption work is done at or near room temperature, where only the lower rotational levels have appreciable populations. This leads to a relatively small number of lines originating from the ground state rotational levels, whereas in the case of emission, the temperature is necessarily much higher, resulting in a large number of rotational levels being populated in the upper state, and a correspondingly greater number of lines. Consequently in practice it is easier to pick out band heads in absorption than in emission.

The absorption spectrum of a gas may be used in an exactly similar fashion to its emission spectrum, for purposes of qualitative identification. The use of absorption spectroscopy for quantitative analysis depends on two physical laws. The first, proposed by Lambert, states that when a beam of radiation passes through a homogeneous absorbing medium the intensity of the radiation is reduced by the same fractional amount in each succeeding unit length of the path. This can be stated in the form

$$-\frac{dI}{I} = k l \quad (1)$$

where I is the intensity at any point and k the fraction by which the absorbing material

reduces the intensity for unit path length; k is known as the absorption coefficient. Integration of this expression between the limits 0 and x , where x is the total path length traversed by the radiation, gives us for the ratio I_0/I_x

$$\log_{10} \frac{I_0}{I_x} = Kx \quad (2)$$

or
$$I_x = I_0 \cdot 10^{-Kx} \quad (3)$$

Here I_0 is the intensity of the incident radiation and I_x the intensity after passing through the thickness x .

The second law, first enunciated by Beer, states that the amount of absorption depends directly on the amount of absorbing species present, or on its concentration if it is in solution. For gases, the second law is incorporated in expression (3) by reducing the gas pressure to S.T.P. and then calculating the hypothetical path length, x , which would give the same absorption as that obtained under the actual experimental conditions.

The factor $\log_{10} I_0/I_x$ in expression (2) is usually known as the optical density, and is designated D .

Some workers prefer to use the absorption coefficient k , obtained from (1) using natural logarithms. Integration of (1) in this way gives us,

$$\log_e \frac{I_0}{I_x} = k \cdot x \quad (4)$$

and
$$I_x = I_0 \exp(-kx) \quad (5)$$

Obviously the two coefficients k and K are related by

$$k = 2.303 K \quad (6)$$

In order to obtain accurate and meaningful values of the absorption coefficient for gases which give a discrete band structure, a resolution is required which can separate individual rotational lines. This is usually the case for simple molecules, *e.g.*, diatomic, triatomic and a few more complex molecules. When the absorption consists of diffuse bands or continua, however, high resolution is not required, and as a rule Beer's law holds rigorously at relatively low pressures. This is the case for most polyatomic molecules. For very sharp bands, such as those obtained in the Schumann-Runge system of oxygen, if the resolution is not good enough to resolve the rotational structure completely, the values of k or K which are obtained will most probably show an apparent variation with pressure. A good review of absorption laws is given by Nielson, Thornton and Dale.⁶

EXPERIMENTAL METHODS OF OBTAINING SPECTRA

(a) Light sources

For work in the visible region of the spectrum, the tungsten filament lamp is still the one most commonly employed. For absorption work the source must be one of stable operating characteristics and high brightness. Various modifications of the simple filament lamp have been developed and are described in the standard texts.^{7,8,9}

For the ultraviolet region down to about 2000 Å, various gas discharge tubes are available, the most commonly used being the hydrogen tube and the xenon tube. One of the most important characteristics that a good discharge tube must possess for such work is the emission of a near uniform continuum with as few atomic lines as possible. Both of the above mentioned tubes fulfil this condition fairly well.

Below 2000 Å, *i.e.*, in the vacuum ultraviolet region, a variety of sources have been tried, with varying degrees of success. Lee and Weissler¹⁰ have employed a low pressure spark for measurement of absorption intensities between 300 Å and 1300 Å, using a photographic technique. They claim a constancy of this source of the order of 2%, but it has the disadvantage of a strong line emission superimposed on the continuum.

The most common source for this region is the hollow cathode discharge tube, modified by the inclusion of a quartz or glass capillary section in the cathode assembly, operating at about 600 V and 0.5 A d.c. The tube may be filled with hydrogen or inert gas (usually xenon) and is fitted with a window of LiF or CaF₂. More recent developments in this field are concerned with the use of electrodeless lamps, the gas being excited by a microwave discharge.¹¹

(b) Absorption cells

The characteristics required of a vessel used to contain the gas to be investigated are principally

- (i) good transmission through the cell windows in the desired spectral region,
- (ii) sufficient path length to give appreciable absorption (this will depend on how intensely a given gas absorbs and the pressure of gas used),
- (iii) ease of manipulation, *e.g.*, for cleaning purposes and degassing of cell walls,
- (iv) reasonable flatness and parallelism of end windows.

The standard texts on absorption spectroscopy give details of the most commonly used types of cell for various purposes. Here it will suffice to say something on the types of window used. For work in the visible region polished glass windows are sufficient; they will transmit radiation in the region 10,000–3500 Å. Below this region polished quartz plates must be employed. The use of quartz extends the spectral range down to about 2100 Å. If it is desired to go to even shorter wavelengths, materials such as LiF or CaF₂ can be used. These materials can be used for wavelengths down to 1200 Å, but to investigate this region all air must be removed from the light path since oxygen begins to absorb strongly below 2000 Å. This necessitates the use of vacuum spectrographs with LiF or CaF₂ optics, or reflection grating instruments.

(c) Measurement of absorption intensity

The measurement of absorption intensity involves essentially the same procedure as emission intensity measurements and this has been discussed in Part I. Again photographic or photoelectric techniques can be used, present trends favouring the use of photoelectric spectrophotometers.

THE ABSORPTION SPECTRA OF GASES AND VAPOURS

Inorganic vapours and gases

The reference work of Pearse and Gaydon¹² lists the wavelengths of the major band heads of the absorption spectra of many inorganic compounds in the vapour

form. Among the absorption spectra listed are those obtained from the halide salts of silver, aluminium, barium, bismuth, calcium, copper, gallium, indium, magnesium, manganese, lead, selenium, tin, strontium, tellurium, thallium and a number of interhalogen compounds. Also listed are the spectra obtained from the oxides of lead, chlorine, selenium, tin and tellurium; the hydrides of aluminium, barium and copper; the sulphides of germanium, lead and tin; and the selenides and tellurides of silicon, tin and lead. The absorption spectra of the vapours of many elements have been examined and those listed include arsenic, bismuth, bromine, cadmium, chlorine, caesium, mercury, iodine, indium, potassium, lithium, phosphorus, lead, antimony, selenium and tellurium.

The same set of wavelength tables record data for the absorption spectra of oxygen, ozone, sulphur dioxide, nitrous oxide, nitrogen peroxide, ammonia, nitrous acid, isocyanic acid, cyanogen and carbon disulphide.

Organic vapours

The absorption spectra of organic vapours have not been so conveniently tabulated as those derived from inorganic species. Pearse and Gaydon¹² only record spectral data for acetylene, benzene, formic acid, formaldehyde, acetaldehyde, propionaldehyde, acetone, benzaldehyde, glyoxal, methyl nitrite and ethyl nitrite. The complexity of the molecular band spectra obtained from organic vapours renders the preparation of a set of tables, similar to those in existence for atomic species and inorganic molecular species, extremely difficult, but as most individual publications include photographs and tables of wavelengths, a source of references to relevant data could prove equally useful. Thus in the following sub-sections, reference is given to recent publications related to the various compounds. In order to restrict the extent of this paper, compounds which absorb in the vacuum ultraviolet have not been included.

A number of models and methods of calculation have been proposed for theoretical studies on the electronic structures of molecules and the prediction of the effect of substituents on the spectrum of a parent compound. This aspect will not be discussed in this paper but details can be found in the publication of Duncan and Matsen⁴ or in recent papers such as that by Moffitt¹³ on the electronic spectra of cata-condensed hydrocarbons; those by Ham and Ruedenberg¹⁴ on the spectra of aromatic hydrocarbons; that by Goodman *et al.*¹⁵ on the spectra of substituted aromatic hydrocarbons; or those by Anno¹⁶ on the electronic structure of the N-containing heterocyclic molecules. Much other relevant material will be found in the publication by Gillam and Stern.²

Benzene: The absorption spectrum of benzene in the region between 2200 Å and 2800 Å was analysed by Spomer *et al.*¹⁷ in 1939; and a year later Radle and Beck¹⁸ determined the wave numbers and relative intensities of five hundred of the absorption bands in the 2600 Å region. In the same year the absorption spectrum of heavy benzene found in the region of 2700 Å–3000 Å was analysed,¹⁹ and this was followed by a study of the absorption spectrum of monodeuterobenzene, which absorbs in the same region as benzene.²⁰ The far ultraviolet absorption spectra and ionisation potentials of C₆H₆ and C₆D₆ were examined by Price and Wood,²¹ and an attempt to give a coherent interpretation of the absorption systems of benzene vapour in this region was made by Nordheim, Spomer and Teller.²² The work of Price and Wood

has been re-examined by Wilkinson²³ using a 21-ft grating instrument and the increased dispersion facilitated the identification of many new weak bands. The variation of the benzene spectrum with temperature was re-examined by Kistiakowsky and Solomon,²⁴ and from the Boltzmann distribution function two fundamental frequencies of the normal state were deduced. A detailed study of the variation in intensity of the main band of three progressions with temperature was included in the study of Radle and Beck.¹⁸ The effect of high pressure was examined by Robertson, Babb and Matsen²⁵ and the benzene absorption bands were found to broaden asymmetrically, and to shift to longer wavelengths on increasing the partial pressure of a foreign gas. In another study²⁶ the absorption spectra was examined in the presence of diluent gases over a wide range of densities, and the red spectral shifts were found to be linear functions of the density.

Halogen substituted benzenes: The absorption spectrum of monochlorobenzene found in the region 2400 Å–2700 Å has been analysed by Sponer and Wollman.²⁷ Detailed interpretations of the spectra of *o*- and *p*-dichlorobenzene vapours which consist of 300 bands in the region 2400 Å–2900 Å, and 400 bands in the region 2400 Å–2950 Å, respectively, are described by Anno and Matubara.²⁸ The absorption spectrum of 1,2,4,5-tetrachlorobenzene vapour was photographed by Matubara and Anno²⁹ and was found to consist of 150 bands in the region 2650 Å–3040 Å, with continuous absorption below 2500 Å.

A re-investigation of fluorobenzene by Wollman³⁰ showed that the spectrum was similar to that of chlorobenzene and was composed of over 280 bands in the region 2380 Å–2750 Å. Cooper³¹ examined the spectrum of *p*-difluorobenzene over a wide range of temperatures and identified over 600 bands between 2350 Å and 2900 Å. The observed wavelength shifts of the O₂ bands in the near ultraviolet spectra of a number of fluorinated benzenes were described by Sponer³² who in conjunction with Rao³³ also reported data for the spectrum of 1,2,4-trifluorobenzene vapour.

Bands in the spectrum of *o*-fluorochlorobenzene were identified by Krishnamachari³⁴ who later reported results on the spectra of *o*-, *m*- and *p*-fluorobromobenzenes.³⁵ Another report on the *m*-isomer of the last compound has been made by Tintea *et al.*³⁶

Alkyl substituted benzenes: An absorption spectrum composed of over 200 bands in the region 2390 Å–2760 Å was observed by Ginsberg *et al.*³⁷ in a study of toluene vapour. The absorption behaviour of *o*- and *m*-chlorotoluenes was investigated by Swamy.³⁸

The absorption spectra of the dimethylbenzenes have been studied by Cooper and co-authors^{39,40} and Singh.⁴¹ The spectra between 2350 Å and 2850 Å were photographed and analysed. The *m*-isomer has the least number of bands and the most diffuse appearance, while the *o*-isomer consists of many very sharp bands.

In the re-examination of aniline, over 500 lines were found in the region 2500 Å–3000 Å.⁴² The presence of a nitro group moves the absorption region to longer wavelengths, so that the bands of *o*- and *m*-nitroaniline were found in the regions 2700 Å–3600 Å and 2550 Å–3250 Å, respectively.⁴³ The absorption bands of the toluidines have been photographed and discussed.⁴⁴

The spectrum of benzonitrile vapour was examined by Hirt and Howe⁴⁵ and found to resemble closely the spectra of other mono-substituted benzenes. The spectrum of toluonitrile vapour has been re-investigated and re-classified by Sen.⁴⁶

Oxy-substituted benzenes: The absorption spectrum of phenol has been shown⁴⁷ to be composed of over 330 bands covering the region 2490 Å–2830 Å. The absorption region for the nitrophenols was found at longer wavelengths, and the wavelength of maximum absorption was found to decrease in the order of *o*- > *m*- > *p*-isomer.⁴⁸

The *p*-cresol spectrum was found by Imanishi *et al.*⁴⁹ to consist of over 170 bands in the 2480 Å–2945 Å region. The thiocresols have been studied by Bapat^{50,51} and bands are reported for the three isomers within the range 2590 Å–2920 Å. The excited state frequencies of these compounds were compared with those of thirteen other disubstituted benzenes.

Benzaldehyde vapour absorption has been investigated by Imanishi, who reports bands in the region 2480 Å–2970 Å,⁵² and a large number of narrow bands in the region 3163 Å–3747 Å.⁴⁹ Weak vapour absorption in the regions 3060 Å–3500 Å and 3270 Å–3510 Å were also found⁴⁹ using acetophenone and benzophenone, respectively.

Dual regions of absorption bands have also been reported for the *o*- and *m*-hydroxybenzaldehydes by Achyuta and Rao.⁵³ The *p*-isomer exhibited bands in only one region, namely 2915 Å–2660 Å. Patel⁵⁴ has demonstrated that the effect of chloro-substitution in benzaldehyde is to shift the long wave benzenoid system to longer wavelengths, the magnitude of the shift being in the order of *o*- > *m*- > *p*-isomer.

The vapour absorption of benzoquinone has been examined by Singh, who records about 130 bands between 2254 Å and 3084 Å⁵⁵ and an even larger number of sharp bands in the region 4100 Å–5000 Å.⁵⁶ A vibrational analysis of the absorption spectrum in the region 4080 Å–5100 Å has recently been published by Anno and Sado.⁵⁷

Heterocyclic Compounds: The absorption spectrum of pyridine in the region 2500 Å–3000 Å has been re-examined by Sponer and Stucklen, who made a vibrational analysis of the 160 bands observed.⁵⁸ Another 60 bands in the region 3000 Å–3300 Å were fitted into a vibrational scheme by Reid,⁵⁹ but these bands were later shown by Brealey⁶⁰ to be caused by a trace of impurity (pyrazine) in the pyridine used in the previous studies. A vibrational analysis of the absorption spectrum of pyrazine vapour has been proposed by Ito *et al.*⁶¹ and another proposed assignment has been published by Hirt,⁶² who included a study of chloropyrazine. The spectrum of pyridine-*N*-oxide was found to be similar in many respects to the spectrum of pyridine, except that the 250 bands are located at longer wavelengths.⁶³

Absorption studies of the three isomeric picolines have been made by Sponer and Rush.^{64,65} All three compounds showed a few diffuse bands in the region 2450 Å–2700 Å, and narrow, relatively sharp bands in the region between 2700 Å and 3000 Å.

The wave numbers of 112 absorption bands of pyrimidine vapour in the 2700 Å–3300 Å region have been determined by Uber.⁶⁶ The absorption spectra of the diazines have also been studied by Halverson and Hirt,⁶⁷ and similar studies were extended by Mason^{68,69} to include sym-triazine, 3,5,6-trimethyl-1,2,4-triazine, *m*-tetrazine and sym-tetrazine. The spectrum of pyrrolidine vapour between 2300 Å and 2800 Å was studied over a range of temperatures by Santhamma,⁷⁰ and 61 broad and diffuse bands were measured.

Condensed ring compounds: The vapour absorption spectra of light and heavy naphthalenes found in the region 2500 Å–2900 Å have been recorded by Sponer

and Cooper,⁷¹ and the spectroscopic behaviour of a large number of methyl derivatives of naphthalene were measured by Wolf.⁷² The spectra of the derivatives were found to be very similar to that of the parent compound. The spectra reported by Deb⁷³ for 1-chloro- and 1-bromonaphthalene also fall within the same wavelength region.

Vibrational assignments were made by Bapat⁷⁴ for the 60 bands in the region 2500 Å–2800 Å found in the absorption spectrum of tetrahydronaphthalene.

The absorption spectra of the vapours of anthraquinone and a number of derivatives are included in the recent work of Borisevich and Gruzinskii.⁷⁵

Miscellaneous compounds: The ultraviolet absorption spectrum of formaldehyde⁷⁶ has been re-investigated, and a complete analysis of the acetaldehyde spectrum reported.⁷⁷ Vibrational assignments have also been made for the bands observed in the spectrum of cyclopentanone,⁷⁸ and spectra have been recorded for crotonaldehyde,⁷⁹ the three isomeric methylphenetoles,⁸⁰ *m*- and *p*-methylanisoles,⁸¹ *o*- and *p*-chlorophenetoles,⁸² and tropolone.⁸³

The absorption spectrum of acetone vapour has been well known for years,⁸⁴ but quite recently a study has been made of the spectra of twenty alkyl-, cyclo-alkyl- and chloro-substituted ketones.⁸⁵ This latter study was made in order to compare the influence of the positive inductive effect of the methyl with the negative inductive effect of the chloro group.

Vibrational analysis of the spectrum obtained from acetylene⁸⁶ and diacetylene^{87,88} have been made, and a spectrum for dicyanoacetylene⁸⁹ has been reported for the first time. The intense absorption of 1,3-cyclohexadiene vapour in the ultraviolet region has been examined by Henri and Pickett,⁹⁰ and the behaviour of the vapours of the three isomers of phenylenediamine has been studied by Sado and Anno.⁹¹ The ester, *n*-butyl benzoate was included in the studies of Deb⁹² who examined the influence of the physical state on the ultraviolet absorption spectra of different compounds.

DISCUSSION

From the preceding review it can be seen that there is a good background of spectral data available which could be used in chemical analysis through adoption of a vapour phase absorption technique. While the spectrographs used for analysis would probably not have the same degree of dispersion as those used in the purely "spectroscopic" studies, identification of a species from its spectrum should be readily achieved. There is the disadvantage that many species absorb in the same wavelength region, and since band spectra are more complex than atomic line spectra, identification of the components of a mixture could become difficult. There is the further disadvantage that relatively high temperatures may be needed to convert some compounds into the vapour phase. On the credit side one may list the high sensitivity of the technique; the characteristic nature of molecular spectra; and the absence of "solvent" effects. In addition, unlike the emission technique previously discussed (Part I), a leak of air into the evacuated cell does not influence the spectrum and does not produce an interfering spectrum.

However, as analysis based on a gaseous phase is usually not so convenient as a method involving liquids, the practicability of vapour phase absorption technique has been examined experimentally. The results of this study will be reported in Part III of this series.

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Zusammenfassung—Die Molekularabsorption von Gasen und Dämpfen wird zusammenfassend behandelt in besonderem Hinblick auf Spektren organischer Molekül.

Résumé—Les auteurs passent en revue les méthodes d'absorption électronique moléculaire des gaz et des vapeurs en insistant particulièrement sur les spectres obtenus avec des molécules organiques.

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ANALYSIS OF GASES AND VAPOURS BY SPECTROSCOPIC TECHNIQUES—III*

APPLICATIONS OF ELECTRONIC ABSORPTION SPECTRA

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Summary—Absorption of ultraviolet radiations by the vapours of organic solvents is proposed as an alternative method of identifying the composition of small volumes of volatile liquids. The limitations of the method are discussed.

IN chemical analysis, absorption spectroscopy has become a major tool but the established techniques almost invariably involve the use of the liquid phase. Absorption by vapours does not appear to have been used in analysis. Accordingly, the possibilities of this technique were examined and were discussed in Part II of this series. Experiments on some organic vapours have now been carried out to test the usefulness of this technique and the results are reported in this paper.

EXPERIMENTAL

Apparatus and reagents

Continuous radiation from a hydrogen lamp was passed through low pressures of organic vapour contained in an absorption cell 15 cm long, 2 cm in diameter and fitted with quartz windows. A small sample container was attached to the cell by means of a ground-glass joint, and the cell was evacuated through a side-arm tap.

Small volumes of liquid (0.01 to 0.20 ml) of Analytical Grade purity were measured into the detachable sample container by means of an Agla Microsyringe and were frozen by immersion of the side-arm in a liquid nitrogen trap. The cell was then evacuated by means of an oil diffusion pump. The cell and side-arm were finally immersed in a water bath fitted with windows, and the vapour pressure in the sealed cell was adjusted by varying the temperature of the water bath.

Measurement of absorption spectra

The absorption spectrum of the vapour was photographed using a Hilger Medium Quartz Spectrograph. The source of continuous radiation used was the hydrogen discharge lamp from a Hilger Uvispek Spectrophotometer and photographs were taken on Ilford N30 plates using a slit width of 0.03 mm. An exposure time of 5 min was found to be satisfactory. The organic vapours examined included benzene, toluene, *o*-, *m*- and *p*-xylenes, benzaldehyde, aniline, ethylbenzene, pyridine and nitrobenzene.

Measurement of absorbance of benzene at 253 m μ

The absorbance of benzene vapour evaporated from benzene-hexane mixtures was measured by removing the lamp housing cover from the Uvispek Spectrophotometer, placing the absorption cell between the entrance slit and focussing the reflecting mirror on the hydrogen lamp. The check (or 100% transmission) adjustment was made using an empty cell in the light path. Known volumes of benzene-hexane mixtures were frozen in the side tube and later allowed to evaporate into the evacuated cell. The absorbance of radiation of wavelength 253 m μ by the vapour was then measured as in normal absorption studies.

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RESULTS

Absorption spectra

From the varied volumes of sample taken, the temperature of the bath and the behaviour of binary mixtures, a list of detectable limits of concentration was compiled and these are recorded in Table I.

TABLE I.—LIMITS OF DETECTION OF ORGANIC SOLVENTS

Solvent	Min. vapour pressure to give spectrum, mm of Hg*	Min. vol. of solvent giving min. vap. press. on evaporation, (50-ml cell) μ l.	Lowest detectable % in binary mixtures at different temperatures		
			20°	40°	60°
Benzene	0.5	0.15	1	0.3	0.2
Benzaldehyde	0.5	0.15	100	25	6
<i>p</i> -Xylene	0.5	0.15	10	3	2
Aniline	0.5	0.15	50	25	10
Pyridine	1	0.3	10	3	1
Toluene	1	0.3	5	2	1
Nitrobenzene†	2	0.6	—	—	80
<i>o</i> -Xylene	3	0.9	75	20	10
<i>m</i> -Xylene	3	0.9	60	20	10
Ethylbenzene	6	1.8	90	20	10

* Above a pressure of 20 mm of Hg many bands tend to broaden into a continuum, hence it is desirable to adjust the temperature to give a vapour pressure of 2–20 mm for the desired species.

† Yields a continuum only.

The photographed spectra were also used to predict the possibility of identifying one component in the presence of a second vapour and the results are recorded in Table II.

TABLE II.—IDENTIFIABLE COMPONENTS OF BINARY MIXTURES OF AROMATIC SOLVENTS (Visual comparison of spectra)

Identifiable component	Diluent solvent*
Benzene	<i>o</i> -, <i>m</i> - or <i>p</i> -Xylene, ethylbenzene, benzaldehyde, aniline, nitrobenzene
Toluene	Benzaldehyde, aniline, nitrobenzene
Pyridine	Benzene, toluene, xylenes, aniline ethylbenzene, nitrobenzene
<i>o</i> -, <i>m</i> - or <i>p</i> -Xylene	Benzene, aniline, nitrobenzene
Benzaldehyde	Benzene, toluene, xylenes, ethylbenzene
Aniline	Benzene, toluene, xylenes, ethylbenzene pyridine, nitrobenzene
Ethylbenzene	Benzene, benzaldehyde, aniline, nitrobenzene

* A third solvent may also be present if it does not absorb in this region of the ultraviolet (e.g. aliphatics like hexane) or if insufficient vapour is present to give a spectrum (nitrobenzene below 50°).

Absorbance of benzene

Using the 15-cm cell (volume \sim 50 ml) and 0.20-ml samples, the optical density

readings were found to increase by approximately 0.1 unit for every 1% increase in benzene content in the mixture. The response varied greatly with the size of sample taken. This is to be expected, since the saturation of the cell with vapour causes a variation in the composition of the liquid phase in equilibrium with the vapour. The smaller the sample, the more marked is the variation in composition as the benzene evaporates; and accordingly the benzene vapour pressure at equilibrium cannot be calculated simply in terms of the composition of the mixture initially admitted to the cell. Correlation of the results using different sample volumes was achieved by calculating the probable value of the equilibrium pressure in each case and plotting optical density *versus* partial vapour pressure. As would be expected from theory, the relationship between absorbance and pressure was linear in the low pressure range examined (< 5 mm of Hg). The precision of the measurements, however, was poor. This can be attributed, *inter alia*, to variations in vapour pressure with temperature, errors in measuring small volumes and losses during introduction of the sample to the cell.

DISCUSSION

It can be observed from Table I that a detectable spectrum can be obtained using vapour absorption by evaporating less than 1 microlitre of solvent. Thus the technique is suitable for identifying very small volumes of pure organic solvent, but in order to achieve a suitable vapour pressure in the absorption cell, the sample and cell may have to be heated.

Since the absorption bands tend to broaden on increasing the vapour pressure and on heating the vapour, the optimum pressures observed in this study were found within the range of from 2 to 20 mm of Hg, and temperatures above 80° were not used.

In binary mixtures, it is still desirable to maintain the partial pressure of the desired component within this pressure range. The vapour pressure of a component in the mixture will be the vapour pressure of the pure component at the ambient temperature, multiplied by the molar fractional volume of the component in the liquid phase at equilibrium. In Table I, an indication is given of the influence of this molar fraction term, for in the final column values are quoted for the limit of detection (in %) of a solvent at different temperatures. It can be seen that at a given temperature (*e.g.*, 20°) the vapour pressure of some pure solvents is so low that any dilution reduces its partial pressure to a value below that detectable by the technique used. In other cases, the vapour pressure of pure solvent is sufficiently high to permit marked dilution of the liquid phase before the lower vapour pressure limit for an absorption spectrum is reached.

A second factor has to be considered if small volumes of sample or very dilute solvent mixtures are used. In these cases it is possible for all of a particular component to evaporate into the cell and still not reach the partial pressure calculated in terms of the molar fraction present in the original liquid. Under these conditions the size of sample should be increased.

The identification of a species in a mixture is complicated by the following facts: (a) the spectra of many benzenoid compounds overlap; (b) the bands of many species broaden readily into continua; and (c) chemical interaction between components is possible. In Table II identifications that have been achieved are recorded.

In making these identifications, the components of a mixed spectrum were identified simply by comparison with the spectra obtained with the pure substances. These standard spectra were sufficiently characteristic to permit such an approach. The identification of a species in a multicomponent system is feasible, but all other components must preferably absorb in a different region of the wavelength scale. Table II is not intended to be exhaustive, and could be extended by including many of the compounds recorded in the review which forms Part II of this series.

The quantitative studies indicate that analysis based on the vapour phase is possible but precision would need to be improved by stricter temperature control, and greater efforts would have to be made to avoid losses of vapour during sample introduction, if results of reasonable reliability are to be achieved. However, quantitative analysis based on vapour absorption does not offer any practical advantage unless the volume of liquid sample present is too small for use in a liquid micro cell or unless the liquid is extremely volatile.

The advantages that could be claimed for this vapour absorption technique are (1) that it is possible to identify the nature of a very small volume of an organic solvent (providing that it absorbs in the ultraviolet or visible range), and (2) that the time required to obtain a photographic spectrum can be much less than the time required to plot an absorption spectrum using a non-recording spectrophotometer. The technique could also prove useful for the identification of small amounts of volatile aromatic compounds present in aliphatic solvents.

However, even these advantages cannot compete in most cases with the facility of analysis now offered by the use of gas chromatography or recording spectrophotometers.

CONCLUSIONS

Vapour phase absorption spectroscopy can be proposed as an alternative method of identification and analysis of small volumes of organic solvents and within a limited range of applications may prove quite useful.

As indicated in Part II of this series, there is a good background of spectral data available, which could be utilised in development of this technique.

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Zusammenfassung—Die UV-Absorption von Dämpfen organischer Solventien wird als eine Methode zur Identifizierung kleiner Volume flüchtiger Substanzen empfohlen. Anwendungsmöglichkeiten der Methode werden diskutiert.

Résumé—Les auteurs proposent l'absorption des radiations ultraviolettes par les vapeurs de solvants organiques comme méthode d'identification de la composition de faibles volumes de liquides volatiles. Les limites de cette méthode sont discutées.

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH DIDODECYLDITHIO-OXAMIDE

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Summary—Didodecyldithio-oxamide reacts with palladium in strong hydrochloric acid solutions to form a yellow water-insoluble complex which can be extracted into chloroform. Optimum conditions for the use of the reagent have been studied. Tolerance limits for other platinum group elements and selected base metals have been determined. The procedure has been successfully applied to the determination of palladium in the presence of high concentrations of diverse ions. The sensitivity of the reaction is 0.005 $\mu\text{g}/\text{cm}^2$.

INTRODUCTION

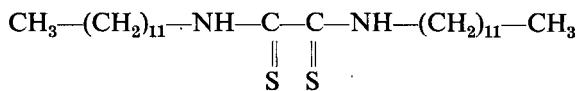
IN recent investigations of the colour reactions of platinum and palladium with a number of symmetrically and unsymmetrically substituted dithio-oxamides,¹ didodecyldithio-oxamide was selected for further study as a reagent for palladium. Indications were that large quantities of platinum relative to palladium could be tolerated. Subsequent investigation of this reagent has shown that in addition to its high tolerance for platinum, much rhodium and ruthenium may be present, as well as high concentrations of base metals commonly associated with palladium.

There is no shortage of sensitive colour reactions for palladium. Many reactions, too numerous to mention, have been reported which exhibit greater or less selectivity. Excellent review articles^{2,3} are available which discuss a variety of these methods. Reagents containing the nitrosophenylamino group, and certain dioximes, have probably found the most widespread use as palladium reagents, the latter type being superior in many respects. With the dioximes, such as α -furildioxime, palladium may be determined in the presence of relatively large concentrations of the other platinum metals. The reaction is carried out in mineral acid medium; close control of pH is not necessary and the palladium complex is readily extractable.

Conditions for colour development in the case of reagents such as *p*-nitrosodimethylaniline and *p*-nitrosodiphenylamine have to be closely controlled. These reagents are, however, among the most sensitive known for palladium.

The present paper describes a colour reaction which is both highly sensitive and not subject to close control of conditions of colour development. Unusually high concentrations of platinum, rhodium, ruthenium, cobalt, nickel, and chromium may be present. At the same time, quantities of iridium, osmium, gold, iron and copper of the order of 1 milligram may be tolerated. The complex is formed in solutions which are approximately 6.8*M* or more in hydrochloric acid. The water-insoluble complex is extracted with chloroform.

Didodecyldithio-oxamide has the following structure:



This compound has been reported to react with cobalt, nickel and copper in alkaline solution.⁴ The complexes formed are water-insoluble and are not extractable by common water-immiscible solvents. With palladium, a bright yellow, water-insoluble complex is formed in the presence of high concentrations of hydrochloric acid, and this may be extracted with chloroform, carbon tetrachloride and most common organic solvents.

EXPERIMENTAL

Apparatus

Spectrophotometers: Beckman spectrophotometers, Model DK-2A and Model DU, with matched 1-cm silica cells, were used for all absorbance measurements.

Separatory funnels: Globe separatory funnels of 125-ml volume were used. The stems were shortened to approximately 1 cm.

Reagents

Standard palladium solution: A standard palladium solution was prepared by dissolving 1 g of palladium^{II} chloride in 500 ml of distilled water containing sufficient hydrochloric acid to give a final solution which was 1M with respect to the acid. This solution was standardised by the dimethylglyoxime gravimetric method. The solution contained 1.15 mg of palladium per ml.

Reagent solutions: The reagent is insoluble in water, only sparingly soluble in ethyl alcohol, but readily soluble in acetone. Three solutions of didodecylidithio-oxamide were prepared which contained 0.5 mg per ml., 2.0 mg per ml, and 5.0 mg per ml, respectively, of the reagent in acetone.

Solutions of diverse ions: Stock solutions containing approximately 1 mg per ml of the ions were prepared from analytical-grade chlorides or nitrates of the metals, except for osmium which was prepared from potassium osmate.

Description of the palladium complex

Colour: Didodecylidithio-oxamide forms a yellow, water-insoluble complex with palladium in the presence of high concentrations of hydrochloric acid. The complex can be extracted into chloroform. Fig. 1 shows absorbance curves for the palladium complex (4.6 ppm) and the reagent ($4.4 \times 10^{-3}M$). The absorbance of the complex was measured against a reagent blank; that of the reagent against a distilled water blank. The palladium complex has an absorbance maximum at 450 m μ .

Effect of hydrochloric acid concentration: The concentration of hydrochloric acid was varied from 0.77M to 9.2M by the addition of 1, 3, 6, 9, and 12M hydrochloric acid to determine the optimum

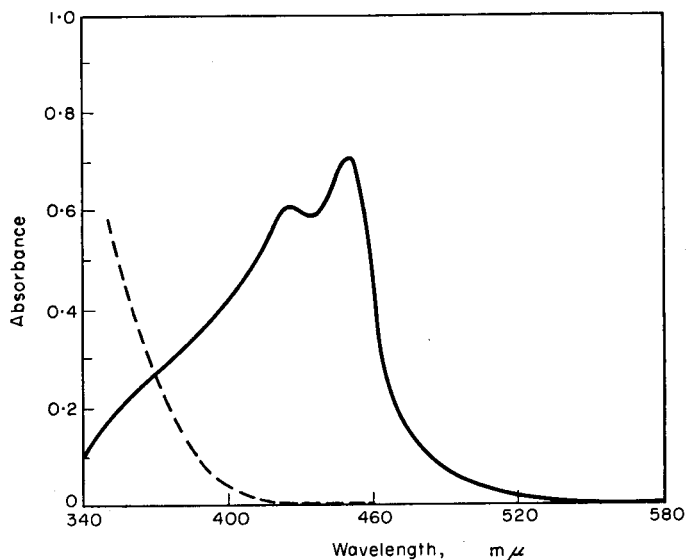


FIG 1.—Absorbance curves for the palladium complex (4.6 ppm) and reagent ($4.4 \times 10^{-3}M$).
 - - - - - Reagent
 ————— Palladium.

concentration for complex formation. Each sample contained 4.6 ppm of palladium, 10 ml of the acid, and 2 ml of the 2 mg/ml reagent solution. The samples were extracted with two 5-ml portions of chloroform, the extracts were diluted to 25 ml with chloroform, and the absorbances were measured. The results of this experiment are shown in Fig. 2. The absorbance of the complex begins to level off above a hydrochloric acid concentration in the aqueous phase of 6.8M. The gain in sensitivity above

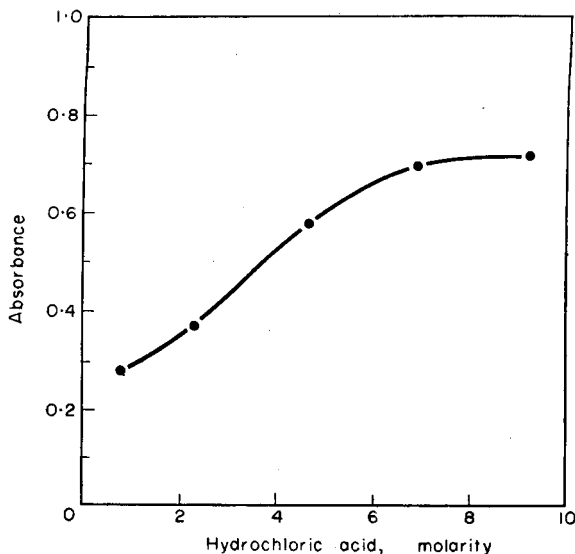


FIG. 2.—Effect of the molarity of hydrochloric acid on the palladium complex.

this acid concentration is so slight that reproducible results are obtained without rigorous control of the acid concentration. In our work, 10 ml of concentrated hydrochloric acid (12M) was used in an approximate volume of 16 ml. This corresponds to an acid concentration in the aqueous phase of about 7.5M.

Rate of colour formation: Although the yellow colour of the palladium complex formed immediately upon the addition of the reagent solution, maximum absorbance was not reached until the colour was allowed to develop for 15 min. To determine the optimum time for colour formation, samples were prepared containing 4.6 ppm of palladium, 10 ml of concentrated hydrochloric acid, and 2 ml of the 2 mg/ml reagent solution. The samples were allowed to develop for varying lengths of time after which they were extracted with two 5-ml portions of chloroform and diluted to 25 ml with chloroform. The absorbances of the samples were measured at 450 m μ against a reagent blank. Table I contains the results of this experiment.

Stability of colour: In order to check the stability of the extracted complex on standing, the absorbance of a sample was measured at intervals of 0.5 hr, 3 hr, 24 hr, and 48 hr. There was no change in absorbance over this period of time. Longer periods were not investigated.

Extraction of the complex: The number of chloroform extractions necessary for complete removal of the complex was determined by the following experiment: 4 samples were prepared which contained 3.68 ppm of palladium, 10 ml of concentrated hydrochloric acid, and 2 ml of the 2 mg/ml reagent solution. Fifteen min were allowed for maximum colour formation. These samples were

TABLE I.—RATE OF COLOUR FORMATION

Time, min	Absorbance at 450 m μ
immediately	0.828
5	0.830
10	0.835
15	0.842
30	0.842
60	0.843

extracted with one, two, three and four 5-ml portions of chloroform, respectively. The results, as shown in Table II, indicate that the complex is completely extracted by the use of two 5-ml portions of chloroform.

TABLE II.—EXTRACTION OF COMPLEX

Number of 5-ml chloroform extractions	Absorbance at 450 m μ
1	0.632
2	0.675
3	0.678
4	0.678

Effect of reagent concentration: Maximum colour formation is attained as long as there is a four-fold or greater excess of the reagent over palladium. Reagent concentrations considerably larger than the theoretical are used in actual practice, for reasons which will be discussed later.

Adherence to Beer's law: The palladium complex obeys Beer's law over the concentration range investigated, 0.46 to 4.6 ppm.

Optimum concentration range: According to Sandell⁵ the most favourable range for making absorbance measurements is from 0.2 to 0.7 absorbance unit. This corresponds to concentrations of palladium ranging from 1.2 to 3.9 ppm.

Sensitivity: The sensitivity of the colour reaction, based upon the Sandell notation,⁶ is 0.005 μg per cm².

Effect of diverse ions: In order to determine the effect of selected ions on the colour reaction, solutions containing approximately 1 mg per ml of the foreign ions were prepared and added individually to solutions containing 115 μg of palladium, 10 ml of concentrated hydrochloric acid, and 5 ml of a 5 mg/ml reagent solution. The samples were extracted with two 5-ml portions of chloroform and diluted to 25 ml with chloroform, and the absorbances were determined at 450 m μ . An interference was arbitrarily chosen as that concentration of the ion which produced an error of 3% or more in the amount of palladium found. The results of this experiment are shown in Table III. In the presence of approximately 1 ml of 1M sodium sulphite, slightly larger concentrations of gold, osmium, and iron could be tolerated. However, if platinum is present, sodium sulphite cannot be used, since the platinum will be reduced to the reactive bivalent state which will react with the reagent.

TABLE III.—EFFECT OF DIVERSE IONS (115 μg of palladium)

Ion added	Amount added, mg	Palladium found, μg	% error
Pt ^{IV}	18.6	120	4.3
Ir ^{IV}	1.3	119	3.5
Rh ^{III}	14.3	116	0.9
Ru ^{III}	14.7	116	0.9
Os ^{VI}	0.2	121	5.2
Os ^{VIa}	0.3	119	3.5
Co ^{II}	10.0	112	2.6
Ni ^{II}	10.0	115	0
Cu ^{II}	1.0	119	3.5
Cr ^{III}	6.0	113	1.7
Fe ^{III}	1.1	118	2.6
Fe ^{IIIa}	2.5	119	3.5
Au ^{III}	0.6	118	2.6
Au ^{IIIa}	3.0	118	2.6
Nitrate	5.0	116	0.9
Sulphate	5.0	116	0.9

^a These samples contained approximately 1 ml of 1M sodium sulphite.

Fourteen mg of rhodium or ruthenium produce practically no interference with the palladium complex. This indicates that still higher concentrations of these ions can be tolerated with the quantity of reagent solution used. The low palladium values for large amounts of cobalt, nickel and chromium indicate that these ions consume so much of the reagent that there is an insufficient quantity for the palladium. By increasing the quantity of reagent solution, larger quantities of these ions probably can be tolerated. Copper, on the other hand, appears to react with the reagent to produce a complex which is extracted to a certain extent, since this element begins to interfere when there is approximately 1 mg present. The outstanding feature of this method is without a doubt the large concentration of platinum which can be tolerated.

Recommended procedure and analysis of synthetic samples

Recommended procedure: Introduce an aliquot of the sample (5 ml or less) which contains 30 to 100 μg of palladium into a 125-ml short-stem separatory funnel. Add 10 ml of concentrated hydrochloric acid and 5 ml of the 5 mg/ml reagent solution. Allow to stand for 15 min and extract with two 5-ml portions of chloroform which has been equilibrated with 6M hydrochloric acid. The use of the equilibrated chloroform gives slightly better results, possibly because it reduces the passage of highly coloured chloro-complexes into the non-aqueous phase. Dilute the sample to 25 ml with chloroform and measure the absorbance of the sample at 450 $m\mu$. Determine the palladium content from a calibration curve. If sodium sulphite is added to increase the tolerance for osmium, iron and gold, it should be added before the addition of the acid. As was mentioned earlier, if platinum is present, sodium sulphite cannot be used.

Analysis of synthetic samples: The procedure outlined above was applied to a series of synthetic samples containing varying quantities of the other platinum metals and selected base metals along with palladium. Since the volumes of these solutions were relatively large (approximately 25 ml), the samples were concentrated by heating on a hot plate to a volume of about 1 ml. The samples were washed into separatory funnels with two 2-ml portions of distilled water and analysed by the recommended procedure. The results are given in Table IV.

TABLE IV.—ANALYSIS OF SYNTHETIC SAMPLES

Sample	Palladium added, μg	Palladium found, μg	Ions added, mg
1	115	124	Pt ^{IV} , 13.8 Ru ^{III} , 4.9 Rh ^{III} , 5.3 Ir ^{IV} , 1.8 Os ^{VI} , 0.3
2	115	122	Same as 1
3	115	114	Pt ^{IV} , 13.8 Ru ^{III} , 4.9 Rh ^{III} , 5.3
4	57.5	59.2	Same as 3
5	115	118	Pt ^{IV} , 13.8 Ru ^{III} , 4.9 Rh ^{III} , 5.3 Ni ^{II} , 4.0 Co ^{II} , 5.0 Fe ^{III} , 1.0 Cu ^{II} , 1.0
6	115	110	Pt ^{IV} , 20.7 Ru ^{III} , 4.9 Rh ^{III} , 5.3 Ir ^{IV} , 0.9
7	57.5	62.3	Same as 6

CONCLUSIONS

Didodecyldithio-oxamide has been shown to react rapidly in strong hydrochloric acid solutions with palladium to give a water-insoluble complex which may be extracted with chloroform. Conditions for the development of colour need not be rigorously controlled. The reaction has a sensitivity which compares favourably with other palladium reagents. The high tolerance for other platinum metals and certain base metals should result in the proposed procedure's extensive use as a method for palladium.

Acknowledgement—Financial assistance from the National Science Foundation in the form of a research grant to W. D. J. is gratefully acknowledged.

Zusammenfassung—Didodecyldithiooxamid reagiert mit Palladium in stark salzsaurem Medium zu einem gelben, wasserunlöslichen Komplex, der in Chloroform ausgezogen werden kann. Die optimalen Bedingungen wurden erarbeitet. Die Störungsgrenzen für andere Platin- und einige weitere Metalle wurden ermittelt. Die Methode wurde auf die Bestimmung von Palladium in Gegenwart hoher Konzentrationen verschiedener, anderer Ionen angewendet. Die Empfindlichkeit der Reaktion ist $0.005 \mu\text{g}/\text{cm}^2$.

Résumé—Le didodecyldithio-oxamide réagit avec le palladium en milieu acide chlorhydrique concentré pour former un complexe jaune, insoluble dans l'eau, qui peut être extrait par le chloroforme. Les meilleures conditions d'utilisation du réactif ont été étudiées. Les limites de tolérance pour les autres éléments du groupe du platine et pour des métaux choisis ont été déterminées. La méthode a été appliquée avec succès au dosage du palladium en présence de grandes concentrations de divers ions. La sensibilité de la réaction est $0,005 \mu\text{g}/\text{cm}^2$.

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PHOTOMETRIC TITRATIONS—VI*

THE DETERMINATION OF SUBMICROGRAM QUANTITIES OF CALCIUM AND MAGNESIUM

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Summary—Three different types of end-point detection in photometric titrations are defined, and their relation to the selectivity problem is discussed. Some of the principles are applied to the determination of calcium and magnesium in quantities down to a few tenths or hundredths of a microgram. Excess dye (Calmagite) is added to the solution containing calcium and magnesium buffered to pH 10, so that both metals are complexed. Then the titration is performed with EDTA. A titration curve is obtained with two end-points, thus allowing the evaluation of each metal present. Changes effected in a photometric titrator previously described are discussed, as well as their relation to increased sensitivity and precision.

END-POINT detection in photometric titrations involves both equilibrium and optical (absorbance) properties of the system. When the discussion is restricted to titrations based on the formation of a 1:1 complex, the following mechanisms of indication can be differentiated:

(1) *Self-indication*: A system is said to exhibit self-indication when a metal ion initially present in a complex (B-complex) is progressively transferred into the titration complex (T-complex) of differing absorbance upon addition of titrant. The conditions which must be satisfied in order that a titration might be possible are: the stability constant of the T-complex must be sufficiently higher than that of the B-complex to allow the transfer to the metal ion to be essentially complete; the stability of the T-complex and also of the B-complex, when the latter is an optically significant variable, must be high enough to ensure that neither is appreciably dissociated; the absorptivities of all species involved must be such that the slopes of the two straight branches of the titration curve are sufficiently different to permit a well-defined intersection to be obtained upon extrapolation.

Example 1: An example of a self-indicating system is the EDTA titration of copper at pH 5.¹ Copper is initially present as the weakly absorbing aquo-complex (B-complex) and during the titration the more stable and more absorbing EDTA complex (T-complex) is formed. Both complex formers, water and EDTA, are colourless and hence do not need to be taken into account optically. The type of curve obtained is shown as curve I in Fig. 1.

Example 2: Copper can also be titrated with EDTA at pH 10 in ammoniacal solution. The highly coloured tetrammine complex is the B-complex, and during the titration the less absorbing EDTA complex (T-complex) is formed. Again, the B- and T-complex formers do not need to be taken into account optically. The concentration of the B-complex former (ammonia), however, affects both the degree of dissociation of the B-complex and the ratio of the stability constants of the two complexes (effect of the β -factor). A curve of type II in Fig. 1 results from such a titration.

* Part IV, *Talanta*, 1962, 9, 76; Part V, *Talanta*, 1961, 8, 885.

(2) *Step-indication:* The term step-indication will be used to describe a system in which a complex forming indicator is employed to obtain a step-like change in absorbance when the end-point is approached. The following conditions must be satisfied: the stabilities of the T-complex and I-complex (indicator-complex) must be sufficient to prevent an unduly high degree of dissociation; the magnitude of the stability constants, for obvious reasons, must be in the order $K_B \ll K_I \ll K_T$, where

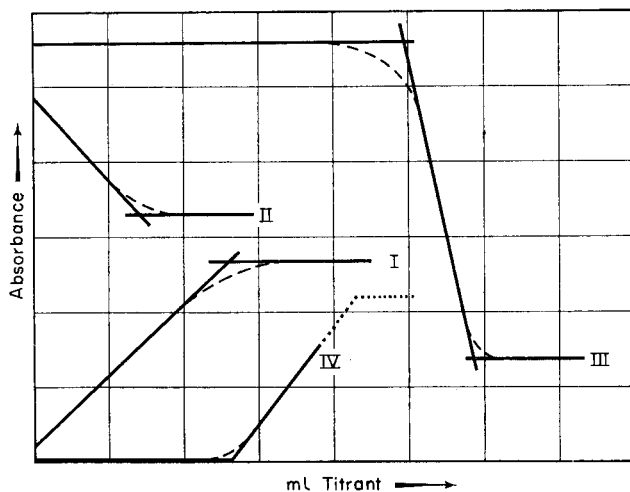


FIG. 1.—Titration curves obtained with various types of indication.

the subscripts refer to the appropriate complexes; the absorptivities of all species involved must be such that a well-defined intersection is obtained upon extrapolation.

Example 3: Step indication is exemplified by the EDTA titration of copper at pH 4 using PAN as indicator.² The type of curve obtained is represented by curve III in Fig. 1. The first horizontal portion of the titration curve results when copper is transferred from the aquo-complex (B-complex) to the EDTA complex (T-complex), neither of which absorbs at the wavelength selected. In contrast with the self-indicating system, this portion of the curve is not used for the extrapolation and hence need not be plotted in practice. The second portion, where an abrupt change in absorbance occurs, is obtained when copper is transferred from the I-complex to the T-complex. The third part results upon the addition of colourless titrant after the end-point has been reached.

It is important to note that a step-indicated system shows two intersection points, the second generally corresponding to the amount of metal determined. The difference between the two points is equivalent to the amount of indicator present.

(3) *Slope-indication:* The term slope-indication will be used to describe end-point location *via* a self-indicating system, the metal of which is titrated after the metal to be determined. Again, the T-complexes must be stronger than the corresponding B-complexes. The T-complexes and any optically significant B-complex must be strong enough to prevent any appreciable dissociation. In addition the condition

$$(K_T/K_B)_s \ll (K_T/K_B)_d$$

must be satisfied, *i.e.*, the ratio of the stability constants of the T- and B-complexes of

the self-indicating system (subscript "s") must be less than the ratio of the stability constants of the corresponding complexes of the metal to be determined (subscript "d"). These conditions ensure that the metal to be determined is complexed before the metal in the self-indicating system. The absorptivities of all species involved must be such that the slopes of the titration curve before and after the end-point differ sufficiently to permit a precise location of the end-point by extrapolation.

Example 4: One of the first systems involving slope-indication was studied by Underwood³ when he titrated bismuth with EDTA using copper as the so-called "photometric indicator".* The type of titration curve obtained is shown as curve IV in Fig. 1. The first horizontal part of the curve corresponds to the transfer of bismuth from the aquo- to the EDTA complex, neither of which absorbs. When all the bismuth is titrated, copper is complexed by the EDTA and the absorbance increases through the formation of the strongly absorbing Cu-EDTA complex. The titration may be stopped at any point of the inclined part of the curve when the number of points recorded suffices for the extrapolation of the straight line.

It may be mentioned that in the case where both bismuth and copper are to be determined, the titration may proceed along the dotted line to a second intersection indicating the end-point of the copper titration.³

In the titration of a metal which is present alone in a solution, the several methods of end-point detection, self-, step- and slope-indication, are equally satisfactory. However, when a metal is to be determined in the presence of others, the method of end-point detection has a very close bearing on the selectivity problem. The following examples will serve to elucidate the situation. Let it be required to determine copper in the presence of aluminium in acetic acid medium. The EDTA complex of copper is more stable than that of aluminium, and copper reacts with the indicator, PAN, whereas aluminium does not. It would seem at first glance that a selective titration of copper under these conditions is possible. However, only the sum of the two metals can be obtained,⁴ as will be apparent from the following considerations. Initially, the species present in the solution will be the aquo- (and/or acetato-) complexes of aluminium and copper, and a very small amount of the copper-PAN complex. Upon addition of EDTA the copper-EDTA complex will be formed first. If all the copper not blocked by the very stable PAN complex is titrated, EDTA will complex the more readily available aluminium. After all the aluminium is titrated, the copper will be taken from the indicator complex, and the end-point will occur when the sum of both metals is titrated. Hence, the stability of the indicator complex plays a decisive role. Thus the copper-PAN-EDTA system is used to indicate visually the end-point in the EDTA titration of many metals which do not form coloured compounds with PAN, and whose EDTA complexes are much less stable than that of copper, e.g., calcium.⁵

Although stability constant data for metal-PAN complexes are not available, it appears from all experimental evidence that copper forms one of the most, if not the most, stable PAN complex. Suppose that instead of employing PAN as indicator, it is used as the titrant; then copper will be complexed preferentially in the presence of other metals. Here, step-indication is replaced by self-indication, with a consequent

* The term *photometric indicator* chosen by Underwood is correct. However, it may be confused with the general expression, *indicator in a photometric titration*, which includes step-indication. In order to avoid this possibility the term *slope indicator* is proposed. While it is true that detection of any end-point in a photometric titration is based on slope changes, the new term will not cause confusion when defined as above.

increase in selectivity. The use of PAN as titrant will be the subject of a further paper in this series.

Another example pertinent to the problem of selectivity is the EDTA titration of calcium using Erio T as indicator. The low absorptivity and low stability of the calcium-Erio T complex makes detection of the end-point exceedingly difficult. Biedermann and Schwarzenbach⁶ pointed out that the addition of at least 5 mole % of magnesium makes possible a precise location of the end-point. However, only the sum of calcium plus magnesium is obtained, and to determine calcium the amount of magnesium added must be known exactly. (A more convenient approach, of course, is the addition of magnesium-EDTA complex). This is an example of step-indication with low selectivity. The selectivity can be increased by replacing step-indication by slope-indication. If any unknown amount of magnesium, and in addition an amount of Erio T is added more than equivalent to the magnesium, the situation is entirely changed. When EDTA is now added the stronger calcium complex will be formed first with only a slight change in absorbance. When all of the calcium is complexed, magnesium will be taken from the Erio T complex, this process being accompanied by a rather large change in absorbance. Thus the calcium end-point is obtained *via* the self-indicating system Mg-Erio T as the slope indicator. As in the case of example 4, only a few points of the Mg-Erio T portion of the titration curve are necessary to enable the determination of its slope. Although the determination of the magnesium present is entirely feasible here, it is irrelevant to the determination of calcium by the slope-indication method.

From this discussion, the significant difference between step- and slope-indication can readily be appreciated. In step-indication the *last* change in slopes is utilised, where the end-point for the titration of *both* metals occurs. In slope-indication the *first* change in slope, when the second metal starts to be titrated, is utilised, thus giving the end-point for the *first* metal only.

A practical application of the principles outlined above is the titration of magnesium in the presence of calcium using Erio T as the titrant. The calcium-Erio T complex is considerably weaker than that of the magnesium, and hence magnesium should complex first when Erio T is added as titrant. The progress of the titration can readily be followed photometrically.

When applying the theoretical considerations to practice, considerable difficulty is encountered because of the low storage stability of the dye. Unless special precautions are taken, a slight but steady drift in the galvanometer readings is observed, indicating decomposition of the dye. Hence, further experiments were performed with Calmagite. This dye, of similar constitution to Erio T,⁷ shows practically identical behaviour in complex formation and colour development, but has a superior storage stability. The stability constant of the magnesium complex⁷ is $10^{5.69}$, which, for titrations in very dilute solutions, is too low to allow a well-developed titration curve. That this is true can be seen from the curves in Fig. 2. The curvature is so great that it is practically impossible to determine the slope of the first, supposedly straight, part of the titration curve when working at $620\text{ m}\mu$, the wavelength at which the metallised and unmetallised dye show the greatest difference in absorbance. This difficulty can be overcome by selecting $650\text{ m}\mu$. At this wavelength only the blue metallised form absorbs, though to a lesser degree. However, it is advantageous to titrate at this wavelength, because it is now unnecessary to determine the slope of the first part,

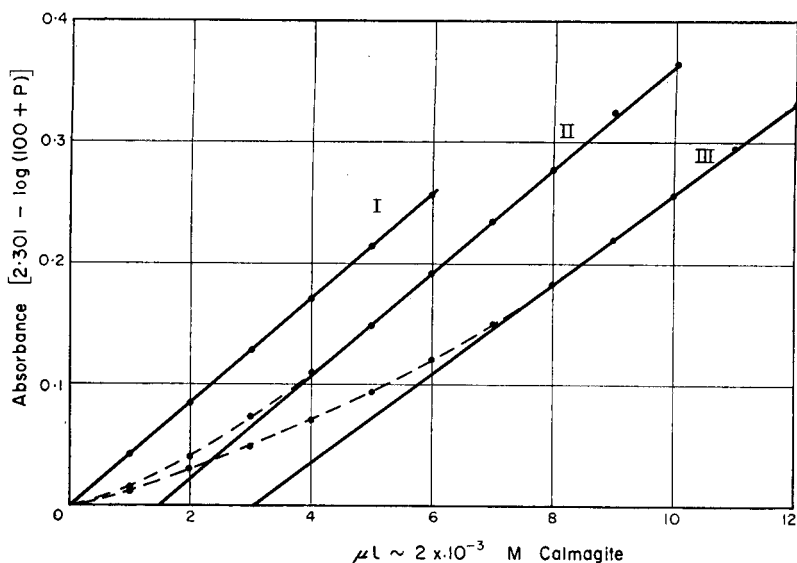


FIG. 2.—Titration of calcium and magnesium with $2 \times 10^{-3} M$ Calmagite solution. (0.5 ml of buffer pH 10: 649 $m\mu$.)
 (I) 50 μl of $5 \times 10^{-4} M$ calcium (Ca does not react); (II) 10 μl , and (III) 20 μl of $5 \times 10^{-4} M$ magnesium.

since it is known to be zero. It is only necessary to titrate with rather large increments until a region beyond the end-point is reached, where the titration curve is straight, and to extrapolate this line to the abscissa. Because a rather long portion of the titration curve is curved, the extrapolation must be carried out from far beyond the end-point, and this lowers the precision considerably.

It was shown that magnesium can be titrated in this way as a self-indicating system and that calcium does not interfere. But the results were not too impressive, and hence no further experiments were performed in this direction. Instead, the more promising possibility of adding excess dye to the sample solution and titrating with EDTA was investigated. Thus the self-indicating system, Mg-Calmagite-EDTA, was created, offering the additional possibility of being used as a slope indicator in the determination of calcium as mentioned above.

EXPERIMENTAL

All chemicals used were of highest available grade of purity. The water to make up the solutions was de-ionised water redistilled through a condenser made from a polyethylene tube.

Stock solutions of 0.1M calcium, magnesium and EDTA were prepared, standardised complexometrically and diluted appropriately. The final calcium and magnesium solutions were $5 \times 10^{-4} M$; the titrant solution was $2.18 \times 10^{-3} M$.

The buffer solution, pH 10, was prepared as follows: 1.14 ml of conc. ammonia, 140 mg of ammonium chloride and 50 mg of potassium cyanide were dissolved in 50 ml of high purity water.

For the dye solution, 20 mg of Calmagite were dissolved in 1 ml of water containing 1 drop of the buffer pH 10. For the daily supply of buffer containing dye, 5 μl of the dye solution were mixed with 5 ml of buffer. This procedure is recommended because in the strongly alkaline solution, over a period of days, the dye slowly fades. The dye titrant solution was prepared by dissolving 7 mg of Calmagite in 10 ml of high purity water. The corresponding solution was about $2 \times 10^{-3} M$.

Whenever possible plastic containers were used to handle and store solutions.

Apparatus: Ultramicro pipettes, calibrated "to contain", were used. The titration was performed with a Beckman/Spinco ultramicro burette, Model 153 A, with a total capacity of 0.12 ml and a precision of about $\pm 0.01 \mu l$. The original burette tip was slightly lengthened, and the holder for the titration vessel was replaced by a removable steel plate.

The photometer used in the present work has been described in Part II of this series.⁸ Some minor modifications were necessary in order to adapt the instrument for the titration of small amounts of material. The 75-mm condenser lens was replaced by a smaller lens having a focal length of approximately 10 mm. Thus a light beam of nearly the same intensity, but with smaller diameter, was obtained, as is necessary when using very small titration vessels.

The titration cell was the bottom section cut from a chipped 1-cm Corex absorption cell originally used in a Beckman DU spectrophotometer. The cell was placed in a cell holder, shown in Fig. 3.

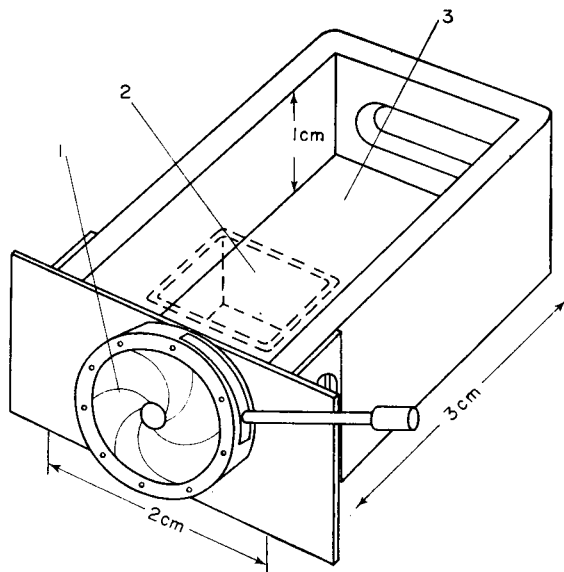


FIG. 3.—Holder for the micro titration cell: (1) iris diaphragm; (2) titration cell; (3) permanent magnet.

The holder was cemented together from sheets of Plexiglass cut to appropriate sizes. A small iris diaphragm was mounted on the front to allow adjustment of the light intensity. The titration cell was held in place by plastic wedges pressed between the side of the cell and the walls of the cell holder. The cell holder was cemented on a permanent magnet. Thus the cell assembly was held firmly on the steel plate of the titrator (see above) but still could be moved in order to obtain the best position within the light beam.

The titration assembly was positioned in the space between the lamp housing and the photoreceptor compartment of the titrator. The entrance opening of the photoreceptor compartment was provided with an aluminium plate having a small hole corresponding to the size and point of entry of the light beam (approximately 0.5 cm in diameter).

To permit shift of the scale (for theory, see later) a zero suppressor circuit was connected in series with the galvanometer and zero adjuster. The wiring diagram is shown in Fig. 4. Its operation is similar to that of the zero adjusting circuit discussed in an earlier paper,⁸ with the exception that the variable resistance R_3 allows a necessarily greater range of current to flow through the galvanometer. The resistance of this circuit is very low in comparison to that of the galvanometer damping resistor, and therefore the zero suppressor has a negligible effect on the damping and sensitivity of the galvanometer.

Procedure

(a) *With no zero suppression:* Place cell assembly in position and adjust zero on the galvanometer with no light reaching the photoreceptor. Place 0.500 ml of buffer containing the dye in the cell, and transfer the sample into the cell with a micropipette, rinsing several times with the buffer in the titration vessel. Insert stirrer and burette. Adjust 100 S.D. (scale divisions) via lamp rheostat and/or iris diaphragm. Titrate in small increments. Plot the results and evaluate in the usual way. For plotting modifications see theory in the following paragraph.

(b) *With zero suppression:* Place the cell assembly in position and adjust zero on the galvanometer with no light reaching the photoreceptor. Adjust 100 S.D. via the lamp rheostat and/or iris diaphragm.

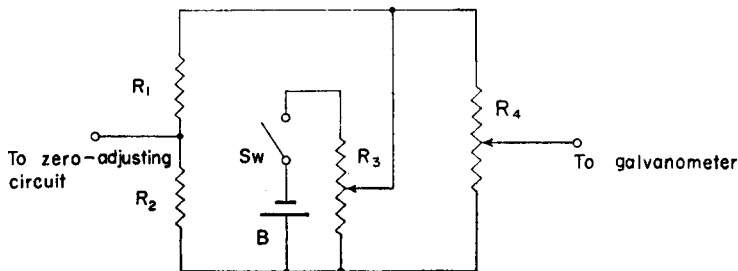


FIG. 4.—Wiring diagram of the zero suppressor: R_1 and R_2 , 500 Ohms; R_3 , 2.5 Megohms; R_4 , 1000 Ohms; Sw, Switch; B, 1.35 volt mercury cell.

Switch on the zero suppression and adjust to zero S.D. by means of the zero suppressor controls.* Now no light reaches the photoreceptor and the pointer moves off scale to -100 S.D. (other values than -100 S.D. may be adjusted in an analogous fashion). Introduce the buffer and sample, insert the stirrer and burette and adjust to 100 S.D. with the initial solution as reference, using the lamp rheostat and/or iris diaphragm. Proceed as described under (a).

Higher precision methods

With a galvanometer reading from 0 to 100 the usual procedure, to set zero S.D. (= Scale Divisions) with no light reaching the photoreceptor and 100 S.D. with water as reference, is inconvenient for titrations involving solutions with a high initial absorbance. The portion of the galvanometer scale used during the titration may be very small even for large changes of absorbance. Adjustment to 100 S.D. with the initial solution is appropriate only when the absorbance increases during the titration. The precision of measurement is thereby increased by a factor of $100/T_i$, where T_i stands for the % transmittance of the initial solution, with water used as 100% T reference.

When the titration is accompanied by a decrease in absorbance the setting of 100 S.D. with the initial solution will result in a galvanometer deflection beyond that point. In order to benefit from increased precision, it is necessary in addition to shift the range of deflection in the negative direction. The possibility that some readings may still fall outside the galvanometer scale is dealt with later.

Discussion of a practical example will elucidate the above statements. In the EDTA titration of the self-indicating system Mg-Calmagite, the initial absorbance of the solution is approximately 1, mainly because of the presence of excess dye. Using water as reference to set 100 S.D., the galvanometer reading with the solution in the cell will be 10 S.D. When all the magnesium is titrated, more of the strongly absorbing dye is released and the final reading is, e.g., 8 S.D. Although this corresponds to a change of approximately 0.1 absorbance unit, the galvanometer will have been deflected only 2 S.D. Obviously, under these conditions it is not possible to obtain sufficiently accurate readings for the construction of a usable titration curve. When the initial solution is used to set the galvanometer to 100 S.D. (e.g., by increasing the light intensity), the precision is increased by a factor of ten, because the 100% T point referred to water is at 1000 S.D. This instrumental manipulation does not, of course, affect the optical properties of the solution, and hence the change in absorbance is still 0.1 unit during the titration. However, the corresponding galvanometer deflection will be from 100 to 80 S.D.

* The setting of a certain zero suppression need be done once only. The selection of operation with or without zero suppression is readily handled by the switch in the zero suppressor circuit.

Heretofore in this discussion reference has been made mainly to galvanometer deflection which is proportional to transmittance; but to obtain a titration curve it is necessary to plot absorbance versus volume of titrant. The question arises whether it is a valid procedure to plot the negative logarithms of the galvanometer readings *versus* volume. The answer is readily obtained by applying a formula derived in a previous paper of this series.⁸ Let M stand for the number of S.D. corresponding to zero transmittance (*i.e.*, no light reaching the photoreceptor). Let N stand for the number of scale divisions corresponding to 100% T set with water as reference, and P for the number of scale divisions read with the sample in the titration cell. Then the % T of the sample can be obtained from the following relation

$$(N - M):100 = (P - M):\%T \quad (1)$$

From this the absorbance is

$$A = -\log (\%T/100) = \log (N - M) - \log (P - M) \quad (2)$$

In the case now under discussion, zero transmittance corresponds to the zero point of the galvanometer scale, and hence $M = 0$. Thus the above expression for the absorbance simplifies to

$$A = \log N - \log P \quad (3)$$

Since $\log N$ (the numerical value need not be known) remains constant during any particular titration, plotting of $\log P$ (it is even not necessary to take account of the minus sign) *versus* volume of titrant is a valid procedure. Addition or subtraction of $\log N$ or any other constant results only in a shift of the titration curve in the direction of the ordinate, which, of course, does not influence the end-point read on the abscissa. Thus by subtracting $\log P$ from 2 it is readily ensured that the titration curve starts at the zero point of the ordinate.

If the galvanometer zero does not correspond to zero light intensity, $M \neq 0$. The first term on the right side of equation (2) is still constant during a particular titration; but plotting the logarithms of scale divisions is no longer a valid procedure. It is now necessary to plot $\log (P - M)$, and hence the value of M (in S.D.) must be known exactly. Regardless of the numerical value of M , it is still possible to subtract $\log (P - M)$ from any arbitrary constant in order that the titration curve again starts at the zero point of the ordinate.

If the zero is shifted to -100 S.D. ($= M$) and the initial solution is used to set 100 S.D., the logarithms of $P - 100$ are subtracted from 2.301 ($= \log 200$) in order to start the titration curve at the zero point of the ordinate. It is convenient, when the setting $M = -100$ (or any other value) is used frequently, to prepare an appropriate table to facilitate the handling of results.

There are two cases in which M is not set equal to zero. First, such a setting may be used in order to achieve an increased precision in measurement. Second, it may be necessary to set M less than zero so that the galvanometer readings do not exceed 100 S.D. during the titration of a system in which the absorbance decreases.

The following example will show why an increased precision results. In the case discussed above, the setting of zero on the galvanometer scale was made with no light reaching the photoreceptor, and the setting of 100 S.D. was made with the initial solution. During the titration a galvanometer deflection from 100 to 80 S.D. was

observed. Suppose the galvanometer setting is adjusted to -100 S.D. with no light reaching the photoreceptor, by moving the scale, by applying an additional voltage, or by some other means. If, now, with the initial solution in the cell the setting is made to 100 S.D. (by increasing the light intensity), the galvanometer deflection during the titration will be from 100 to 60 S.D. Thus the precision with which the galvanometer can be read is doubled.

For a system whose absorbance decreases during the titration, the zero point (*i.e.*, the galvanometer setting with no light reaching the receptor) may, for example, be adjusted to -100 S.D. ($= M$). If the solution is now placed in the cell and the initial setting is made to be zero on the galvanometer scale (*via* change in light intensity), the galvanometer will deflect up the scale during the titration. When large changes in absorbance are involved, the pointer may still leave the galvanometer scale during the course of the titration. This can be avoided by decreasing the sensitivity through selection of a less negative value of M .

In order to find a suitable value for M , several pre-titrations may be necessary. To circumvent this inconvenience it is much simpler to operate with a sectioned titration curve. Whenever the pointer approaches 100 S.D. a re-setting to the zero point of the galvanometer scale is performed by changing the light intensity.

Sectioning the curve is also an appropriate procedure for a titration in which the absorbance increases. Whenever the pointer approaches the zero point of the galvanometer scale it is brought back to 100 S.D. by increasing the light intensity. An example of such a sectioned titration curve is shown in Fig. 5. A close inspection of

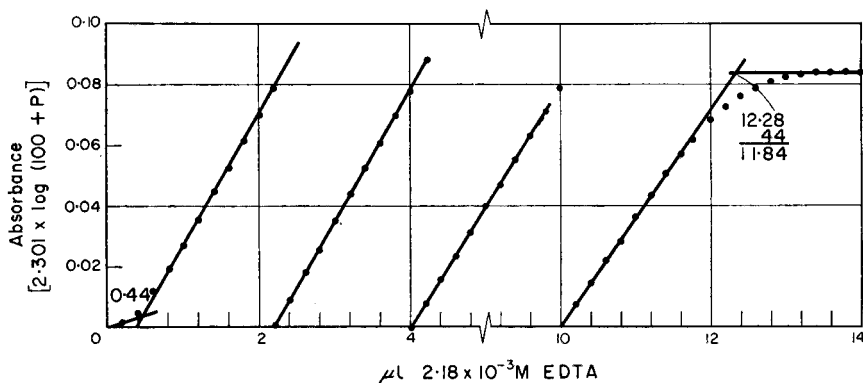


FIG. 5.—Dissection of a titration curve.
($50 \mu\text{l}$ of $5 \times 10^{-4} M$ magnesium: 0.5 ml of buffer, pH 10: $622 m\mu$.)
The calcium blank is readily seen at the beginning of the titration curve.

the figure reveals that each succeeding section has a lower slope. This results from the dilution.

Correction for dilution

To correct for dilution generally, the absorbance values have to be multiplied by the factor $F = (V + b)/V$, where V is the initial volume and b the volume of titrant added. As discussed in the preceding paragraph the titration curve results from a plot of $-\log(P - M)$ versus volume of titrant. In order to have the titration curve start conveniently at the zero point of the ordinate one may even plot $R - \log(P - M)$, where R is an arbitrary constant, as discussed for the case where the

absorbance increases during the titration. It is obvious that the correction factor has to be applied to the true absorbance, A , and not to the term, A' , which is actually plotted, and which for brevity, but incorrectly, is called absorbance.

From a comparison of the two equations,

$$A = \log (N - M) - \log (P - M)$$

$$A' = R - \log (P - M),$$

it can readily be seen that the application of the dilution factor to A' only gives correct results when by chance $R = \log (N - M)$. The more the two terms differ numerically, the more incomplete is the correction. It is possible to determine the numerical value of the term $\log (N - M)$ and then to calculate the true absorbance and to apply the correction to it. However, this is highly inconvenient.

From these considerations, it follows that the most practical way is to employ titrant solutions with sufficiently high concentrations, obviating the necessity of applying a correction.

Blank and impurities

The smaller the amount of calcium and magnesium to be determined, the greater is the influence of impurities. It is hence essential to determine the magnitude of the blank and other corrections necessary with the highest possible accuracy. The magnitude of the blank varies greatly with each preparation of the buffer solution. In only one case was it possible to obtain a buffer solution free from a calcium blank. With appropriate care, however, one may keep the blank within reasonable limits.

Glass vessels for storage of solutions should be rejected, and only plastic containers should be used. When the use of a glass container is unavoidable (volumetric flasks) the contact time should be kept as short as possible. Special treatment of the containers before use is highly recommended (see later).

The main sources of extraneous calcium and/or magnesium are water and dust. De-ionised water has not been proven to be blank free. The most reliable water was obtained by distillation through a condenser made from a plastic tube. When such water is used to prepare the buffer solution only a very small blank can be observed initially. But after some time the blank may increase because of the introduction of calcium and/or magnesium from dust particles.

It is nearly impossible to obtain good results with the smallest amounts of metal ion titrated when the titration is performed in a room where smoking is permitted and many people are moving about. It is readily possible to obtain a correct titration curve up to a certain point and then to observe erratic readings when a dust particle falls into the solution. The erratic readings may not arise entirely from the optical interference caused by the particle. To eliminate this interference, the stirrer may be switched off and the reading made when the particle has left the region of the light beam. If the particle contains any titratable metal ion, erroneous changes in absorbance will deform the titration curve from that point on.

Besides being capable of introducing a chemical interference, dust is a nuisance because it is extremely tedious to wait after each addition of titrant for dust particles to leave the light beam, and with numerous and very small ones such a procedure becomes entirely impossible. Hence, freedom from dust is essential. Filtration is helpful in removing the particles, but very readily increases the blank considerably.

The most suitable filter medium is sintered-glass or porcelain boiled in conc. nitric acid and then treated with warm alkaline EDTA solution for several hours. Extensive rinsing with high-purity water follows the chemical treatment. The same treatment is necessary for the suction flask and the filter holder of the filter assembly. A plastic stopper is recommended for the filter outfit, since rubber particles are easily detached and are a ready source of metal ions. It is essential to bring the solution, after filtration, immediately from the filter flask to the plastic container for permanent storage.

Only small portions of buffer and other solutions should be transferred to a smaller plastic bottle for the daily supply, in order to avoid introduction of dust by too frequent opening of the bottle containing the main portion.

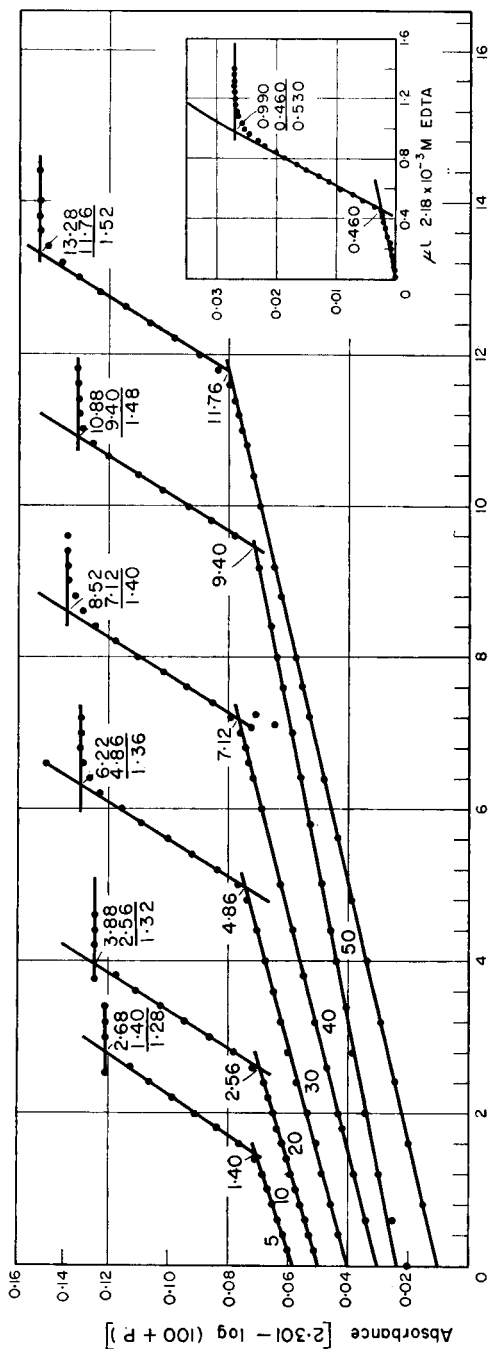
In order to check that the newly developed method would work, it was necessary to prepare calcium and magnesium solutions (in the present case $5 \times 10^{-4}M$ and $5 \times 10^{-5}M$) from more concentrated stock solutions, the molarities of the latter being determined by well-established complexometric procedures. Initial experiments revealed some trends in the results indicating a systematic error. The cause of that error was found in the fact that the water used for the preparation of the dilute solutions was not blank-free, and that calcium had been introduced into the magnesium solution and *vice versa*. These amounts had to be taken into account, and were determined in a similar fashion to the blank of the buffer solution. An example is shown in the results in Fig. 6. Clearly the value for magnesium increases with increasing calcium content. The amount of magnesium in this particular calcium solution was calculated from the results as being approximately equivalent to $0.05 \mu\text{l}$ of EDTA per $10 \mu\text{l}$ of the calcium solution. This series of experiments was performed in the initial phase of the investigation; later, with appropriate care, this type of impurity was maintained at a much lower level. In a practical calcium-magnesium analysis, correction for such impurities may become important, but only when standardising an extremely dilute solution of EDTA against an extremely dilute metal standard solution. With titrant concentrations of $0.001M$ and higher, the standardisation need not be performed on the ultramicro scale; when large amounts of solutions are involved, the minute amounts of impurities do not cause interference. Using the results of Fig. 6, as collected and processed in Table I, the determination of the calcium blank in the buffer becomes evident.

There is a much simpler procedure for determining the calcium and magnesium blank of the buffer, in which the concentration of the calcium and magnesium

TABLE I.—PROCESSING OF THE RESULTS FOR DETERMINATIONS OF CALCIUM ACCORDING TO FIG. 2.

Given, μl $5.07 \times 10^{-4}M$ Ca	5.00	10.0	20.0	30.0	40.0	50.0
Calculated, μl $2.18 \times 10^{-3}M$ EDTA	1.15	2.29	4.59	6.88	9.18	11.47
Found, μl $2.18 \times 10^{-3}M$ EDTA	1.40	2.56	4.86	7.12	9.40	11.76
Difference (= Blank)	0.25	0.27	0.27	0.24	0.22	0.29
μl EDTA corrected for blank (0.257)	1.14	2.30	4.60	6.86	9.14	11.50
Difference, μl EDTA (Corr.—Calcul.)	-0.01	+0.01	+0.01	-0.02	-0.04	+0.03
Difference, %	-0.88	+0.44	+0.22	-0.15	-0.44	+0.26

solutions involved need not be known. The procedure is as follows: A solution containing calcium and magnesium in about equimolar amounts is prepared, and a certain number of μl of this solution is transferred into the titration cell using 0.500 ml of buffer solution. The amount of metal solution should be such that sufficient titrant is required to allow the recording of a reliable titration curve. Several titrations



$\mu\text{L } 2.18 \times 10^{-3} \text{ M EDTA}$

FIG. 6.—Titration of increasing amounts of calcium (5, 10, 20, 30, 40, 50 μl of $5 \times 10^{-4} \text{M}$) in presence of a constant amount (5 μl of $5 \times 10^{-4} \text{M}$) of magnesium.

(0.5 ml buffer, pH 10; 622 m μ .)

Insert: Typical titration curve for very small amounts. 1 μl of Ca and 2 μl of Mg.

are performed using exactly the same amount of buffer and sample in each experiment. The results are averaged. Then another series of titrations is performed in exactly the same way, the only difference being that 1.00 ml of buffer is used. If any significant blank is present the corresponding results in the second series must be higher and the differences correspond to the blank value of calcium and magnesium respectively in 0.500 ml of buffer. A typical example is presented in Table II.

TABLE II.—TYPICAL DATA TO DETERMINE THE CALCIUM AND MAGNESIUM BLANK OF THE BUFFER

$\mu\text{l } 2.18 \times 10^{-3}M \text{ EDTA}$		$\mu\text{l } 2.18 \times 10^{-3}M \text{ EDTA}$	
For calcium	For magnesium	For calcium	For magnesium
using 0.500 ml buffer		using 1.00 ml buffer	
1.12	1.25	1.15	1.28
1.14	1.23	1.17	1.27
1.10	1.23	1.16	1.26
1.13	1.24	1.18	1.27
Average 1.122	1.238	1.165	1.270
A	B	C	D

Calcium blank per 0.500 ml buffer: $C - A = 0.043 \mu\text{l EDTA}$

Magnesium blank per 0.500 ml buffer: $D - B = 0.032 \mu\text{l EDTA}$

CONCLUSIONS

The determination of submicrogram quantities of calcium and magnesium with a surprisingly high precision and accuracy (Tables I and III) is readily achieved by evaluation of a single titration curve. The lower limits shown in this investigation are not the ultimate amounts titratable. With appropriate modifications of the titration cell, smaller amounts can be titrated as far as the sensitivity of the instrument and the readability of the burette will allow. However, a considerable increase in difficulties with sampling, purity of reagents, blank values and their constancy, dust, *etc.* will occur. No studies have been made with regard to interferences by other metals, because these can be predicted from the vast body of information about titrations on the micro and macro scale.

TABLE III.—TITRATION OF SMALL AMOUNTS OF $5 \times 10^{-4}M$ SOLUTIONS OF CALCIUM AND MAGNESIUM BY $2.18 \times 10^{-3}M$ EDTA 0.5 ML OF BUFFER 10.622 M μ

Calcium					Magnesium				
μl	μg				μl	μg			
	given	found	diff.	$\Delta\%$		given	found	diff.	$\Delta\%$
1.00	0.0203	0.0200	-0.0003	-1.48	1.00	0.0122	0.0113	-0.0009	-7.38
2.00	0.0406	0.0425	+0.0019	+4.68	1.00	0.0122	0.0121	-0.0001	-0.82
3.00	0.0609	0.0585	-0.0024	-3.94	1.00	0.0122	0.0131	+0.0009	+7.38
4.00	0.0812	0.0803	-0.0009	-1.11	1.00	0.0122	0.0141	+0.0019	+15.6
5.00	0.1015	0.1036	+0.0021	+2.07	1.00	0.0122	0.0119	-0.0003	-2.46
1.00	0.0203	0.0203	-0.0001	-0.49	2.00	0.0244	0.0250	+0.0006	+2.46

It should be emphasised that the titration curves show a very low degree of curvature near the end-point. This seems surprising at first glance, when it is considered that the concentration of metal in the solution finally titrated is of the order of 10^{-7} – $10^{-6}M$ and that the stability constant of the magnesium-dye complex is only $10^{5.69.7}$. Since the dye is not used in relatively small quantities as an indicator, but is added in a considerable excess over the metal ions in order to create a self-indicating system, a very favourable shift of the equilibria, opposing the dissociation of the metal-dye complexes, is achieved. The curvature is considerably less than could otherwise be expected. With no excess dye, dissociation is large, as can be seen from the rather extensive curvature near the end-point in Fig. 2.

Since the handling of the samples and the operation of the instrument are simple compared with similar methods, practical application of these titrations seems feasible in many cases. For example, under the conditions described in this paper the titration of about $1\ \mu\text{g}$ of calcium and $0.5\ \mu\text{g}$ of magnesium present no difficulty in routine analysis, because in this range the effect of impurities and any blank is not serious. The amount of metals mentioned above correspond to those present in approximately 0.01 ml of blood serum. Thus, the two metals can readily be determined starting with one small drop of blood obtained from the finger. No puncturing of veins is necessary. Further, only one titration need be performed to determine both metals.

The principles developed here and tested experimentally are by no means restricted to the system calcium-magnesium. Any binary mixture of metal ions showing the appropriate optical and chemical behaviour can be treated in an analogous manner. A mixture of copper and zinc, *e.g.*, in the presence of excess PAN, could be titrated similarly with EDTA. There are even cases where one may determine three metals from one titration curve. Further examples are under investigation.

The principle applied here to small amounts of substances and to small volumes is not restricted to those conditions, and similar titrations may be performed with considerably higher amounts of material and in larger volumes. In some practical cases the solubility of the complexes, or the price of the dye may set the limit.

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Zusammenfassung—Drei verschiedene Typen von Endpunktsmechanismen bei photometrischen Titrationen, die auf Komplexbildung basieren, werden definiert und ihre Beziehung zum Selektivitätsproblem wird diskutiert. Einige der entwickelten Prinzipien werden auf die Bestimmung von Ultramikromengen Calciums und Magnesiums angewendet. Überschuss an Farbstoff (Calmagite) wird zu einer die beiden Metall enthaltenden, auf pH 10 gepufferten Lösungen zugesetzt, sodass die Metalle vollständig komplexiert sind. Die Titration wird mit ÄDTE durchgeführt. Eine Titrationskurve wird erhalten, die zwei Sprünge aufweist und somit gestattet beide Metalle in einem Zuge zu bestimmen. Änderungen an einem schon früher beschriebenen Phototitrator werden mitgeteilt und die dadurch erzielte Steigerung der Empfindlichkeit und Präzision wird besprochen.

Résumé—Les auteurs définissent trois méthodes différentes de détection du point équivalent dans les titrages photométriques et discutent du problème de la sélectivité. Certains de ces principes sont appliqués au dosage du calcium et du magnésium en quantités allant jusqu'à quelques dixièmes ou quelques centièmes de microgrammes. Un excès de colorant (calmagite) est ajouté à la solution tamponnée à pH 10, contenant le calcium et le magnésium de sorte que ces deux métaux soient complexés. Ensuite le titrate est réalisée avec l'EDTA. On obtient ainsi une courbe de titrage avec deux points équivalents permettant la détermination de chaque métal présent. Les changements effectués dans un photomètre précédemment décrit sont discutés, ainsi que l'accroissement de sensibilité et la précision.

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THE ELECTROLYTIC OXIDATION OF OXALATE ION IN THE DETERMINATION OF CALCIUM AND MAGNESIUM

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Summary—A graphite anode has been found suitable for the electrolytic removal of excess oxalate ion following precipitation of calcium as oxalate and prior to determination of magnesium as phosphate or quinolate. Magnesium in concentrations as low as 5 mg in 250 ml of solution can be precipitated quantitatively when the solution is electrolysed for 20–30 min at 4 A. The method is applicable to limestone analysis according to the procedure of Kolthoff and Sandell.¹

In a procedure used for limestone analysis the precipitation of calcium oxalate is performed by neutralising with ammonia a hot hydrochloric acid solution containing a large excess of ammonium oxalate.¹

High concentrations of oxalate render the precipitation of magnesium as the phosphate or quinolate incomplete because of the formation of complex ions. Quantities of ammonium oxalate of the order of 1 g in 100 to 200 ml do not interfere seriously.² Since a large excess of ammonium oxalate is employed in the precipitation of calcium, it must be destroyed before the determination of magnesium. Many textbooks maintain that oxalate can be destroyed by the use of concentrated nitric acid. A number of experiments have proved, however, that neither nitric acid nor *aqua regia* is a sufficiently strong oxidising agent for the destruction of oxalate ion.³ Ammonium oxalate may be completely removed by volatilisation over a free flame after the solution is evaporated to dryness. Bromine has been found satisfactory for the oxidation of oxalate in aqueous solution and, although the procedure is laborious, it is probably the most time-saving method available.³

It has been found that 85% of the ammonium oxalate in a stirred acetic acid solution is oxidised in 30 min at cylindrical platinum gauze electrodes when the current is 1.5 A. The amount of ammonium oxalate remaining in solution is not sufficient to interfere with the precipitation of magnesium as phosphate or quinolate.

A number of tests indicated that graphite was suitable as an anode in a hydrochloric acid solution when the effective anode area was 160 cm² and the applied current was 4 A. More than 85% of the ammonium oxalate in a hydrochloric acid solution is destroyed in 25 min and the electrolysis is over 75% efficient at a simply fabricated sixteen rod graphite electrode. As shown in Fig. 1, the electrode requires no ring-stand or clamp and eliminates losses of solution caused by spattering. Experiments proved that magnesium can be precipitated quantitatively as phosphate and quinolate when the solutions are electrolysed for 20–30 min. Magnesium in concentrations as low as 5 mg in 250 ml of solution can be recovered and weighed as pyrophosphate.

Electrolytic removal of oxalate has been found applicable for the separation of calcium and magnesium in limestone analysis. After the removal of hydrous oxides, calcium is precipitated by neutralising a hydrochloric acid solution containing an

excess of ammonium oxalate. The solutions are electrolysed with stirring for 25 min at 4 A using the graphite electrode. The solutions are then filtered to remove any carbon particles which may be dislodged from the electrode surface and magnesium is precipitated as phosphate or quinolate.

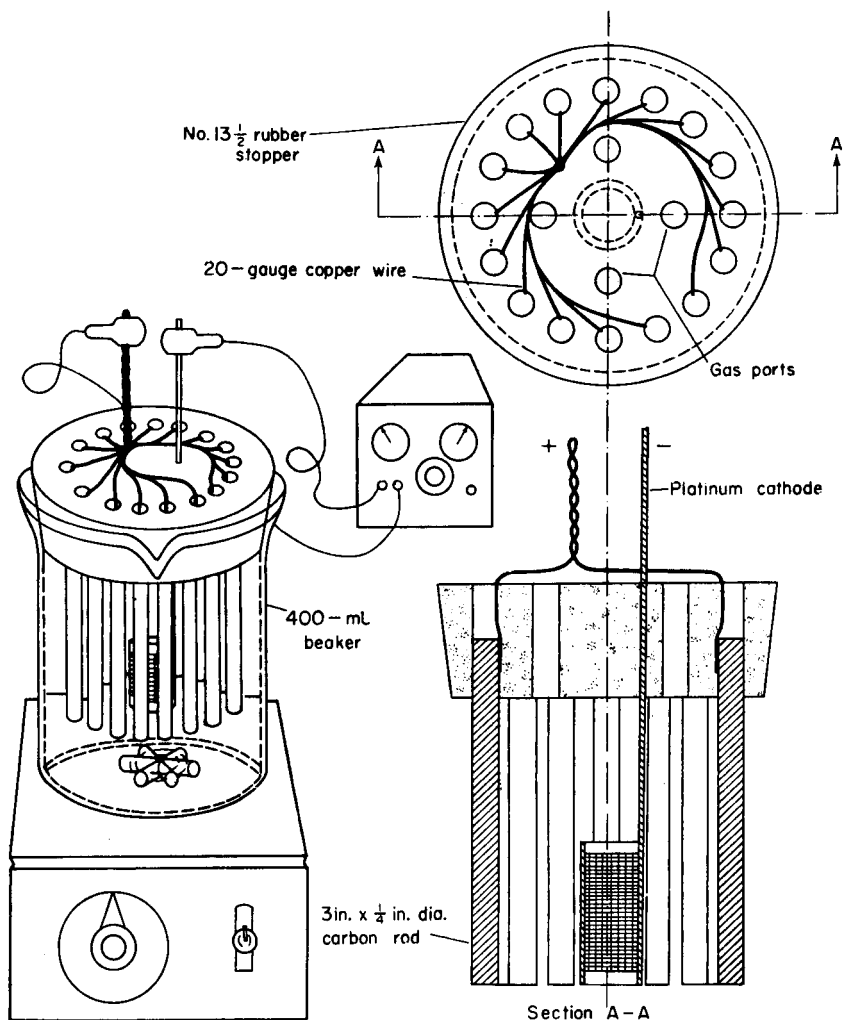


FIG. 1.—Sixteen rod graphite electrode assembly.

EXPERIMENTAL

The rectifier used as a source of direct current operated on 115 V of 60 cycle, single phase a.c. It furnished 25 A of rectified, filtered d.c. at 6 V with powerstat voltage control from zero to full voltage. Electrolysis time was measured with a stopwatch and solutions were stirred with a magnetic stirrer.

Electrolytic Oxidation of Oxalate

A number of coulometric experiments were performed in acetic acid and hydrochloric acid solutions to determine the efficiency and suitability of various electrodes as well as the time required for oxidation of a representative amount of ammonium oxalate. The composition of the experimental solutions corresponded approximately to that of solutions obtained from calcium oxalate precipitation

prior to magnesium determination. For precipitation in acetic acid solution 1.5 to 2 g of ammonium oxalate is used while 3 to 4 g is required in hydrochloric acid solution.

Oxidation in acetic acid solution

Seven solutions containing 50 ml of ammonium oxalate solution (40 g/l.), 10 ml of magnesium acetate solution (0.1 g of MgO/10 ml), 10 ml of glacial acetic acid and 125 ml of distilled water were prepared in beakers. The solutions were electrolysed for varying times at 1.5 A with platinum

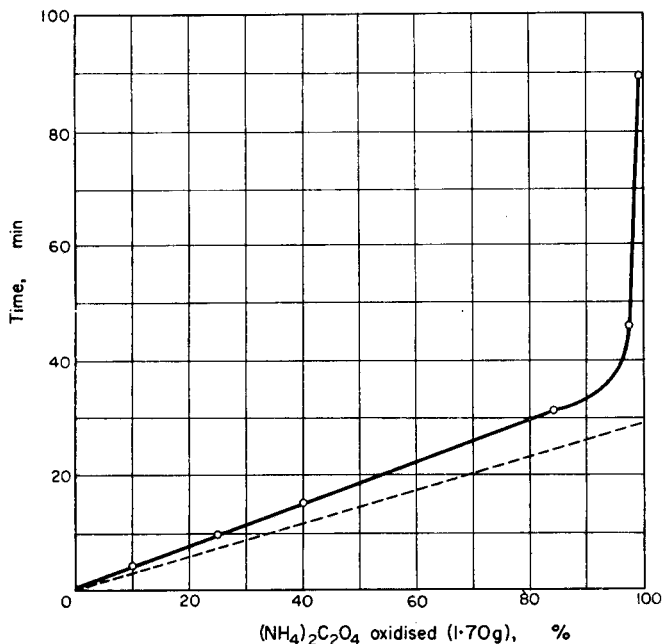


Fig. 2.—Efficiency of oxalate oxidation at platinum electrodes in acetic acid:
 - - - theoretical (Faraday's law)
 —○— experimental.

cylindrical gauze electrodes. The electrolysis was executed at room temperature with stirring. The weight of ammonium oxalate remaining after electrolysis was determined by titration with standard permanganate. The results (Fig. 2) indicate that 85% of the ammonium oxalate is oxidised in 30 min leaving approximately 0.25 g in solution which does not interfere appreciably with precipitation of magnesium ammonium phosphate or quinolate.

Oxidation in hydrochloric acid solution

Similar experiments were conducted in hydrochloric acid using electrodes other than platinum since it dissolves anodically. Solutions were prepared containing 100 ml of ammonium oxalate solution (40 g/l.), 10 ml of magnesium chloride solution (0.1 g of MgO/10 ml), 17 ml of concentrated hydrochloric acid, 12 ml of concentrated ammonium hydroxide and 150 ml of water. The solutions were electrolysed with stirring for varying times using graphite rod anodes in conjunction with a platinum cathode. The applied current was 4 A and the corresponding voltage was 5 V. Fig. 3 shows the effect of varying the current density by increasing the number of graphite rods. More than 85% of the oxalate was oxidised in 25 min with the sixteen rod anode and the electrolysis was over 75% efficient up to that point. The electrode did not disintegrate to any great extent and gas evolution was smooth.

Experiments were performed for the purpose of determining the time that the solutions should be electrolysed in order to obtain a quantitative precipitation of magnesium as phosphate or quinolate. Solutions with the same composition as in the previous experiment were prepared and electrolysed for varying times at 4 A with stirring at the sixteen rod graphite anode. After electrolysis the electrodes were rinsed thoroughly with distilled water and the solutions were filtered to remove the few carbon particles which were dislodged from the electrode. Magnesium was then precipitated and determined

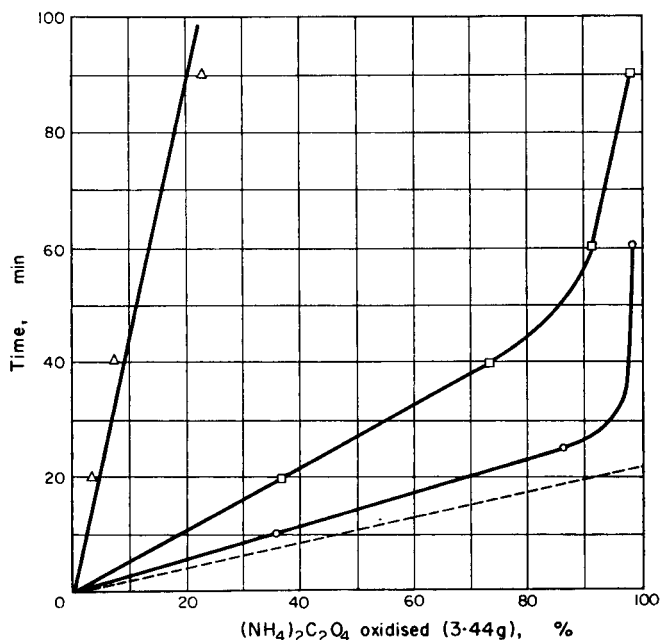


FIG. 3.—Oxidation efficiency at graphite electrodes in hydrochloric acid:
 - - - theoretical (Faraday's law)
 —△— single rod graphite anode
 —□— eight rod graphite anode
 —○— sixteen rod graphite anode.

TABLE I.—DETERMINATION OF MAGNESIUM WITH VARYING TIMES OF ELECTROLYSIS

Time of electrolysis, <i>min</i>	(NH ₄) ₂ C ₂ O ₄ present, <i>g</i>	Magnesium found* as pyrophosphate, <i>g</i>	Magnesium found* as quinolate, <i>g</i>
10	2.20	0.0537	0.0464
10	2.20	0.0540	0.0472
20	0.98	0.0545	0.0539
20	0.98	0.0545	0.0543
30	0.10	0.0546	0.0544
30	0.10	0.0545	0.0540

* 0.0545 g of magnesium present.

TABLE II.—DETERMINATION OF MAGNESIUM IN LIMESTONES

Thorn-Smith Sample No.	Magnesium oxide present, %	Magnesium oxide found as pyrophosphate, %	Magnesium oxide found as quinolate, %
71(a)	4.19	4.26	
71(b)	4.19		4.15
78(a)	10.97	11.08	
78(b)	10.97		10.99
90(a)	21.61	21.48	
90(b)	21.61		21.60

as phosphate and quinolate. Results shown in Table I indicate that precipitation is quantitative when the solutions are electrolysed for 20–30 min.

An investigation was carried out to ascertain if variable quantities of magnesium could be determined quantitatively after the solutions were electrolysed for 25 min. Results indicated that as little as 5 mg of magnesium can be detected as the pyrophosphate.

Finally the results of the analysis of three limestone samples in which the excess oxalate was destroyed electrolytically showed (Table II) that the subsequent determination of magnesium is quantitative.

Zusammenfassung—Der Ueberschuss der Oxalationen, der von der Bestimmung des Kalziums als Kalziumoxalat herruehrt, kann elektrolytisch zerstoert werden u.zw. mit Hilfe einer Graphit-elektrode. Dies ist in der Regel notwendig vor der Bestimmung des Magnesiums entweder als Phosphat oder Oxinat. Magnesium in einer Konzentration von fuenf Milligramm per 250 Milliliter kann noch quantitativ gefaellt werden, wenn die Loesung vorher durch 25–30 Minuten mit einem Strom von 4 Ampère elektrolysiert wurde. Diese Arbeitsweise kann zur Analyse des Kalksteines verwendet werden nach der Methode von Kolthoff und Sandell.

Résumé—On a découvert une anode de graphite pour détruire par l'électrolyse l'excédent des ions d'oxalate à la suite de la précipitation du calcium pour former de l'oxalate et avant la résolution du magnésium en phosphate ou quinolate. Le magnésium dans des concentrations même de la faiblesse de 250 ml. peut se précipiter quantitativement si on électrolyse la solution de vingt à trente minutes à quatre amperes. Cette méthode peut s'appliquer à l'analyse de la pierre de chaux selon le procédé de Kolthoff et Sandell.

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OXIDIMETRIC DETERMINATION OF ORGANIC COMPOUNDS BY MEANS OF STRONG OXIDISING AGENTS

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Summary—A survey of the complete oxidation in aqueous solutions of organic compounds by means of strong oxidising agents is presented. A discussion of the influence of acidity and of the possibilities of working at higher temperatures are given, as well as some general remarks for further research in this field.

INTRODUCTION

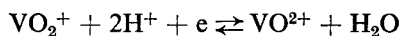
Of the various types of chemical reactions that may underlie a titrimetric determination, oxidation-reduction reactions are the most important, especially those reactions in which the substance to be determined is oxidised by the reagent.

Although in organic chemistry titrimetric analysis, in general, is less important than in inorganic chemistry, because of the smaller rate of the reactions, still many attempts have been made to develop titrimetric procedures for the determination of organic compounds. It is the aim of this review to collect the most important results obtained in oxidimetric analysis of organic compounds and to discuss them in a critical way in order to obtain some lines of conduct for fruitful further investigations in this field of analysis.

Two types of oxidation of an organic compound can be distinguished:

- (1) Moderate oxidation by a moderate or sometimes a strong oxidising agent.
- (2) Complete oxidative breakdown *e.g.* into carbon dioxide and water. These reactions can only be carried out by means of very strong oxidising agents.

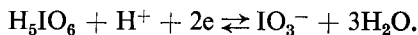
As the first example of the moderate type of oxidation may be mentioned some recently published oxidimetric determinations by means of vanadium^V, belonging to the half reaction:



with a normal potential of 1.00 V at pH = 0.¹ In strong sulphuric acid solutions West and Skoog² determined α -hydroxy acids by means of oxidation with vanadium^V to the corresponding carboxylic acid with one carbon atom less and carbon dioxide. Rao *et. al.*³ described a similar determination of α -amino acids after prior de-amination. They claim the formation of formic acid instead of carbon dioxide. The determination of uric acid by means of oxidation with vanadium^V to alloxan is described by Rao and Murty.⁴

A second example is the well-known "Malaprade" reaction, the determination of α -diols, α -diketones and similar compounds by means of potassium periodate.⁵ At room temperature in approximately neutral solution these organic compounds are stoichiometrically oxidised within a few min, *e.g.* in the case of α -diols by means of a cleavage of the C—C bond between the carbon atoms that bear the hydroxyl groups

and formation of the respective aldehydes. Periodate is reduced to iodate according to the half reaction:



Although the normal potential of the periodate-iodate couple is 1.6 V at pH = 0, and periodate is, therefore, a very strong oxidising agent, the oxidation does not proceed beyond the aldehyde state. Thus it is a moderate oxidation by means of a very strong oxidising agent.

A third and last example of these moderate oxidations is the excellent determination of formaldehyde by oxidation to formate in alkaline solution by the strong oxidising reagent hypiodite, according to Romijn.⁶

These examples of moderate stoichiometric oxidations are a completely arbitrary choice. There are a number of other reactions of the same type in use in titrimetric organic analysis. It is not the aim of this review, however, to sum up all reactions of this type, because it is not possible to do it in a systematic way.

Every oxidising agent has its own typical aspects and it is better in this respect to review the reactions of each oxidising agent; this has been carried out in some textbooks^{7,8} and in some reviews.^{9,10}

The main difficulty in moderate oxidations, as mentioned above, is that the reactions are, in general, not stoichiometric and that very often empirical factors are needed for obtaining correct results. This lack of stoichiometry does not occur in oxidations of the second type, *i.e.*, complete oxidative breakdown, usually to carbon dioxide and water. This type of oxidation can only be carried out by means of very strong oxidising agents. Accordingly, this review is limited to this second type of oxidation in aqueous solution. The various strong oxidising reagents will be compared with respect to this type of reaction and the influence of the acidity of the solution on the oxidation of organic compounds will be discussed.

SURVEY OF THE VARIOUS STRONG OXIDISING REAGENTS

From the thermodynamic point of view the strength of an oxidising reagent is determined by the normal potential of the half reaction combining the oxidising reagent and the substance to which it is reduced.

As is well known, it must be realised that the rate of a thermodynamically possible oxidation-reduction reaction may be and is, in many cases, negligible, especially the oxidation of organic compounds. Although the rate of oxidation of any compound is by no means related to the oxidation potential of the oxidising reagent involved, oxidative breakdown of organic compounds is, in general, exclusively brought about by very strong oxidising agents, although the opposite, of course, does not hold. Therefore, we can limit ourselves in the second type of oxidation of organic compounds to oxidations by means of very strong oxidising agents and only to those oxidising agents which are stable in aqueous solution, preferably also at higher temperatures.

The normal potential of the majority of half reactions strongly depends on the acidity of the solution. Therefore a distinction will be drawn between very strong oxidising agents in acidic and in alkaline solution.

An oxidising agent will be called a very strong oxidising agent when it belongs to a half reaction having a normal potential > 1.3 V at pH = 0 or of > 0.3 V at pH = 14.

There is still another important reason to distinguish between redox reactions in acidic and alkaline solution, because the rate of these reactions frequently depends strongly on the acidity of the solution.

A great number of compounds, organic as well as inorganic compounds, are exclusively or preferably oxidised in either alkaline or acidic solution, *e.g.*

- (1) Hydrogen cyanide is stable towards strong oxidising agents in an acidic medium. In neutral and alkaline solutions quantitative oxidation to cyanate takes place fairly rapidly.
- (2) Oxidation of formic acid is only very slow in an acidic medium; in an alkaline medium quantitative determinations can be carried out by means of oxidation of formate to carbon dioxide and water.
- (3) Oxalic acid behaves in an exactly opposite manner. In alkaline solution no oxidation occurs, in an acidic medium a quantitative determination by means of oxidation to carbon dioxide and water can be carried out with several strong oxidising agents.

In order to see which oxidising agents have to be considered in oxidations of the second type, those half-reactions that have the qualifications mentioned above are listed in Tables I and II. Table I refers to half-reactions in an acidic medium and corresponding normal potentials at $\text{pH} = 0$, whilst Table II does the same for alkaline solutions and $\text{pH} = 14$. The values given are those recorded by Latimer.¹

TABLE I

Half reaction	E_0, V
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e \rightleftharpoons 2\text{H}_2\text{O}$	1.77
$\text{MnO}_4^- + 4\text{H}^+ + 3e \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	1.69
$\text{HClO}_2 + 2\text{H}^+ + 2e \rightleftharpoons \text{HClO} + \text{H}_2\text{O}$	1.64
$\text{HClO} + \text{H}^+ + e \rightleftharpoons 0.5\text{Cl}_2 + \text{H}_2\text{O}$	1.63
$\text{Ce}^{4+} + e \rightleftharpoons \text{Ce}^{3+}$	1.61
$\text{H}_5\text{IO}_6 + \text{H}^+ + 2e \rightleftharpoons \text{IO}_3^- + 3\text{H}_2\text{O}$	1.60
$\text{HBrO} + \text{H}^+ + e \rightleftharpoons 0.5\text{Br}_2 + \text{H}_2\text{O}$	1.59
$\text{BrO}_3^- + 6\text{H}^+ + 5e \rightleftharpoons 0.5\text{Br}_2 + 3\text{H}_2\text{O}$	1.52
$\text{MnO}_4^- + 8\text{H}^+ + 5e \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
$\text{Mn}^{3+} + e \rightleftharpoons \text{Mn}^{2+}$	1.51
$\text{HIO} + \text{H}^+ + e \rightleftharpoons 0.5\text{I}_2 + \text{H}_2\text{O}$	1.45
$\text{Cl}_2 + 2e \rightleftharpoons 2\text{Cl}^-$	1.36
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33

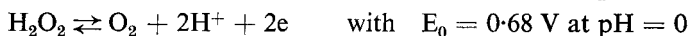
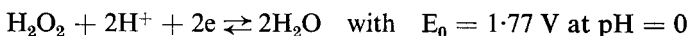
TABLE II

Half reaction	E_0, V
$\text{ClO}^- + \text{H}_2\text{O} + 2e \rightleftharpoons \text{Cl}^- + 2\text{OH}^-$	0.89
$\text{HO}_2^- + \text{H}_2\text{O} + 2e \rightleftharpoons 3\text{OH}^-$	0.88
$\text{BrO}^- + \text{H}_2\text{O} + 2e \rightleftharpoons \text{Br}^- + 2\text{OH}^-$	0.76
$\text{H}_5\text{IO}_6^{2-} + \text{H}_2\text{O} + 2e \rightleftharpoons \text{IO}_3^- + 3\text{OH}^-$	0.70
$\text{ClO}_2^- + \text{H}_2\text{O} + 2e \rightleftharpoons \text{ClO}^- + 2\text{OH}^-$	0.66
$\text{BrO}_3^- + 3\text{H}_2\text{O} + 6e \rightleftharpoons \text{Br}^- + 6\text{OH}^-$	0.61
$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2e \rightleftharpoons \text{MnO}_2 + 4\text{OH}^-$	0.59
$\text{MnO}_4^- + e \rightleftharpoons \text{MnO}_4^{2-}$	0.56
$\text{IO}^- + \text{H}_2\text{O} + e \rightleftharpoons \text{I}^- + 2\text{OH}^-$	0.49
$\text{Fe}(\text{CN})_6^{3-} + e \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	0.36
$\text{ClO}_4^- + \text{H}_2\text{O} + 2e \rightleftharpoons \text{ClO}_3^- + 2\text{OH}^-$	0.36
$\text{ClO}_3^- + \text{H}_2\text{O} + 2e \rightleftharpoons \text{ClO}_2^- + 2\text{OH}^-$	0.33

In the remaining part of this section the results obtained in oxidations of organic compounds by means of the oxidising agents included in Tables I and II will be briefly mentioned, especially with respect to oxidations of the second type *viz.* complete breakdown of organic compounds. Only those aspects of the oxidising agents necessary for a comparative discussion of these reagents later in this paper will be mentioned. For a complete picture of the applications of every reagent, reviews and textbooks are available.^{7,8,9,10}

Hydrogen peroxide

Although hydrogen peroxide is a very strong oxidising agent in an acidic as well as in an alkaline medium and although it is under certain conditions fairly stable in aqueous solutions at room temperature so that a few quantitative determinations of inorganic compounds appear to be possible,^{11,12} it will not be possible to carry out any quantitative oxidation of a more complicated character with this reagent. For, hydrogen peroxide is unstable with respect to its own disproportionation into oxygen and water, which is evident from the half-reactions:



and similar half reactions in alkaline media.

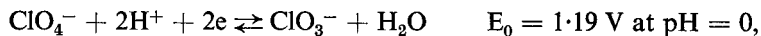
Although under certain conditions this disproportionation only takes place at an extremely small rate, it will give rise to loss of oxygen and thus to titration errors when the time for an oxidation becomes long or when reactive intermediates occur or when heating is necessary for a completely stoichiometric oxidation.

Halogens, their oxyacids and their oxyanions

The halogens, their oxyacids and their oxyanions belong, in acidic as well as in alkaline solution to the strong oxidising agents as is clear from Tables I and II. Because of the many disproportionation reactions taking place and because in many of the half reactions involved more than one of these compounds occur, it is best to treat these compounds together.

Chlorine, oxyacids and oxyanions of chlorine

To Table I the following half reactions can be added:



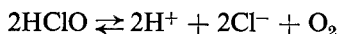
From Tables I and II and the two half reactions mentioned above a number of important conclusions can be drawn.

Although from a thermodynamic point of view perchlorate and chlorate ions are strong oxidising agents in alkaline solution, the reactivity of these ions in this medium, as well as in an acidic medium, is very poor, *e.g.* perchlorate ion is only reduced at a very slow rate in an acidic medium by such a very strong reducing agent as chromium^{II}. Chlorous acid and chlorite ions are more reactive and recently quantitative oxidations of some compounds by means of chlorite have been examined by Minczewski and Glabisz.¹³ Although it is possible that chlorites and chlorous acid may be valuable oxidising agents in some cases, the authors feel that for the complete oxidation of

organic compounds, hypochlorous acid and hypochlorites are to be preferred not only from the thermodynamic but also from the reactivity point of view.

Hypochlorous acid in acidic solution and hypochlorite ion in alkaline solution are very strong oxidising agents. Both are thermodynamically unstable with respect to disproportionation to chlorine and chlorate and perchlorate ions in acidic solution, and to chloride ion on the one hand and to chlorate and perchlorate ions on the other in alkaline solution. However, these disproportionation reactions are slow and, under ordinary conditions, do not pass beyond the chlorate state so that the reaction will not necessarily give rise to titration errors when using hypochlorous acid or hypochlorite in titrimetric analysis, because in a back titration all chlorine compounds left can be brought to the chloride state without any loss of oxygen.

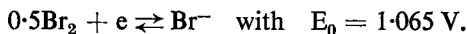
There is, however, a decomposition reaction that can cause serious errors namely:



which takes place in acidic and in alkaline solution. Pierron¹⁴ showed that the decomposition caused by this reaction increases in the order: LiOCl, NaOCl, KOCl. In all cases the rate of decomposition reaches a minimum in neutral solution, but even then the decomposition is from 5 to 25% when the solutions are heated for a few hr at 100°. Although this decomposition reaction is very slow and even negligible under less extreme conditions, e.g. room temperature, it looks as if it is responsible for the fact that no complete oxidations of organic compounds by hypochlorite or hypochlorous acid are described in the literature. Only several simple quantitative oxidations by means of these reagents are known.^{15,16} More complex oxidation reactions with these reagents do not seem to take place at an appreciable rate at room temperature, although some further research on this subject is warranted, especially in an alkaline medium and perhaps particularly in lithium hydroxide solution, because there are few strong oxidising agents in alkaline medium.

Bromine, oxyacids and oxyanions of bromine

To Table I the following half reaction can be added:



The stable oxidising compounds of bromine are less in number than those of chlorine. Bromate acts in an acidic and in an alkaline solution as oxidising agent, hypobromous acid in an acidic solution only, hypobromite in an alkaline solution and elementary bromine in an acidic solution, the latter being only a moderate oxidant.

Bromate, although belonging to a half reaction with a large normal potential in acidic and in alkaline media, is only slightly reactive.¹⁰ It is often used in an acidic medium together with bromide ions and it then acts as elementary bromine which shows a greater reactivity than bromate, but it has scarcely any significance in organic oxidimetry.

Hypobromous acid and hypobromites are strong oxidising agents. They have lower oxidation potentials than the corresponding chlorine compounds but, in general, they show a greater reactivity. They are also less stable than the corresponding compounds of chlorine. This means that in oxidation processes that require much time or that have to be carried out at higher temperatures, oxygen losses will make a quantitative analysis impossible.

The best results are obtained by means of the chlorine compounds to which bromide ions are added, in which case the solutions act as solutions of hypobromous acid or hypobromites.^{17,18,19}

The authors feel that in an acidic medium there is no place for this reagent besides the well known stable oxidimetric reagents, but that hypobromite may be of value in alkaline solution in simple oxidation processes, although up to the present hardly any applications of bromine compounds are known in oxidimetric organic analysis.

Iodine, oxyacids and oxyanions of iodine. Only two valency states of iodine act as strong oxidising agents, in acidic as well as in alkaline solution.

Hypo-iodous acid and the hypo-iodites are for the same reasons as in the cases of the corresponding chlorine and bromine compounds unsuitable for oxidations at higher temperatures or of long duration. Some quantitative processes in an alkaline medium are known, however, including a few oxidations of organic compounds e.g. aldehydes.^{6,20}

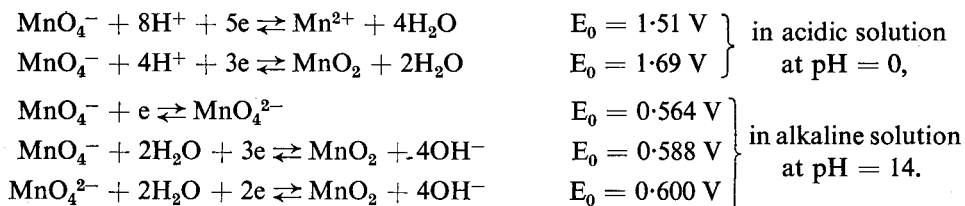
Periodate and periodic acid have already been mentioned in the *Introduction*. These compounds are of interest in a great number of specific oxidations of organic compounds, e.g. "Malaprade" reactions.³ No applications are known, however, of further stoichiometric oxidations of organic compounds by means of these reagents.

Higher valency states of manganese

Tervalent, hexavalent and heptavalent manganese are very strong oxidising agents either in acidic or in alkaline solution, or in both of them.

Manganese^{III} is of no practical importance in quantitative analysis. Apart from its stability in a few complexes, when it is no longer a strong oxidising agent, it only shows any definite stability in strongly acidic solutions and then insufficient for practical purposes.

The discussion will, therefore, be restricted to manganate and permanganate. The half reactions in which these two ions take part are summarised below:



In alkaline solution it is seen that at pH 14 three half reactions are possible. In solutions of lower alkalinity the normal potential of the permanganate-manganate couple does not change, while the other two normal potentials rise, the result being that with decreasing alkalinity manganate becomes thermodynamically unstable with respect to disproportionation to permanganate and manganese dioxide. The actual behaviour of manganate solutions is in accordance with these calculations. Manganate is only stable in solutions more than 1M in alkali hydroxide. At lower alkalinities disproportionation of manganate takes place, increasing in rate with decreasing alkalinity. Therefore, permanganate is the only strong oxidising agent of manganese of practical importance in an acidic solution. It takes part in two half reactions, one producing manganese dioxide and occurring in slightly acidic solution, the other proceeding to manganese^{II} and taking place at higher acidities.

The significance of manganate and permanganate will be discussed separately.

Permanganate. Permanganate is the best known strong oxidant. It owes its important place in analytical chemistry to several excellent properties: it can easily be obtained, it is intensely coloured, it is a very strong oxidising agent in both acidic and alkaline solution from the thermodynamic (normal potentials of the half reactions in question) and from the reactivity point of view. One of the most important properties of a reagent to be used in oxidimetric analysis, *viz.* stability under various conditions, will first be discussed. Especially in oxidation processes taking up much time or requiring higher temperatures, oxidant stability is of great importance. Permanganate solutions are most stable in neutral solution. The addition of manganese^{II} or manganese dioxide, increasing acidity and rise in temperature decrease the stability of permanganate solutions. Some experimental evidence is given in Table III. †

TABLE III

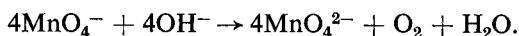
Expt.	Initial permanganate concentration, <i>M</i>	Acidity	Temp., °C	Time	Decompn., %
1	0.01	neutral	100	1 hr	0.0
2	0.002	neutral	100	1 hr	1.0
3	0.01 (Mn ^{II} *)	neutral	100	1 hr	0.4
4	0.01	neutral	20	1 year	0.0
5	0.01	0.2 <i>M</i> H ₂ SO ₄	20	24 hr	0.7
6	0.01 (Mn ^{II} *)	0.2 <i>M</i> H ₂ SO ₄	70	1 hr	10

* Mn^{II} was added in experiments 3 and 6, causing formation of MnO₂.

Summarising, to avoid titration errors in titrimetric procedures involving permanganate in an acidic medium and taking much time, it is absolutely necessary to work at low acidities and at room temperature. Without manganese^{II} or manganese dioxide being present these conditions would not be stringent, but in oxidations with permanganate these compounds are formed directly from the beginning of the process.

In alkaline solution the behaviour of permanganate is different. The stability of permanganate now depends on the alkalinity of the solution, the permanganate concentration, the temperature and the time. Manganese dioxide does not influence the stability of alkaline permanganate solutions.

Several investigations^{23,24,25,26} dealing with this stability have been carried out. It was found that the decomposition of alkaline solutions of permanganate is exclusively caused by the reaction:



As already stated, at lower alkalinities manganate shows a disproportionation but this is a reaction without loss of oxygen and it does not, therefore, result in titration errors.

The extent to which an alkaline permanganate solution is converted to manganate is outlined in Table IV.

The main characteristics for the decomposition from this table and also from a great number of other decomposition experiments^{23,24,25,26} are:

- (1) Decomposition is very large in the beginning. When a certain amount of manganate is formed, the decomposition decreases markedly (expt. 1 and 2).
- (2) Decomposition increases with decreasing initial concentration of permanganate (expt. 3, 4 and 5).

- (3) Decomposition increases with increasing alkalinity (expt. 4 and 6).
 (4) Decomposition increases with increasing temperature (expt. 1 and 3).

Elimination of titration errors in titrimetric procedures involving alkaline permanganate only seems possible at room temperature, at low alkali hydroxide concentration ($< 1M$) and at large permanganate concentration ($> 0.1M$ permanganate). After this discussion of the stability of permanganate solutions a survey of the most important investigations on titrimetric procedures involving strong oxidations of organic compounds by means of permanganate is given. Only those investigations will be mentioned which present a new aspect to this field.

The application of permanganate to quantitative analysis dates from 1846²⁷ and in the next 80 years a great number of analyses, including that of organic compounds, has been described, e.g. those by Péan de St. Gilles²⁸ and Lenz.²⁹ Some authors reveal

TABLE IV

Expt.	Initial permanganate concentration, M	Alkali hydroxide concentration, M	Time, hr	Temp., $^{\circ}C$	Decompn. into manganate, %
1	0.01	1	2	20	4
2	0.01	1	48	20	4
3	0.03	2	1	35	10
4	0.003	2	1	35	25
5	0.0003	2	1	35	60
6	0.003	4	1	35	70

their knowledge of the sometimes essentially different behaviour of some compounds towards oxidation in alkaline and acidic media, but the investigators have not, in general, succeeded in developing stoichiometric determinations of organic compounds and only carry out quantitative analysis of more complicated organic compounds by using empirical factors. The first to state that oxidimetric processes with permanganate taking much time should be carried out at room temperature was Kolthoff.²¹ Subsequently, Imhof³⁰ carried out a systematic investigation of the oxidation of many organic compounds, mainly to carbon dioxide and water, by permanganate in acidic and in alkaline media at room temperature. He also indicated that in many cases it is of great value to begin an oxidation in an alkaline medium, then to continue for a certain time in an acidic medium.

Imhof collected much valuable data about oxidisibility of organic compounds in acidic and alkaline solutions and also obtained a number of correct results for quantitative analysis according to his procedures. The main drawbacks to Imhof's methods are that his standard procedure requires more than 24 hr, that still there are in many cases titration errors amounting to a few percent, and that his method is not suitable for the determination of small amounts of organic material because of the larger oxygen losses at lower permanganate concentrations.

Some years later, Stamm³¹ made new progress in this field. He looked for a means to overcome the long reaction time of Imhof's procedure. He turned his attention to the fact that the reduction of permanganate to manganese dioxide in an alkaline solution takes place in two distinct steps, *viz.* the rapid reduction of permanganate to manganate and a much less rapid reduction of manganate to manganese dioxide. To limit the reaction time of oxidations by permanganate in an alkaline solution he

proposed the addition of so much permanganate to the organic material to be oxidised, that the reduction to manganate is sufficient for the desired oxidation. Indeed, Stamm succeeded by means of this idea to decrease the reaction time in some cases from several hr to several min, thus overcoming one of the major drawbacks of Imhof's procedures. To avoid oxygen losses Stamm carries out his analysis at large permanganate concentration (0.1M) and in as short a reaction time as possible. Although the reaction times are shorter in this case, still smaller permanganate concentrations have to be avoided because oxygen losses especially occur immediately after mixing permanganate and alkali (see Table IV and *Conclusions*).

Other valuable oxidimetric determinations of organic compounds by means of permanganate have been described since Stamm's work, but none of them has added new aspects to the solution of the problems mentioned above.

It may be concluded that sufficient experimental evidence is available to state that complicated oxidimetric determinations by means of permanganate taking much time should always be carried out at room temperature in solutions of which neither the acidity nor the alkalinity should be large (e.g. between 1M acid and 1M alkali). Titration errors caused by oxygen losses can never be corrected by running a blank, because an acidic blank loses only a little oxygen when no manganese^{II} or manganese dioxide (to catalyse the self-decomposition of permanganate in the determination itself) are present in the blank; an alkaline blank always develops more oxygen than the determination itself, because the stabilising manganate is formed, not only by the self-decomposition as in the blank, but also, and in many cases mainly, by means of reduction of permanganate by the compound to be determined.

Manganate. It has already been stated that the self-decomposition of permanganate in an alkaline solution does not pass beyond the manganate state. This means that manganate should be stable, with respect to loss of oxygen, in alkaline solutions. Although the normal potential of the manganate–manganese dioxide couple at pH 14 does not differ much from the permanganate–manganate and permanganate–manganese dioxide couples and manganate in this medium is, therefore, an oxidising reagent of the same strength as permanganate, Stamm's experimental work³¹ demonstrates that permanganate is far more reactive than manganate. The smaller reactivity may, however, be compensated, or even over-compensated, by the greater stability resulting in the possibility of carrying out oxidations at higher temperatures without the loss of oxygen.

After preliminary work by den Boef,^{26,32} in which the applicability of manganate for some quantitative inorganic oxidations and the stability at room temperature of manganate solutions were demonstrated, (results which were in accordance with results obtained by Issa *et al.*³³ somewhat later), Polak and den Boef³⁴ investigated the stability of manganate solutions at higher temperatures. Negligible loss of oxidative power was found when a 0.03M manganate solution was heated for 12 hr at 70° in 1 to 4M alkali hydroxide solution. Similar stability occurs on heating the same solutions at 100° for a few hr. Decreasing the manganate concentration to 0.006 M does not affect the stability under these conditions. This stability could be expected from the results of the decomposition of permanganate.²⁶

It is of great practical importance that the presence of manganese dioxide does not affect the stability of manganate solutions. This means that when it is necessary to heat for a very long time so that some decomposition and loss of oxidative power

takes place, correction by means of a blank is possible, in contrast with analysis by means of permanganate. In alkali hydroxide solutions of concentration lower than 2M a slow disproportionation of manganate into permanganate and manganese dioxide takes place but this reaction does not, of course, bring about titration errors.

Polak³⁵ described a number of ways in which determinations with manganate can be carried out and applied them to the determination of formate ions, obtaining very accurate results with very small amounts of formate ions. A great number of other organic compounds can also be analysed with the same accuracy.³⁶

Quadrivalent cerium

Cerium^{IV} compounds have been used extensively in oxidimetric processes since the work of Willard and Young,³⁷ although limited to strongly acidic solutions. The normal potential of the cerium^{IV}-cerium^{III} couple largely depends on the acidity and on the nature of the acid. It varies from 1.8 V in perchloric acid via 1.60 V in nitric acid and 1.45 V in sulphuric acid to 1.28 V in 1M hydrochloric acid. Thus cerium^{IV} is always a strong oxidising agent with an average of about the same strength as potassium permanganate. As a strong oxidant in an acidic medium it has, in general, surpassed its competitors for the following reasons:

- (1) In a sulphuric acid medium (not in nitric or perchloric acids), solutions of cerium^{IV} sulphate can be boiled for several hr without any decomposition. This is a great advantage in slow oxidation processes, e.g. of organic compounds.
- (2) The half reaction of the cerium^{IV}-cerium^{III} couple is a one electron transfer and therefore there are no unstable and highly reactive intermediates as is the case in the reduction of permanganate and dichromate in an acidic medium, so that induced reactions do not disturb the stoichiometry of an oxidation with cerium^{IV}.

There are also a few arguments against the use of cerium^{IV}:

- (1) In spite of the high oxidation potential there is sometimes a lack of reactivity, so that catalysts are necessary to bring about the desired reaction, e.g. with arsenic^{III}.
- (2) The limitation of its applicability to acidic solutions makes it unsuitable for the determination of compounds preferably or exclusively oxidised in neutral or alkaline solutions.

The latter limitation has been one of the main difficulties in the determination of organic compounds by complete oxidation with cerium^{IV}. Very often formic acid is one of the products of such oxidations and this compound is only incompletely oxidised by means of cerium^{IV} under normal conditions, so that correct results in the analysis of organic compounds could only be obtained by means of empirical factors.

Recently, Sharma and Mehrotra^{38,39,40} indicated some new possibilities in solving this problem by means of the use of chromium^{III} as a suitable catalyst for the oxidation of some organic acids by means of cerium^{IV} to carbon dioxide and water in boiling 60% sulphuric acid. Without a catalyst Sharma⁴¹ reported correct results for the oxidation of some carbohydrates to formic acid.

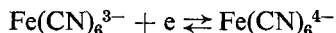
Very recently Mathur *et al.*⁴² proposed potassium bromide as a catalyst in oxidations with cerium^{IV} of those organic compounds which normally yield formic acid without a catalyst. With bromide added, a few hr are sufficient for complete oxidation to carbon dioxide and water in 1M sulphuric acid.

In conclusion, the incomplete oxidation of organic compounds in an acidic medium is the main problem in the determination of organic compounds by complete

oxidative breakdown. As the work of the Indian investigators has already demonstrated, this problem has to be solved by means of the use of suitable catalysts.

Hexacyanoferrate (III)

The normal potential ($E_0 = 0.356$ V) of the half reaction:



is independent of the pH of the medium. Therefore, hexacyanoferrate (III) is a strong oxidising agent in alkaline solutions only. The reactivity is, however, not very large and the applications to organic analysis have been limited to some moderate oxidations, which have been reviewed recently.⁹

Potassium dichromate

The dichromate–chromium^{III} couple with a normal potential of 1.33 V at pH = 0 is only of interest in an acidic solution. In an alkaline solution dichromate is converted into chromate, which is not a strong oxidising agent.

For rapid oxidations dichromate has no advantage over permanganate and cerium^{IV}, but for slow processes it may be of interest because potassium dichromate is available in a very pure state, it does not decompose upon boiling in sulphuric acid solution and the difference between the normal potential of the cerium^{IV}–cerium^{III} couple and dichromate–chromium^{III} couple is too small to leave dichromate out of consideration for that reason alone. One must always, however, be prepared for induced side reactions.

Several quantitative determinations are known in which organic compounds, especially alcohols, are oxidised to carbon dioxide and water, but in many other processes the reaction is not stoichiometric.⁴³

DISCUSSION

With this survey of the powerful oxidising agents in mind, some general rules of conduct for the complete oxidation of organic compounds will now be attempted, *i.e.* to see which oxidising agent should be selected and what should be the experimental conditions such as temperature and acidity.

Experimental results published by Pode and Waters⁴⁴ and by Imhof³⁰ and other data well known from organic chemistry give some knowledge about the pH at which organic compounds are preferably oxidised. Although there are exceptions, oxidations of some aliphatic acids *e.g.* malic acid, malonic acid, and nearly all aromatic acids, including phenolic compounds, proceed better in acidic than in alkaline media. On the contrary some other aliphatic acids, *e.g.* formic acid, lactic acid, alcohols, aldehydes and enolisable ketones can be better oxidised in an alkaline solution.

It is obvious that the oxidation of a complicated organic compound in a certain medium may result in products that are not further oxidised under the same conditions, so that for a further oxidation it will be necessary to change the conditions. For such a change, the pH of the solution must be particularly considered.

Imhof³⁰ has already described such a change in his standard procedure, consisting of a 24-hr oxidation of the organic compound in an alkaline medium with permanganate, followed by acidification of the reaction mixture and another 1 hr for further oxidation. This is a good procedure, for example, for oxidation of organic compounds that result in oxalic acid, which is not oxidised in an alkaline solution. The procedure should not, however, be generalised and in other cases the order

alkaline-acid might be better reversed *e.g.* in the oxidation of compounds being oxidised to formic acid in an acidic medium. The oxidation of formic acid is, as stated already, slow in an acidic medium and rapid in alkaline solution.

One can easily imagine that there could be oxidations in which a second change of medium would be useful to obtain a complete oxidation. Polak³⁶ demonstrated that the order alkaline oxidation-acid oxidation is in many cases not the best one and is in some cases without purpose, namely when no reaction occurs in an alkaline medium, *e.g.*, citric acid. He therefore critically examined every organic compound to be analysed before deciding to oxidise in either acid or alkaline solution only, or in both media. Thus, tartaric acid, fumaric acid and maleic acid are oxidised completely to carbon dioxide and water when the oxidation is started with acidic cold permanganate solution, continued in warm alkaline manganate solution and finished with a back titration in an acidic solution. On the other hand, pyruvic acid can be oxidised using in turn warm alkaline manganate-cold acid permanganate.

The data about the influence of the medium on the oxidation of organic compounds can also be applied to the analysis of mixtures. Some examples are:

- (1) For a mixture of oxalic acid, formic acid and acetic acid,³⁴ the sum of oxalic acid and formic acid is determined by oxidation in an alkaline medium, then continued in an acidic medium; acetic acid remains unchanged. In an alkaline solution only formic acid is oxidised. The total acid can be obtained by means of an alkalimetric titration.
- (2) For a mixture of formaldehyde and formic acid,³⁵ in an alkaline solution oxidation by manganate yields carbon dioxide and water. In the same medium formaldehyde can be determined by oxidation to formic acid according to Romijn.⁶ by manganate proceeds to carbon dioxide and water. In the same medium formaldehyde can be determined by means of oxidation to formic acid according to Romijn.⁶
- (3) The same procedure can be applied to formaldehyde-methanol mixtures,³⁵ which are of practical importance.

When the influence of the medium on the oxidation of organic compounds is set aside and some attention given to the effect of temperature, it is obvious that the possibility of a high temperature is a great advantage.

In the survey of oxidising agents, it was seen that in an acidic medium only three of them had practical applications in the complete oxidation of organic compounds, namely permanganate, dichromate and cerium^{IV}, of which only the latter two can be used at boiling temperature in a sulphuric acid medium. In an alkaline solution only permanganate and manganate were of importance in the analysis under consideration, of which only the latter one could be used at higher temperatures.

When the influences of temperature and medium are combined it may be stated that permanganate is stable in an acidic and to a certain extent also in an alkaline medium, and that this is one of the reasons for its wide application in this field. However, the impossibility of working at higher temperatures requires further research in this field with other reagents *e.g.* by making use of an oxidation in two media of different acidity by means of two different reagents. An oxidation could be begun in a boiling sulphuric acid medium with cerium^{IV} or dichromate and continued in a warm alkaline solution with manganate or the reverse procedure. Better results appear possible by means of such procedures.

There is another section of this field in which attention has at present been revived, namely catalysis. To this process further attention should be given. It often opens up possibilities for new oxidations or it offers a more elegant procedure for an already known analysis. Very recently a number of investigations^{19,42,45,46,47,58} using catalysts have been published.

Note. Apart from applications, already mentioned in this paper, the quantitative oxidation of an organic compound to carbon dioxide and water may be of value in its purity control. Very often the control of the purity of an organic acid is carried out by means of an alkalimetric determination. When, however, an acidic impurity is present false results are obtained. There is more certainty when a second procedure, e.g. an oxidimetric one, gives analogous results.

Zusammenfassung—Es wird eine Übersicht gegeben über die kräftige Oxidation organischer Substanzen in wässriger Lösung mittels sehr starker, zur quantitativen Analyse geeigneter, Oxydationsmittel. Deruss Einfl der Säuregrad der Lösung und die Möglichkeit bei höheren Temperaturen zu arbeiten werden besprochen.

Résumé—On présente une mise au point de l'oxidation forte en solutions aqueuses de corps organiques. Les influences de l'acidité des solutions et la possibilité de travailler à des températures élevées sont discutés.

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IMPROVED RADIOCHEMICAL DETERMINATION OF COBALT*

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Summary—A shortened procedure for the radiochemical determination of cobalt is described. The precipitation of cobalt mercury^{II} thiocyanate for the final yield determination, proposed by Hahn and Smith,¹ has been verified. Decontamination from 5-hr cooled fission products and 1-day cooled stainless steel activation products is complete.

RECENTLY Hahn and Smith¹ surveyed the then existing procedures for the radiochemical determination of cobalt. They concluded that the method of Burgus,² with a changed yield determination, was best. The change in yield determination was from the electrodeposition of cobalt to precipitation as cobalt mercury^{II} thiocyanate, $\text{Co}[\text{Hg}(\text{SCN})_4]$.

At the time their article appeared, research in our laboratory had resulted in a method using this same precipitate. Our reasons for the selection of this precipitate are in complete agreement with those stated in the article. However, in our method the separation steps prior to the yield determination require only 45 min, resulting in a saving of over 1 hr in the overall procedure with no significant change in decontamination. Omitting the potassium cobaltinitrite and sulphide precipitations, two of the more tedious steps, accounts for most of the time saving.

EXPERIMENTAL

Procedure

1. Place an aliquot of sample in a 50-ml centrifuge containing 1 ml of cobalt carrier [10 mg/ml as $\text{Co}(\text{NO}_3)_2$]. Add sufficient sodium hydroxide to precipitate $\text{Co}(\text{OH})_2$ completely. Centrifuge and discard the supernatant solution.
2. Dissolve the precipitate in a minimum (*ca.* 2 drops) of conc. sulphuric acid. Heat, if necessary, until dissolution is complete and the cobalt red colour appears. Cool, add 2 ml of conc. ammonium hydroxide solution, and dilute to 10 ml with water.
3. Slowly add 10 drops of 10 mg/ml iron^{III} holdback while vigorously swirling the solution. Centrifuge and decant (or filter) into a 125-ml separatory funnel.
4. Add 2 ml of glacial acetic acid, 20 ml of 25% ammonium thiocyanate solution (pH 7.0), and 10 ml of methyl isobutyl ketone. Extract for 1 min. Discard the aqueous phase.
5. Add 20 ml of 25% ammonium thiocyanate solution and scrub the organic phase for 1 min. Discard the aqueous phase. Repeat.
6. Strip the cobalt with 5 ml of water for 30 sec. Drain the aqueous phase into a clean 50-ml centrifuge tube. Repeat the strip with an additional 5 ml of water, combining the aqueous portions. Add 3 drops of conc. hydrochloric acid.
7. Heat nearly to boiling and add 2 ml of 1M ammonium mercury^{II} thiocyanate. Swirl until precipitation of the blue cobalt thiocyanate is complete, as evidenced by the lack of red colour in solution.
8. Cool in an ice bath and filter onto a tared filter. Wash with water, ethanol, and ether. Dry for 5 min in a vacuum desiccator and weigh as $\text{Co}[\text{Hg}(\text{SCN})_4]$ (11.98% by weight cobalt).

* Work performed under contract At(10-1)-205 for the U.S. Atomic Energy Commission.

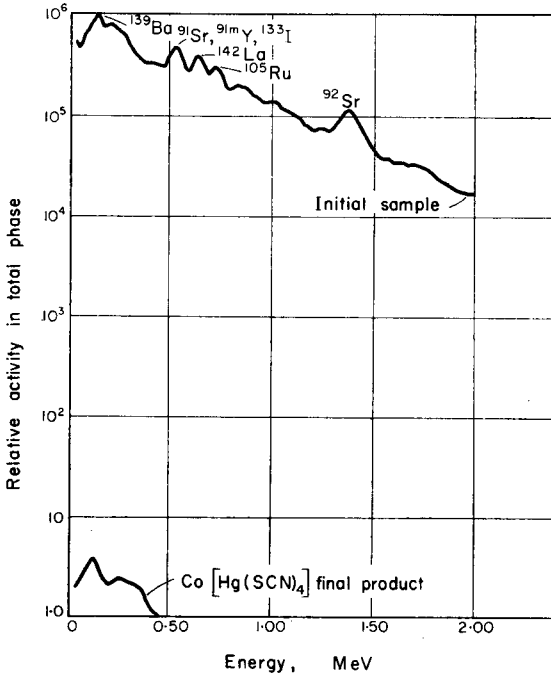


FIG. 1.—Decontamination from 5-hr cooled fission products.

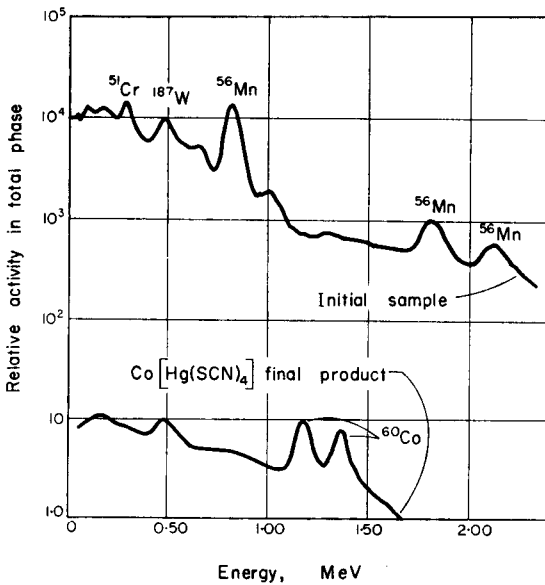


FIG. 2.—Decontamination from 1-day cooled stainless steel activation products.

The gamma ray spectra shown in Figs. 1 and 2 illustrate the decontamination of cobalt from 5-hr cooled fission products and 1-day cooled stainless steel (Bureau of Standards Sample No. 123-A) activation products.

Zusammenfassung—Es wird ein gekurztes Verfahren zur radiochemischen Bestimmung von Kobalt beschrieben. Die Fällung von Kobalt mercurirhodanid wird nach Hahn und Smith für die endliche Bestimmung bestätigt. Die Entgiftung ist aus 5-Stunde-gekühlt Spaltprodukten und 1-Tag-gekühlt-Nichtröstende-stahl-Aktivierungsprodukten völlig.

Résumé—Les auteurs décrivent une méthode simplifiée de dosage radiochimique du cobalt. La précipitation du mercurithiocyanate de cobalt pour le dosage final, proposée par Hahn et Smith, a été vérifiée. La décontamination des produits de fissions refroidis pendant 5 heures et des produits d'activation de l'acier inoxydable refroidis pendant 1 jour est complète.

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TITRIMETRIC DETERMINATION OF VANADIUM^{IV} WITH CERIUM^{IV} SULPHATE AT ROOM TEMPERATURE USING RHODAMINE 6G AS FLUORESCENT INDICATOR

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Summary—The titration of vanadium^{IV} has been carried out with cerium^{IV} sulphate at room temperature in a medium containing sulphuric acid and syrupy phosphoric acid, using Rhodamine 6G as an internal fluorescent indicator. At the equivalence point the greenish-yellow fluorescence of the indicator is suddenly quenched with a slight excess of the oxidant.

FROM a potentiometric study of the titration of vanadium^{IV} with cerium^{IV} sulphate, Furman¹ found that accurate results are obtained at room temperature only when the titration is carried out slowly in the neighbourhood of the end-point and waiting for several min for the potential to become constant. Furman reported that the titration can be carried out at 50–60° as the rate of reaction is rapid at this temperature, and that the titration is as satisfactory as the permanganate titration is at 80°. According to Furman the break in potential at the end-point per 0.05 ml of 0.05*N* cerium^{IV} solution varies from 25 to 100 mV as the initial volume of the solution is varied between 200 and 25 ml, respectively. Willard and Young² independently studied the same titration and found that titrations at 70–80°, using 5–15 ml of sulphuric acid per 100 ml of the titration mixture, give accurate results when carried out in either direction, although the break in potential at the end-point decreases as the acidity is increased.

Kolthoff and Belcher³ state that no visual end-point methods appear to have been described for the determination of vanadium^{IV}. Willard and Young⁴ appear to have investigated without success the use of ferroin as an internal indicator in this titration.

From the experiments of Furman (*loc. cit.*) and Willard and Young (*loc. cit.*) it appears that the reaction between vanadium^{IV} and cerium^{IV} sulphates is slow at room temperature. During a study of the possible influence of various catalysts, we observed that orthophosphoric acid (overall concentration 0.30–0.45*M*) markedly accelerates the reaction in dilute sulphuric acid, so that the titration of vanadium^{IV} with cerium^{IV} sulphate can then be made at room temperature using Rhodamine 6G as a fluorescent indicator. The equivalence point is indicated by a sudden quenching of the fluorescence of Rhodamine 6G with the addition of a very slight excess of cerium^{IV} sulphate solution. Without the presence of the phosphoric acid catalyst, Rhodamine 6G gives a correct indication of the end-point when the titration is carried out at 70–80°.

EXPERIMENTAL

Reagents

Vanadium^{IV} Sulphate Solution, approximately 0.05*N*: Prepared by reducing an aliquot volume of about 0.1*N* sodium vanadate solution in a sulphuric acid medium with sulphur dioxide at boiling temperature, then making up the solution to the desired volume after having driven off the sulphur dioxide completely by passing a rapid stream of carbon dioxide.

Cerium sulphate solution approximately 0.05*N*: Prepared in the usual manner from B.P. cerium oxalate free from iron, and standardised against B.D.H. AnalaR quality sodium oxalate.

Orthophosphoric acid: Syrupy phosphoric acid of Pro Analyti grade supplied by E. Merck (Germany).

0.035% *Rhodamine 6G solution*: Prepared from Rhodamine 6G supplied by B.D.H. Ltd. and stored in an amber coloured bottle.

All other chemicals used in this investigation were of analytical reagent grade.

Catalytic effect of orthophosphoric acid

The following experiments were made to demonstrate the accelerating action of orthophosphoric acid on the reaction between vanadium^{IV} and cerium^{IV} sulphates: 0.5 ml of approximately 0.01*N* vanadium^{IV} sulphate solution was added to 50 ml of 2.0*N* sulphuric acid. To this mixture was added 0.2 ml of 0.035% Rhodamine 6G solution. The resulting mixture had a greenish-yellow fluorescence in the diffuse light of the laboratory. Such a mixture was treated with varying volumes of approximately 0.01*N* cerium^{IV} sulphate solution, while being stirred with a magnetic stirrer, and the observations are recorded in Table I. Similar experiments were also made in the presence of 1.0 ml of syrupy phosphoric acid.

In the above experiments, the concentration of vanadium^{IV} was equivalent to what obtains

TABLE I

Serial no.	Volume of cerium ^{IV} sulphate solution added, ml	Observations	
		A—In absence of phosphoric acid	B—In presence of 1.0 ml of syrupy phosphoric acid
1	0.10	Intensity of fluorescence decreases somewhat; original intensity restored after 20 sec.	No change in intensity of fluorescence
2	0.20	Fluorescence nearly completely quenched, but begins to reappear in 20 sec, reaching original intensity in about 40 sec.	No change in intensity of fluorescence.
3	0.30	Fluorescence completely quenched, but begins to reappear after 25 sec; maximum intensity is reached in 60 sec, but original intensity not regained.	Intensity of fluorescence decreases somewhat, but regains original intensity almost immediately.
4	0.40	Fluorescence completely quenched; feeble fluorescence reappears after 45 sec and intensifies with time; original intensity not regained.	Intensity of fluorescence decreases somewhat, but begins to intensify almost immediately, reaching original intensity in 5 sec.
5	0.50	Fluorescence completely quenched; fluorescence begins to appear in 85 sec and intensifies in 120 sec; original intensity not regained.	Fluorescence completely quenched, but almost immediately reappears, reaching original intensity in about 10 sec.
6	0.55	Fluorescence completely quenched; very feeble fluorescence reappears after 150 sec but does not intensify with time.	Fluorescence completely quenched, but reappears after 5 sec; intensity low and does not increase with time.
7	0.60	Fluorescence immediately quenched, and does not reappear even after 5 min.	Fluorescence immediately quenched and does not reappear even after 5 min.

towards the equivalence point of a titration of 0.05*N* solution. The amount of vanadium^{IV} taken was equivalent to 0.51 ml of the cerium^{IV} sulphate solution used in these experiments.

Rhodamine 6G appears to undergo ready oxidation by cerium^{IV} sulphate to an intermediate oxidation product, which may be in the nature of a free radical and is practically non-fluorescent. The intermediate oxidation product can undergo reduction by vanadium^{IV} sulphate somewhat slowly, or undergo further oxidation by cerium^{IV} sulphate to an irreversible state which is also non-fluorescent. In experiments 2A and 3A it is seen that the fluorescence is almost completely quenched, immediately on the addition of cerium^{IV} sulphate, although there is vanadium^{IV} sulphate present in excess of the amount of cerium^{IV} sulphate added. From this observation, it is concluded that the reaction between Rhodamine 6G and cerium^{IV} sulphate is much more rapid than the vanadium^{IV}-cerium^{IV} sulphate reaction. Consequently, the cerium^{IV} sulphate added reacts with Rhodamine 6G in preference to vanadium^{IV}. In the corresponding experiments 2B and 3B, where phosphoric acid is present, it is observed that the fluorescence is practically unaffected. This observation leads to two conclusions:¹ that cerium^{IV} sulphate reacts rapidly with vanadium^{IV} in the presence of phosphoric acid, and² that any oxidised Rhodamine 6G is rapidly reduced back to the original fluorescent form by vanadium^{IV}, this reduction being more rapid in the presence of phosphoric acid than in its absence. These conclusions receive further support from experiments 5A and 5B. In experiment 5A, the amount of cerium^{IV} sulphate added is nearly equivalent to the vanadium^{IV} present, but the fluorescence of Rhodamine 6G is completely quenched, a feeble fluorescence reappearing only after 85 sec. This shows that in the absence of phosphoric acid: (1) Rhodamine 6G is oxidised in preference to vanadium^{IV}, and (2) reduction of the intermediate oxidised product of Rhodamine 6G by vanadium^{IV} is so slow that it is further oxidised by cerium^{IV} to the irreversible product. However, in the corresponding experiment 5B where phosphoric acid is present, it is noted that although the fluorescence of the dye is quenched immediately on the addition of cerium^{IV}, it reappears almost immediately, reaching the original intensity in about 10 sec. This result indicates that: (1) the vanadium^{IV}-cerium^{IV} reaction is accelerated by phosphoric acid, and (2) although Rhodamine 6G is oxidised to the intermediate state, it is very quickly reduced back to the fluorescent dye because of the acceleration by phosphoric acid. In experiment 7B, the fluorescence is completely quenched although there is phosphoric acid present. This is so because the cerium^{IV} sulphate added is in excess of that required for the complete oxidation of the vanadium^{IV} present. The amount of Rhodamine 6G added to the solution requires about 0.08 ml of 0.01*N* cerium^{IV} sulphate for complete oxidation.

Experiments similar to those recorded in Table I have been conducted with more concentrated solutions of vanadium^{IV} and cerium^{IV} and the observations recorded in Table II.

The observations recorded in Table II lead to the same conclusions as those in Table I. In experiments 1B, and 2B, there is no quenching of the fluorescence whereas in experiments 3B, 4B and 5B, even though the fluorescence is quenched, it is very rapidly regained. Evidently phosphoric acid present in the mixture accelerates the reaction between vanadium^{IV} and cerium^{IV} so much that there is no cerium^{IV} left for the oxidation of Rhodamine 6G; or even if the dye is oxidised, it is only to the intermediate free radical state, which is again rapidly reduced back to the fluorescent dye by the vanadium^{IV} present, because this reaction is also accelerated by phosphoric acid. In experiment 6B, the cerium^{IV} salt added is slightly in excess of the vanadium^{IV} present, so that the dye is oxidised to the irreversible non-fluorescent state.

In view of the above findings, it may be concluded that the titrimetric determination of vanadium^{IV} is possible at room temperature using orthophosphoric acid as catalyst and Rhodamine 6G as internal indicator.

Factors influencing the oxidation of Rhodamine 6G by cerium^{IV}

In order to ascertain the optimum conditions for the best functioning of the indicator, the following experiments were made on the speed of the reaction between cerium^{IV} sulphate and Rhodamine 6G at various acidities in the presence and absence of phosphoric acid, cerium^{III} sulphate and vanadium^{IV}. The observations are recorded in Table III.

The observations in Table III show that the oxidation of Rhodamine 6G by cerium^{IV} sulphate is retarded by phosphoric acid but the retardation decreases as the acid concentration is increased. When the concentration of sulphuric acid is 2.0*N*, the oxidation of the dye is immediate even in the presence of 2.0 ml of syrupy phosphoric acid.

Because phosphoric acid is necessary for the acceleration of the reaction between vanadium^{IV} and cerium^{IV}, it is seen that for a satisfactory titration of vanadium^{IV} with cerium^{IV} using Rhodamine 6G as internal indicator, the acidity should be between 1.5 and 2.0*N*. In these limits of sulphuric acid concentration, 1.0 to 1.5 ml of syrupy phosphoric acid is sufficient to accelerate the reaction between vanadium^{IV} and cerium^{IV}; the acidity is sufficient to counteract the retarding influence of phosphoric acid on the oxidation of the dye by cerium^{IV}. However, the acidity cannot be made too high, because vanadium^V itself is capable of oxidising the dye in 4.0*N* sulphuric acid or in 3.0*N* sulphuric acid in the

presence of phosphoric acid, as shown in the last two experiments of Table III. The addition of cerium^{III} sulphate has been observed to have no effect on the speed of oxidation of the dye.

Factors influencing the reduction of Rhodamine 6G by vanadium^{IV}

It has already been stated that the immediate quenching of the fluorescence of Rhodamine 6G by cerium^{IV} appears to be caused by the oxidation of the dye to an intermediate free radical state, which is non-fluorescent and that the dye in the free radical state can be reduced back to the original

TABLE II

Serial no.	Volume of cerium ^{IV} sulphate solution added, ml	Observations	
		A—In absence of phosphoric acid	B—In presence of syrupy phosphoric acid
1	0.10	Fluorescence disappears but begins to reappear after 4 sec and reaches maximum intensity in 10–15 sec.	No change in the intensity of fluorescence.
2	0.20	Fluorescence completely quenched but begins to reappear after 8 sec, reaching maximum intensity in 20 sec.	Intensity of fluorescence decreased somewhat but almost immediately regains original intensity.
3	0.30	Fluorescence completely quenched; begins to reappear after 13 sec, reaching maximum intensity after 30 sec.	Fluorescence quenched but almost immediately reappears, regaining original intensity in 5 sec.
4	0.40	Fluorescence completely quenched but begins to reappear after 25 sec, reaching maximum intensity after 50 sec but much lower than original intensity.	Fluorescence completely quenched but begins to reappear in 2 sec, and intensifies in 10 sec.
5	0.45	Fluorescence completely quenched but begins to reappear after 60 sec; intensity of fluorescence very feeble even after long time.	Fluorescence completely quenched but begins to reappear in 3 sec, regaining original intensity in 10 sec.
6	0.51	Fluorescence completely quenched, and does not reappear even after 5 min.	Fluorescence completely quenched, and does not reappear even after 5 min.

50 ml of 2.0*N* sulphuric acid + 0.5 ml of vanadium^{IV} solution (0.05443*N*) + 0.2 ml of 0.035% Rhodamine 6G solution. Concentration of cerium^{IV} sulphate solution = 0.05539*N*.

fluorescent dye by vanadium^{IV} or other suitable reductant. Unless the speed of this reduction is rapid, the indicator cannot function properly. If the indicator is oxidised rapidly by cerium^{IV} to the intermediate oxidation product (or even to the final irreversible product) and if the speed of reduction of the intermediate product by vanadium^{IV} is not very fast, it is obvious that premature end-points will result. Hence experiments were made to ascertain the factors which control the reduction of the partially oxidised dye by vanadium^{IV} in the following way: To 50 ml of dilute sulphuric acid, 0.2 ml of 0.035% Rhodamine 6G solution was added, followed by 0.5 ml of 0.005*N* cerium^{IV} sulphate solution, then 0.5 ml of 0.005*N* vanadium^{IV} sulphate solution. If the influence of phosphoric acid was to be studied, it was added before the vanadium^{IV}. Observations were made concerning the times of first appearance of fluorescence of the dye and these are recorded in Table IV. The fluorescence intensifies gradually after the time indicated.

In the experiments marked by an asterisk, the fluorescence is restored by the mere addition of phosphoric acid, without the addition of any vanadium^{IV}. This is probably caused by the acceleration of the disproportionation of the partially oxidised dye by phosphoric acid. The accelerated disproportionation is observed only in media containing sulphuric acid of a concentration not exceeding 1.0*N*.

At higher acid concentrations, the fluorescence is restored only on adding vanadium^{IV}. From the results in Table IV, it is seen that: (1) the reduction of the partially oxidised dye by vanadium^{IV} is a somewhat slow reaction, (2) the speed of reduction is decreased by increasing the concentration of sulphuric acid, and (3) the speed of reduction of the partially oxidised dye by vanadium^{IV} is accelerated by phosphoric acid. A volume of 0.5–1.0 ml of syrupy phosphoric acid is sufficient to accelerate

TABLE III

Additives	Time of quenching of fluorescence of Rhodamine 6G, <i>sec</i>						
	0.2N H ₂ SO ₄	0.5N H ₂ SO ₄	1.0N H ₂ SO ₄	1.5N H ₂ SO ₄	2.0N H ₂ SO ₄	3.0N H ₂ SO ₄	4.0N H ₂ SO ₄
0.05 ml of 0.05N Ce ^{IV}	immediate	immediate	immediate	immediate	immediate	immediate	immediate
0.05 ml of 0.05N Ce ^{IV} + 0.50 ml of syrupy phosphoric acid	135	40	2	immediate	immediate	immediate	immediate
0.05 ml of 0.05N Ce ^{IV} + 1.0 ml of syrupy phosphoric acid	180	80	5	immediate	immediate	immediate	immediate
0.05 ml of 0.05N Ce ^{IV} + 2.0 ml of syrupy phosphoric acid	480	130	20	2	immediate	immediate	immediate
5.0 ml of 0.1N of sodium vanadate	—	—	—	—	—	—	30
5.0 ml of 0.1N sodium vanadate + 1.0 ml of syrupy phosphoric acid	—	—	—	—	—	15	5

Total volume of the reaction mixture 50 ml + 0.2 ml of 0.035% Rhodamine 6G solution.

TABLE IV

Volume of syrupy phosphoric acid added, <i>ml</i>	Time of restoration of fluorescence, <i>sec</i>						
	0.2N H ₂ SO ₄	0.5N H ₂ SO ₄	1.0N H ₂ SO ₄	1.5N H ₂ SO ₄	2.0N H ₂ SO ₄	3.0N H ₂ SO ₄	4.0N H ₂ SO ₄
nil	7	10	12	15	20	30	35
0.5	*	*	*	immediate	immediate	10	12
1.0	*	*	*	immediate	immediate	8	10
2.0	*	*	*	immediate	immediate	5	8

the speed of reduction in a 1.5–2.0N sulphuric acid medium. Moreover, it has also been observed that, in the presence of phosphoric acid, the fluorescence restored by vanadium^{IV} intensifies much more quickly than in the absence of phosphoric acid.

Recommended procedure for the titrimetric determination of vanadium^{IV} using Rhodamine 6G as indicator and phosphoric acid as catalyst

From 5 to 20 ml of 0.05N vanadium^{IV} solution are transferred to an Erlenmeyer flask and sufficient dilute sulphuric acid is added to give an overall acidity of 1.5–2.5N when diluted to 50 ml. The mixture is then treated with 1.0–1.5 ml of syrupy phosphoric acid and 0.2 ml of 0.035% Rhodamine 6G solution and titrated at room temperature with a standard solution of 0.05N cerium^{IV} sulphate, containing sulphuric acid at about 1.0N. The titration is carried out with the usual speed until the greenish-yellow fluorescence of the mixture is quenched. Towards the end of the titration,

it is better to add the cerium^{IV} sulphate in fractions of a drop to avoid any indicator correction when working with 0.05*N* solutions of vanadium^{IV} and cerium^{IV}. Titrations can be made normally in a well-lighted laboratory, without the need for an artificial source of illumination; on a cloudy day, however, titrations should be made with the use of a 100 W incandescent lamp. It should be noted that the light transmitted by Rhodamine 6G is red, whereas the fluorescence light is greenish-yellow. Observations of the change in intensity of the fluorescent light are facilitated by holding a piece of black paper behind the titration flask. When phosphoric acid is used as a catalyst, titrations cannot be made in 0.5–1.0*N* sulphuric acid media, because of the possibility of the precipitation of cerium^{IV} phosphate and of the retardation of the oxidation of the indicator.

Some typical results from a large number of determinations of vanadium^{IV} are presented in Table V. Titrations of 0.01*N* solutions of vanadium^{IV} are also possible under the conditions described above. An indicator correction of 0.08 ml of 0.01*N* cerium^{IV} sulphate solution should be applied.

TABLE V

Titration with 0.05 <i>N</i> vanadium ^{IV} solution		Titration with 0.01 <i>N</i> vanadium ^{IV} solution	
Vanadium ^{IV} taken, <i>mmole</i>	Vanadium ^{IV} found, <i>mmole</i>	Vanadium ^{IV} taken, <i>mmole</i>	Vanadium ^{IV} found, <i>mmole</i>
0.2674	0.2681	0.02927	0.02908
0.3553	0.3538	0.04060	0.04080
0.4454	0.4448	0.05286	0.05277
0.5554	0.5554	0.06042	0.06033
0.6368	0.6401	0.06609	0.06591
0.8600	0.8568	0.07647	0.07656
1.0070	1.0020		
1.0230	1.0200		

Titration of vanadium^{IV} with cerium^{IV} sulphate at 70–80°

Titrations of vanadium^{IV} can be carried out with cerium^{IV} sulphate in a 0.5–2.5*N* sulphuric acid medium at 70–80°, using 0.2 ml of 0.035% Rhodamine 6G solution as indicator. At this high temperature, there is no need for the use of phosphoric acid as a catalyst, because both reactions—the oxidation of vanadium^{IV} by cerium^{IV} sulphate and the reduction of the semi-oxidised indicator by vanadium^{IV}—are very fast. There is no need to use an inert atmosphere. Titrations are not possible in media containing sulphuric acid at 3.0*N* and above, because higher acid concentrations tend to destroy the fluorescence of Rhodamine 6G. Some typical results are given in Table VI.

TABLE VI

Amount of vanadium	
Taken, <i>mmole</i>	Found, <i>mmole</i>
0.2402	0.2412
0.2952	0.2947
0.3128	0.3121
0.4303	0.4204
0.6005	0.5985

Titrations in hydrochloric acid media

Titrations of vanadium^{IV} in hydrochloric acid media using phosphoric acid as catalyst and Rhodamine 6G as indicator have been found to be possible only when the hydrochloric acid concentration is about 2.5–3.5*N*. Below 2.5*N* acid concentration, there is some slight precipitation of cerium^{IV} phosphate and above 3.5*N* hydrochloric acid concentration, the fluorescence of Rhodamine 6G decreases because of the acid itself. Without the use of phosphoric acid, titrations of vanadium^{IV} are possible at 80° in a 0.5*N* hydrochloric acid medium, using the Rhodamine 6G indicator. When the acid concentration is higher, the fluorescence of Rhodamine 6G is decreased because of the combined effect of the increased acid concentration and higher temperature.

Interferences

Iron^{III} and chromium^{III}: The results in Table VII show that iron^{III} does not interfere in the cerimetric determination of vanadium^{IV} using Rhodamine 6G as indicator and phosphoric acid as catalyst at room temperature. With chromium^{III} there is no interference up to about 5 ml of 0.05M chromium^{III} sulphate in 50 ml of the titration mixture, but above this concentration it is difficult to note the fluorescence of Rhodamine 6G. It will also be seen from the results in Table VII that iron^{III} and chromium^{III} do not interfere even when present together at the maximum limits.

TABLE VII

Additive, ml 0.05M solution	Vanadium ^{IV} found, mmole
2.0 of iron ^{III}	0.2859
3.0 of iron ^{III}	0.2859
5.0 of iron ^{III}	0.2880
10.0 of iron ^{III}	0.2869
2.0 of chromium ^{III}	0.2880
3.0 of chromium ^{III}	0.2859
5.0 of chromium ^{III}	0.2880
2.0 ml of iron ^{III} + 3.0 ml of chromium ^{III} }	0.2869

Amount of vanadium^{IV} taken = 0.2869 mmole.

Uranium^{IV}, molybdenum^V and iron^{II}: Uranium^{IV}, molybdenum^V and iron^{II} also react quantitatively with cerium^{IV} sulphate under the conditions prescribed for the titration of vanadium^{IV} in the presence of phosphoric acid at room temperature, using the Rhodamine 6G indicator.

Use of other catalysts

Osmium^{VIII}, iron^{III}, chromium^{III}, and manganese^{II} do not accelerate the reaction between vanadium^{IV} and cerium^{IV} sulphate in 1.0N sulphuric acid.

Zusammenfassung—Die Titration von Vanadin(IV) mit Cer(IV) sulfate bei Raumtemperatur wurde mit Rhodamin 6G als Fluoreszenzindicator durchgeführt. Das Titrationsmedium enthielt konzentrierte Schwefelsäure und sirupöse Phosphorsäure. Beim Äquivalenzpunkt wird die gelbgrüne Fluoreszenz des Indicators abrupt gelöscht, wenn ein kleiner Überschuss von Oxydationsmittel anwesend ist.

Résumé—Les auteurs ont effectué le titrage du vanadium(IV) par le sulfate de cérium(IV) à température ambiante dans un milieu contenant de l'acide sulfurique et de l'acide phosphorique concentré; la rhodamine 6G est utilisée comme indicateur fluorescent interne. Au point équivalent, la fluorescence jaune grisâtre de l'indicateur disparaît brusquement pour un faible excès d'oxydant.

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ANALYTICAL POTENTIAL OF SEPARATIONS BY LIQUID ION EXCHANGE

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Summary—While extractions by liquid anion exchange with alkylamines or quaternary ammoniums and by liquid cation exchange with (especially) organophosphorus acids are being developed intensively for chemical processing, they appear as yet to be used considerably less than other types of extractions in analytical chemistry. It is suggested that this results from chance and habit rather than from any lack of potential usefulness, and that liquid ion exchange warrants increased attention from analytical chemists. Some of the advantages that have proved important in chemical processing should apply also to analytical use. When extractions reported from process and physicochemical applications are included along with analytical reports, a considerable range of extractions is already available to suggest and guide further uses. A representative compilation of such extractions is summarised, and the controlling variables in some of the typical liquid ion-exchange systems are reviewed.

FOR the purpose of this paper, *liquid ion exchange* refers to those liquid-liquid extraction systems that operate, at least formally, by interchange of ions at the interface between an aqueous solution and an immiscible solvent, with negligible distribution of the extracting agent to the aqueous phase. Neither of these criteria is precise. *Negligible* is an elastic description, and some of the extraction systems (as also some resinous ion-exchange systems) can involve transfer of a neutral species followed by further complexing within the organic phase instead of actual interchange of ions. However, those equilibria can still be validly represented as the equivalent exchange of complex ion for free ligand ion, and the definition is useful to distinguish extractions by ionic systems from extractions by chelation systems, by neutral reagents like ethers, esters, and phosphine oxides, and by distribution of complex species already formed in the aqueous phase.

While the preference emphasised for extraction reagents showing only negligible transfer to the aqueous phase is not as essential to analytical extractions as it is to process extractions, it still has advantages to offer. These include avoiding the loss of extraction power by loss of reagent or by competition from that portion of the reagent transferred to the aqueous phase, reproducibility over changing extraction conditions, constant reagent concentration through multistage extractions, and constant composition for final colorimetric determinations in the organic phase.

In comparison with the recent rapid expansion of analytical use of other extraction systems, liquid ion exchange has not yet been much exploited. In a review by Morrison and Freiser in 1960,⁷⁵ only 4 of about 150 analytical extractions tabulated are of this type, and none in their review in 1958.⁷⁴ Instead of accepting that as evidence of low potentiality, it is a purpose of this paper to suggest that liquid ion exchange warrants increased attention, and to summarise a range of liquid ion exchange extractions from process and physicochemical as well as analytical studies

* Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

exchange. Only the cation exchange extends into the alkaline earth and alkali elements. Anion exchange extends further into the metalloids and, of course, includes the hydro- and oxygen acids. Both have been used extensively for the transition metals. It is also noticeable that there has been much attention devoted to the actinides and lanthanides. This reflects the intensive study of these extractions in reactor fuels, raw materials and reprocessing. A blank does not necessarily indicate non-extractability—it may be only lack of information. For instance, the lanthanides missing for some of the extractant classes (Figs. 2–4) certainly must behave somewhat like their neighbours, but they are the rarer ones and were not actually analysed in the studies cited.

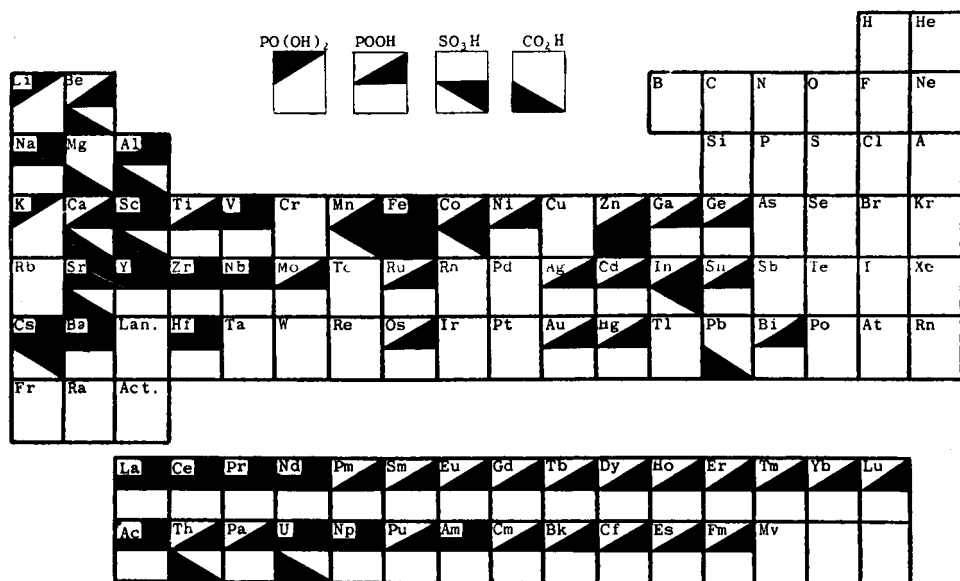


FIG. 2—Extractions with acids.

The reagents and conditions of these extractions are sorted out a step further in Figs. 2–4. Fig. 2 shows the cation-exchange extractions, comparing the use of (1) dibasic monoalkylphosphoric and -phosphonic acids, (2) monobasic dialkylphosphoric and -phosphinic acids, (3) sulphonic acids, and (4) carboxylic acids. Dialkylphosphoric acids have the major share of these reported extractions. Sulphonic and carboxylic acids have as yet been tested to only a slight extent, but probably have an important future.

Fig. 3 shows the extractions with primary amines from solutions in which the major anion was nitrate, chloride, sulphate, or phosphate. The nature of the aqueous anions is more significant here than in cation exchange, where they only exert varying degrees of competition with the reactant, since in anion exchange they often must contribute to forming the extractable species. It is characteristic that primary amine extraction of the transition metals is most important from sulphate and phosphate solutions. The exceptions are those that readily form oxygen anions, *e.g.*, molybdate and pertechnetate. Extractions with tertiary amines and quaternaries (Fig. 4)

TABLE I—LIQUID CATION EXCHANGE EXTRACTIONS

Element	Aqueous phase ^a	Extractant ^c		Reference
		(Type) ^b	Acid/Diluent	
<i>Alkalis</i>				
Li, Na, K, Cs	Nitrate	(H ₂ P)	DDPA/kerosene	24
		(H ₂ P)	HDPA/kerosene	24
Na	CsNO ₃	(HP)	D2EHPA/kerosene	24
Na	Nitrate	(HP)	D2EHPA/Amsco 125-82	24
Cs	Chloride	(HP)	D2EHPA/benzene	5
		(HS)	Dinonylnaphthalene-sulphonic/ benzene	17
	Nitrate	(HS)	Dinonylnaphthalene-sulphonic/ Amsco 125-82	25
<i>Alkaline earths</i>				
Be	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88
	Sulphate	(HP)	D2EHPA/kerosene	51
Ca	0.01M HCl	(HP)	D2EHPA/toluene	53
Be, Mg, Ca	Nitrate, perchlorate	(HCF)	Perfluoro-octanoic/ethers	63
Sr, Ba	Nitrate	(H ₂ P)	DDPA/kerosene	24
	Chloride	(HP)	D2EHPA/toluene	82
		(HP)	D2EHPA/Amsco 125-82	26
Sr	Acetate	(HP)	D2EHPA/benzene	5
	Acetate	(HP)	D2EHPA/Amsco 125-82	24
	Perchlorate	(HP)	D2EHPA/hexanol-Amsco	62
		(HCF)	Perfluoro-octanoic/CCl ₄ + hexone	40
		(H ₂ P)	Various alkyl and aryl acids and acid esters	81
		(HP)		
		(H ₂ Ph)		
		(HPn)		
<i>Group III</i>				
Al	Nitrate	(HP)	D2EHPA + TBP/Amsco	111
	HNO ₃ , pH > 1	(HP)	D2EHPA/Amsco 125-82	54
	Nitrate, perchlorate	(HCF)	Perfluoro-octanoic/ethers	63
	Sulphate	(H ₂ P)	M2EHPA/kerosene	14
		(H ₂ P)	DDPA/kerosene	14
		(H ₂ P)	Various monoalkylphosphoric acids/kerosene	45, 57
		(HP)	D2EHPA/kerosene	51

TABLE I—Cont.

Element	Aqueous phase ^a	Extractant ^c		Reference	
		(Type) ^b	Acid/Diluent		
Rare earths	HNO ₃ , pH <0 Chloride, perchlorate	(HP)	D2EHPA/Amsco 125-82	54	
		(H ₂ P)	M2EHPA/toluene	78	
Sc	Perchlorate	(H ₂ P)	Mono-octylphenylphosphoric/toluene	78	
		(HP)	D2EHPA/toluene	78	
		(HP)	Dioctylphenylphosphoric/toluene	78	
		(HCF)	Perfluoro-octanoic/CCl ₄ + hexone	40	
		(HPn)	Hydrogen 2-ethylhexylphenacyl-phosphonate/cyclohexanol	100, 101	
		(H ₂ P)	Various monoalkylphosphoric acids/ amyl alcohol	102	
Y	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88	
		(HP)	DBP/CHCl ₃	40	
	Perchlorate	(HP)	D2EHPA/toluene	79	
		(H ₂ P)	M2EHPA/toluene	82	
	Chloride, perchlorate	(H ₂ P)	Mono-octylphenylphosphoric/toluene	78	
		(HP)	DBP/toluene	77	
	Lanthanides ^{III}	Nitrate, chloride, sulphate	(HP)	D2EHPA/toluene	77
			(HP)	Dicyclohexylphosphoric/toluene	77
		Perchlorate	(HP)	Dioctylphenylphosphoric/toluene	78
			(HP)	Diphenylphosphoric/toluene	77
Chloride, sulphate		(HP)	D2EHPA/kerosene	23	
		(HP)	D2EHPA/Amsco 125-82	54	
HNO ₃ , pH >0.5		(HP)	D2EHPA/Amsco 125-82	54	
		(HP)	D2EHPA/Amsco 125-82	54	
HNO ₃ , pH >0.3		(HP)	D2EHPA/Amsco 125-82	54	
		(HP)	Several mono- and dialkylphosphoric acids/kerosene	23	
HNO ₃ , pH >0.1	(H ₂ P)(HP)	D2EHPA/ <i>n</i> -heptane	82		
	(HP)	D2EHPA + TBP/Amsco	111		
Nitrate	Perchlorate	(HP)	DBP/dibutyl ether	39	
		(HP)	DBP/CHCl ₃	40	
Lanthanides ^{III}	Chloride	(H ₂ P)	M2EHPA/toluene	77	
		(HP)	D2EHPA/toluene	77	
Lanthanides ^{III}	0.1-1M HCl	(HP)	D2EHPA/toluene	53	
		(HS)	Dionylmaphthalene-sulphonic/ benzene	17	
Lanthanides ^{III}	Nitrate	(HP)	D2EHPA/toluene	79	

	Chloride, perchlorate	(H ₃ P) (H ₂ P) (HP) (HP) (HP) (HP) (HP) (HP) (HP) (HP)	M2EHFA/toluene Mono-octylphenylphosphoric/toluene D2EHFA/toluene Dioctylphenylphosphoric/toluene D2EHFA/kerosene D2EHFA/ <i>n</i> -heptane D2EHFA/Amsco 125-82 D2EHFA/ <i>n</i> -heptane D2EHFA/kerosene + 2-ethylhexanol	78 78 78 77, 78 23 82 23 59 14
Ce ^{IV}	Chloride, sulphate Nitrate 10M HNO ₃ Sulphate	(H ₃ P) (H ₂ P) (HP) (HP) (HP)	M2EHFA/toluene Mono-octylphenylphosphoric/toluene D2EHFA/toluene Dioctylphenylphosphoric/toluene	78 78 78 78
Actinides Ac	Perchlorate	(H ₃ P) (H ₂ P) (HP) (HP)	M2EHFA/toluene Mono-octylphenylphosphoric/toluene D2EHFA/toluene Dioctylphenylphosphoric/toluene	78 78 78 78
Th ^{IV}	HClO ₄ , HNO ₃ , HCl	(HP) (HP)	D2EHFA/toluene Bis (<i>p</i> -tert-octylphenyl) phosphoric/ toluene	80 80
	Nitrate 10M HNO ₃ Nitrate Sulphate 3M H ₂ SO ₄ ≤10M HNO ₃	(HP) (HP) (HC) (HP) (HP) (HP) (HP)	Bis (<i>p</i> -tert-octylphenyl) phosphoric + TBP/toluene D2EHFA/cyclohexane D2EHFA/ <i>n</i> -heptane Salicylic or cinnamic/hexone D2EHFA/kerosene + 2-ethylhexanol D2EHFA + DBBP/Amsco 125-82 DBP/benzene DBP + TBP/kerosene D2EHFA/kerosene	80 80 88 59 48 14 49 46 46 46
Pa ^V	HCl	(H ₃ P) (H ₂ P) (HP) (HP)	M2EHFA/toluene M2EHFA + TBP/toluene D2EHFA/kerosene D2EHFA/kerosene	83 83 15 15
U ^{IV}	< 8M HCl 3M H ₂ SO ₄ 3-5M H ₃ PO ₄	(HP) (HP) (HP) (HP)	D2EHFA/kerosene D2EHFA + TBP/kerosene D2EHFA + DBBP/Amsco 125-82 Bis(3,5,5-trimethylhexyl)phosphoric/ kerosene	49 49 49 12
	Perchlorate	(HP) (HP) (HP) (HP) (HCF)	Bis(di-isobutylmethyl)phosphoric/ kerosene Bis(di-isobutylmethyl)phosphoric + Bu ₃ PO/kerosene D2EHFA/ <i>n</i> -hexane DBP/CHCl ₃ Perfluorobutyric/ethers	12 12 12 8 40 63
U ^{VI}				

TABLE I—Cont.

Element	Aqueous phase ^a	Extractant ^c		Reference	
		(Type) ^b	Acid/Diluent		
U ^{VI}	Nitrate	(HP)	DBP/variou diluents	46	
	<6M HNO ₃ , NaNO ₃	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14	
	<8M HNO ₃	(HP)	D2EHPA + TBP/kerosene	15	
	10M HNO ₃	(HP)	D2EHPA/ <i>n</i> -heptane	59	
	Nitrate	(HC)	Salicylic or cinnamic/kerosene	48	
	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88	
	6M HCl	(H ₂ F)	DDPA/kerosene	12	
	<12M HCl	(H ₂ F)	M2EHPA/toluene	83	
	<8M HCl	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14	
	<12M HCl	(HP)	D2EHPA + TBP/kerosene	15	
	Sea-water	(HP)	D2EHPA + TBP/kerosene	12	
		(HP)	DBP/CCl ₄	96	
		(HP)	D2EHPA/CCl ₄	87	
		(HP)	D2EHPA/CCl ₄	64	
	H ₂ SO ₄	(H ₂ F)	Various monoalkylphosphoric acids/ kerosene	45	
	Sulphate, phosphate		(H ₂ F)	Various combinations of acids, esters or R ₃ PO and diluents	11, 14, 15, 20, 88
			(H ₂ Ph)		
		(HP ⁱⁿ)			
Np ^{VI}	0.1M H ₂ SO ₄	(HP)	DBP + TBP/CCl ₄	41	
	2-5M H ₂ SO ₄	(HP)	D2EHPA + DBBP/Amsco 125-82	49	
	<8M H ₂ SO ₄	(HP)	D2EHPA + TBP/kerosene	15	
	<2M H ₃ PO ₄	(H ₂ P)	Various combinations of acids and diluents	12, 14	
	<10M HNO ₃	(HP)	D2EHPA + TBP/kerosene	15	
	<12M HCl	(HP)	D2EHPA/Amsco 125-82	105	
Np ^{IV}	<2.5M H ₂ SO ₄	(H ₂ P)	M2EHPA/toluene	83	
	10M HNO ₃ -1M KBrO ₃	(HP)	M2EHPA + TBP/toluene	83	
	<12M HCl	(H ₂ F)	D2EHPA/Amsco 125-82	105	
	<8M HNO ₃	(HP)	D2EHPA/ <i>n</i> -heptane	59	
	<10M HNO ₃	(HP)	M2EHPA/toluene	83	
	2M UO ₂ (NO ₃) ₂ + 1M HNO ₃	(HP)	D2EHPA/Amsco 125-82	49	
	3-5M H ₂ SO ₄	(HP)	D2EHPA/Amsco 125-82	49	
		(HP)	D2EHPA + TOPO/Amsco 125-82	49	
		(HP)	D2EHPA + DBBP/Amsco 125-82	49	
		(HP)		49	

Pu ^{VI}	4M HNO ₃	(HP)	D2EHPA/Amsco 125-82	49	
	2-8M HNO ₃	(HP)	D2EHPA/Amsco 125-82 + tridecanol	49	
Am ^{III}	2-4M HNO ₃	(HP)	D2EHPA + TOPO/Amsco 125-82	49	
	10M HNO ₃ + 1M KBrO ₃	(HP)	D2EHPA/ <i>n</i> -heptane	59	
	5M H ₂ SO ₄	(HP)	D2EHPA/Amsco 125-82	49	
	0-1M HNO ₃	(HP)	D2EHPA + TOPO/Amsco 125-82	42	
	Perchlorate, chloride	(H ₂ P) (H ₂ P)	DBP/ <i>n</i> -hexane or CCl ₄ M2EHPA/toluene	77, 78 77, 78	
Am, Cm, Bk, Cf	Nitrate, chloride	(HP)	Mono-octylphenylphosphoric/toluene	77, 78	
	HCl	(HPn)	D2EHPA/toluene Diphenylphosphoric/toluene 2-Ethylhexylphenylphosphonic/ diethylbenzene	78, 79 77 9	
Cm ^{III}	Perchlorate	(HP)	D2EHPA/toluene	77	
	8-10M HNO ₃	(HP)	Diocylphenylphosphoric/toluene	77, 78	
Bk ^{IV}	Chloride	(HP)	D2EHPA/ <i>n</i> -heptane	84	
	8-10M HNO ₃	(HP)	D2EHPA/toluene	77	
Bk ^{III}	8-10M HNO ₃	(HP)	D2EHPA/ <i>n</i> -heptane	84	
	8-10M HNO ₃	(HP)	D2EHPA/ <i>n</i> -heptane	84	
Cf, Es, Fm	Chloride	(HP)	D2EHPA/toluene	77	
	Chloride	(HP)	DBP/toluene	77	
<i>Transition metals</i>	Tl ^{IV}	Nitrate, chloride, sulphate	D2EHPA/cyclohexane	88	
		0-5M HCl	D2EHPA/toluene	53	
		0-5M Na ₂ SO ₄	D2EHPA/kerosene + 2-ethyl- hexanol	14	
	Zr ^{IV}	Nitrate	(H ₂ P-HP)	MBP + DBP/dibutyl ether	89
		Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88
	Zr-Nb ^e	HF in mixed acids, + A(NO ₃) ₃	(HP)	DBP/CHCl ₃	86
		Nitrate	(H ₂ P-HP)	MBP-DBP/dibutyl ether	89
		10M HNO ₃	(HP)	D2EHPA/ <i>n</i> -heptane	59
	Hf ^{IV} V ^{IV}	Perchlorate	(HP)	DBP/CHCl ₃	40
		0-5M Na ₂ SO ₄	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14, 37
Nb ^v	Sulphate	(H ₂ P)	Various monoalkylphosphoric acids/ kerosene	45	
	Nitrate	(H ₂ P-HP)	MBP + DBP/dibutyl ether	89	
	1M HCl	(HP)	D2EHPA/toluene	53	

TABLE I—Cont.

Element	Aqueous phase ^a	(Type) ^b	Extractant ^c		Reference
			Acid/Diluent		
Mo ^{VI}	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88	
	·10M HNO ₃	(HP)	D2EHPA/ <i>n</i> -heptane	59	
	9M HCl	(HP)	D2EHPA/ <i>n</i> -heptane	59	
	0·5M HCl	(HP)	D2EHPA/toluene	53	
	0·5M Na ₂ SO ₄	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14	
Mn ^{II}	Perchlorate	(HS)	Dinonylnaphthalene sulphonic/ heptane	107	
	HNO ₃ , pH > 1·1	(HP)	D2EHPA/Amsco 125-82	54	
Fe ^{II}	<0·01M HCl	(HP)	D2EHPA/toluene	53	
	Sulphate	(H ₂ P)	Various monoalkylphosphoric acids/ kerosene	45, 57	
Fe ^{III}	Perchlorate	(HP)	D2EHPA/ <i>n</i> -octane	7	
	Perchlorate, chloride	(HS)	Dinonylnaphthalene sulphonic/heptane	106, 107	
Ru ^{III}	HNO ₃ , pH < 0	(HP)	Perfluorobutyric/ethers	63	
	<10M HCl	(HP)	Dinonylnaphthalene sulphonic/ benzene	17	
	Nitrate, chloride, sulphate	(HP)	D2EHPA/Amsco 125-82	54	
	0·5M Na ₂ SO ₄	(HP)	D2EHPA/toluene	53	
	HNO ₃ , pH > 1·3	(H ₂ P)	D2EHPA/cyclohexane	88	
	<1M HCl	(HP)	DDPA/kerosene	14	
	Perchlorate	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14	
		(HP)	D2EHPA/Amsco 125-82	54	
		(HP)	D2EHPA/toluene	53	
		(HS)	Dinonylnaphthalene sulphonic/ heptane	107	
Ni ^{II}	HNO ₃ , pH > 2	(HP)	D2EHPA/Amsco 125-82	54	
	HNO ₃ , pH > 3	(HP)	D2EHPA/Amsco 125-82	54	
Group B elements	HNO ₃ , pH > 2	(HP)	D2EHPA/Amsco 125-82	54	
	10M HCl	(HP)	D2EHPA/toluene	53	
	Perchlorate	(HS)	Dinonylnaphthalene sulphonic/ heptane	107	
Ag ^I	Perchlorate, chloride	(HCF)	Perfluoro-octanoic/ethers	63	
	HNO ₃ , pH > 0·9	(HS)	Dinonylnaphthalene sulphonic/benzene	17	
	<0·01M HCl	(HP)	D2EHPA/Amsco 125-82	54	
		(HP)	D2EHPA/toluene	53	

Cd ^{II}	HNO ₃ , pH > 1.2	(HP)	D2EHPA/Amsco 125-82	54
Hg ^I	HNO ₃ , pH < 0	(HP)	D2EHPA/Amsco 125-82	54
Ga ^{III}	< 0.1M HCl	(HP)	D2EHPA/toluene	53
In ^{III}	Perchlorate	(HS)	Dinonylnaphthalene sulphonic/ heptane	106, 107
	Nitrate, sulphate	(HP)	D2EHPA/cyclohexane	88
	HNO ₃ , pH < 0	(HP)	D2EHPA/Amsco 125-82	54
	< 1M HCl	(HP)	D2EHPA/toluene	53
	8M HCl	(HP)	D2EHPA/toluene	53
Ge	Nitrate, chloride	(HP)	D2EHPA/cyclohexane	88
Sn ^{IV}	Perchlorate	(HCF)	Perfluoro-octanoic/ethers	63
Pb ^{II}	0.01M HCl	(HP)	D2EHPA/toluene	53
Bi	< 0.1M HCl	(HP)	D2EHPA/toluene	53

^a Aqueous phase salts listed include neutral to moderately acidic solutions.

^b Types of acid extractants:

- (H₃P) Monoalkylorthophosphoric (diacidic)
- (HP) Dialkylorthophosphoric (monoacidic)
- (H₃Pn) Monoalkylphosphonic
- (HPn) Alkyl monoalkylphosphonic
- (HPin) Dialkylphosphinic
- (HS) Sulphonic
- (HC) Carboxylic
- (HCF) Perfluorocarboxylic

^c Extractants are more fully identified in Table III.

^d Extraction of plutonium present in the aqueous phase as Pu^{IV} may involve oxidation to Pu^V enhanced by strong stabilisation of Pu^V by the extraction system.

^e "Zr-Nb" refers to simultaneous extraction of fission-product or tracer zirconium and niobium, measured by γ -count without differentiation between the two.

TABLE II—Cont.

Element	Aqueous phase ^a	Extractant ^c		Reference
		Class ^b	Amine/Diluent	
Pu ^{VI}	8M HNO ₃	(3)	TIOA/Gulf Solvent BT-decanol	110
	8M HNO ₃	(Q)	Roccal/Gulf Solvent BT-decanol	110
	1-12M HNO ₃	(3)	TOA/Xylene	52, 92
	1-4M HNO ₃	(3)	TLA/Amsco- <i>n</i> -Octanol	108
	0.1 to 10M NO ₃ ⁻ , acid to salt	(1) (2) (3) (Q)	(Many amine-diluent combinations, all classes)	49
Pu ^{VI}	3-6M HNO ₃	(3)	Tris(3,5,5-trimethylhexyl)/Xylene	10
	3M HNO ₃	(Q)	Tetrabutylammonium/CHCl ₃ -benzene	97
	0.5-3M [H ₂ SO ₄ + (NH ₄) ₂ SO ₄]	(1) (2) (3)	(Various amine-diluent combinations)	49
	1-14M HNO ₃	(3)	TOA/Xylene	52
	2-8M HNO ₃	(1) (2) (3) (Q)	(Various amine-diluent combinations)	49
Am, Cm ^{III} Am, Cm, Bk, Cf, Es	6-9M HCl	(3)	Tribenzyl/CHCl ₃	67
	5M HCl	(3)	TIOA/Xylene	68
	1M HOAc	(3)	TIOA/Xylene	69
	10M LiCl	(3)	TIOA/Xylene	70
	>10N LiCl-AlCl ₃	(3)	Alamine 336/di-isopropylbenzene	9
Transition metals Ti ^{IV}	5M NH ₄ SCN	(Q)	Tetra- <i>n</i> -heptyl/Amsco 125-82	103
	1M Na ₂ SO ₄	(3)	TOA/Xylene	92
Zr ^{IV} (and Hf)	0-5M Na ₂ SO ₄	(1)	Amine 21F81/Amsco D-95	72
	>8M HCl	(2)	Dilauryl/Amsco D-95-octanol	72
		(1)	Amine 21F81/kerosene	72
		(3)	MDOA/Xylene	67
		(3)	TIOA/Xylene	68
	1M Na ₂ SO ₄	(3) (1) (2) (3)	TOA/cyclohexane (Various amine-diluent combinations)	31 32

VIII	0.1-1M H ₂ SO ₄	(3)	TOA/kerosene-tridecanol	23
VV	0.5M Na ₂ SO ₄	(1)	Primene JM-T/kerosene	35
	1M Na ₂ SO ₄	(1)	(Various amine-diluent combinations)	19
	(Strongly dependent on pH)	(2)		
Nb ^v	>6M HCl	(3)	MDOA/Xylene	56
	11M HCl	(3)	TIOA/Xylene	68
	1.5M H ₂ SO ₄	(3)	Tribenzyl/CHCl ₃	43
	4M H ₃ SO ₄	(3)	MDOA/trichloroethylene	71
	~2M H ₃ PO ₄	(3)	Tribenzyl/CH ₂ Cl ₂	43
	Carboxylic acids	(3)	MDOA/trichloroethylene	43
Ta ^v	>4.8M H ₂ SO ₄	(3)	Tribenzyl/CHCl ₃	43
	Carboxylic acids	(3)	Tribenzyl/CH ₂ Cl ₂	43
Cr ^{VI}	Aqueous H ₂ CrO ₄	(3)	MDOA/CHCl ₃	94
	6M HCl	(3)	Tribenzyl/CHCl ₃	67
		(3)	TIOA/Xylene	68
Mo ^{IV}	<1M HNO ₃	(1)	(Various amine-diluent combinations)	99
		(2)		
		(3)		
Tc ^{VII}	Aqueous Solutions	(Q)	B-104/kerosene	16
	(acid, neutral, or basic)			
	Acid Solutions	(1)	(Various amine-diluent combinations)	16
		(2)		
		(3)		
Fe ^{III}	6N Al(NO ₃) ₃	(3)	Alamine 336 or TLA/Amsco 125-82-tridecanol	33
	>1M HCl	(3)	MDOA/trichloroethylene	58
		(3)	TIOA/Xylene	68
	<1-12M HCl	(1)	(Various amines in CHCl ₃ and in benzene)	44
		(2)		
		(3)		
Co ^{II}	1M Na ₂ SO ₄	(1)	Amine 21F81/Amsco D-95	32
	<0.5M Na ₂ SO ₄	(1)	Di- <i>n</i> -decyl/benzene	6
	(strongly dependent on pH)	(2)		
	>6M HCl	(3)	MDOA/trichloroethylene	58
		(3)	TIOA/Xylene	68
		(3)	TOA/benzene	23
		(3)	TLA/toluene	70
Ru ^{IV}	2M HNO ₃	(3)	TIOA/Xylene	68
	0.1-9M HCl	(3)		

TABLE II—Cont.

Element	Aqueous phase ^a	Extractant ^c			Reference
		Class ^b	Amine/Diluent		
"B Group" metals					
Cu ^{II}	>4M HCl	(3)	MDOA/trichloroethylene	58	
Ag ^I	LiCl, HCl	(3)	MDOA/trichloroethylene	90	
Zn ^{II}	>1M HCl	(3)	MDOA/Xylene	58, 68	
		(3)	Tribenzyl/CHCl ₃	58	
	2M HCl	(3)	TIOA/hexone	91	
	LiCl, HCl	(3)	MDOA/trichloroethylene	90	
	1-5M HCl	(Q)	Aliquat 336/benzene	85	
Pb^{II}					
Nonmetals					
Po ^{IV}	6M HCl	(3)	Tribenzyl/CHCl ₃	67	
N	HNO ₃	(3)	Tris(3,5,5-trimethylhexyl)/Xylene	10	
		(2)	Amine S-24, Amberlite LA-1, ditiiridecyl/Xylene	49	
		(1)	Primene JM-T/Xylene	49	
S	H ₂ SO ₄	(2)	Di- <i>n</i> -decyl/benzene	3	
		(3)	TOA/benzene	2	
Cl	HCl	(3)	TIOA/toluene	76	
Br	HBr	(3)	MDOA/trichloroethylene	90	

^a Aqueous phase salts listed include neutral to moderately acidic solutions.

^b Classes of amines: (1) Primary
(2) Secondary
(3) Tertiary
(Q) Quaternary ammonium

^c Extractants are more fully identified in Table III.

^d Extractions of plutonium present in the aqueous phase as Pu^{IV} may involve oxidation to Pu^{IV} enhanced by strong stabilisation of Pu^{IV} by the extraction system.

TABLE III—REAGENTS

Class or type ^a	<i>Amines</i>
(1)	<p><i>Amine 21F81</i>, 1-(3-Ethylpentyl)-4-ethyloctylamine (Union Carbide Chem. Co.)</p> $\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ \text{H}_2\text{N}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_3 \\ \\ \text{CH}_2\text{CH}_3 \end{array}$
(1)	<p><i>Primene JM-T</i> (Rohm and Haas Co.) $\text{H}_2\text{N}-\text{C}(\text{R})(\text{R}')\text{R}''$ trialkylmethylamine; $\text{R} + \text{R}' + \text{R}'' = 17-23$ carbon atoms.</p>
(1)	<p>1-<i>Heptyloctylamine</i> (Armour Chemical Division)</p> $\begin{array}{c} \text{H}_2\text{N}-\text{CH}-(\text{CH}_2)_6\text{CH}_3 \\ \\ \text{CH}_2(\text{CH}_2)_5\text{CH}_3 \end{array}$
(1)	<p>1-<i>Undecyllaurylamine</i> (Armour Chemical Division)</p> $\begin{array}{c} \text{H}_2\text{N}-\text{CH}-(\text{CH}_2)_{10}\text{CH}_3 \\ \\ \text{CH}_2(\text{CH}_2)_9\text{CH}_3 \end{array}$
(2)	<p><i>Amberlite LA-1</i>, previously <i>Amine 9D-178</i> (Rohm and Haas Co.)</p> $\begin{array}{c} \text{C}(\text{R})(\text{R}')\text{R}'' \\ \\ \text{HN} \\ \\ \text{CH}_2\text{CH}:\text{CHCH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ <p>N-dodeceny!(trialkylmethyl)amine; $\text{R} + \text{R}' + \text{R}'' = 11-14$ carbon atoms.</p>
(2)	<p><i>Amberlite LA-2</i> (Rohm and Haas Co.)</p> $\begin{array}{c} \text{C}(\text{R})(\text{R}')\text{R}'' \\ \\ \text{HN} \\ \\ \text{CH}_2(\text{CH}_2)_{10}\text{CH}_3 \end{array}$ <p>N-Lauryl(trialkylmethyl)amine; $\text{R} + \text{R}' + \text{R}'' = 11-14$ carbon atoms.</p>
(2)	<p><i>Amine S-24</i> (Union Carbide Chem. Co.) bis(1-isobutyl-3,5-dimethylhexyl)amine</p> $\left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_2\text{CHCH}_2\text{CHCH}_3 \\ \\ \text{HN}-\text{CH} \\ \\ \text{CH}_2\text{CHCH}_3 \\ \\ \text{CH}_3 \end{array} \right]_2$
(2)	<p><i>Di-n-decylamine</i> (Eastman Organic Chemicals, No. p7724)</p> $\text{HN}-[(\text{CH}_2)_9\text{CH}_3]_2$
(2)	<p><i>Ditridecylamine</i> (Union Carbide Chem. Co.)</p> $\text{HN}-[-\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}_{10}\text{H}_{21}]_2$ <p>"Tridecyl" = Mixture of 13-carbon alkyls from tetrapropylene</p>

TABLE III—Cont.

Class
or
type

Amines

- (2) *Dilaurylamine* (Eastman Organic Chemicals, No. p4519)
 $\text{HN}—\left[—(\text{CH}_2)_{11}\text{CH}_3\right]_2$
- (2) *Di(2-propyl-4-methylpentyl)amine* (Eastman Chemical Products)
 $\text{HN}—\left[\begin{array}{c} —\text{CH}_2\text{CHCH}_2\text{CHCH}_3 \\ | \quad | \\ \text{C}_3\text{H}_7 \quad \text{CH}_3 \end{array} \right]_2$
- (2) *Di(1-heptyloctyl)amine* (Armour Chemical Division)
 $\text{HN}—\left[\begin{array}{c} —\text{CH}—(\text{CH}_2)_6\text{CH}_3 \\ | \\ \text{CH}_2(\text{CH}_2)_5\text{CH}_3 \end{array} \right]_2$
- (2) *Di(1-nonyldecyl)amine* (Armour Chemical Division)
 $\text{HN}—\left[\begin{array}{c} —\text{CH}—(\text{CH}_2)_8\text{CH}_3 \\ | \\ \text{CH}_2(\text{CH}_2)_7\text{CH}_3 \end{array} \right]_2$
- (2) *N-(1-nonyldecyl)laurylamine* (Armour Chemical Division)
 $\begin{array}{c} (\text{CH}_2)_{11}\text{CH}_3 \\ | \\ \text{HN} \\ | \\ \text{CH}—(\text{CH}_2)_8\text{CH}_3 \\ | \\ \text{CH}_2(\text{CH}_2)_7\text{CH}_3 \end{array}$
- (2) *N-(1-undecyllauryl)laurylamine* (Armour Chemical Division)
 $\begin{array}{c} (\text{CH}_2)_{11}\text{CH}_3 \\ | \\ \text{HN} \\ | \\ \text{CH}—(\text{CH}_2)_{10}\text{CH}_3 \\ | \\ \text{CH}_2(\text{CH}_2)_9\text{CH}_3 \end{array}$
- (2) *NBHA*, N-benzylheptadecylamine (Union Carbide Chem. Co.)
 N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine.
 $\begin{array}{c} \text{CH}_2\text{C}_6\text{H}_5 \\ | \\ \text{HN} \\ | \quad | \\ \text{CH}—\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \quad | \\ \text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_3 \\ | \\ \text{CH}_2\text{CH}_3 \end{array}$
- (2) *N-Benzyl-(1-nonyldecyl)amine* (Armour Chemical Division)
 $\begin{array}{c} \text{CH}_2\text{C}_6\text{H}_5 \\ | \\ \text{HN} \\ | \\ \text{CH}(\text{CH}_2)_8\text{CH}_3 \\ | \\ \text{CH}_2(\text{CH}_2)_7\text{CH}_3 \end{array}$

TABLE III—Cont.

Class or type	<i>Amines</i>
(2)	<p><i>N</i>-Benzyl-1-undecyllaurylamine (Armour Chemical Division)</p> $\begin{array}{c} \text{CH}_2\text{C}_6\text{H}_5 \\ \\ \text{HN} \\ \\ \text{CH}(\text{CH}_2)_{10}\text{CH}_3 \\ \\ \text{CH}_2(\text{CH}_2)_9\text{CH}_3 \end{array}$
(3)	<p><i>TLA</i>, trilaurylamine (Archer-Daniels-Midland Co.; General Mills, Inc.; Eastman Organic Chemicals, No. 7727)</p> $\text{N}-\left[-(\text{CH}_2)_{11}\text{CH}_2\right]_3$
(3)	<p><i>Alamine 336</i> (General Mills, Inc.)</p> $\text{N}-\left[-(\text{CH}_2)_{7-11}\text{CH}_2\right]_3$ <p>straight chain alkyls, principally octyl and decyl.</p>
(3)	<p><i>TOA</i>, tri-<i>n</i>-octylamine (Eastman Organic Chemicals, No. P7723)</p> $\text{N}-\left[-(\text{CH}_2)_7\text{CH}_2\right]_3$
(3)	<p><i>TIOA</i>, Tri-<i>iso</i>-octylamine (Union Carbide Chem. Co.)</p> $\text{N}-\left[\begin{array}{c} -\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CHCH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}\right]_3$ <p>"iso-octyl" = mixture of dimethylhexyls and methylheptyls, etc., principally 3,5-, 4,5-, and 3,4-dimethylhexyl.</p>
(3)	<p><i>Tri-isononylamine</i>, trist(3,5,5-trimethylhexyl)amine [I.C.I. (Heavy Organic Chemicals) Ltd., Billingham, Eng.]</p> $\text{N}-\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CCH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}\right]_3$
(3)	<p><i>Amberlite XE-204</i>, didodecenyln-<i>n</i>-butylamine (Rohm and Haas Co.)</p> $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3(\text{CH}_2)_8-\text{N}-\left[-\text{CH}_2\text{CH}:\text{CHCH}_2\text{CCH}_2\text{CCH}_3\right]_2 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
(3)	<p><i>Butyldilaurylamine</i> (Laboratory preparation)</p> $\text{CH}_3(\text{CH}_2)_8-\text{N}-\left[-(\text{CH}_2)_{11}\text{CH}_2\right]_2$
(3)	<p><i>Tribenzylamine</i> (Eastman Organic Chemicals, No. 1015)</p> $\text{N}-\left[-\text{CH}_2\text{C}_6\text{H}_5\right]_3$
(Q)	<p><i>Aliquat 336</i> (General Mills, Inc., as chloride)</p> $\left[\text{CH}_3-\text{N}-\left(-(\text{CH}_2)_{7-11}\text{CH}_2\right)_3\right]^+$ <p>Trialkylmethyl ammonium, straight chain alkyls, principally octyl and decyl.</p>
(Q)	<p><i>B-104</i>, Experimental Quaternary B-104 (Rohm and Haas Co., as chloride)</p> $\left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ (\text{CH}_3)_2-\text{N}-\left(-\text{CH}_2\text{CH}:\text{CHCH}_2\text{CCH}_2\text{CCH}_3\right)_2 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}\right]^+$ <p>Dimethyl-didodecenyllummonium.</p>

TABLE III—Cont.

Class or type	<i>Amines</i>
(Q)	<i>Roccal</i> , (Sterwin Chemicals, Inc., as chloride) $\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5\text{CH}_2-\text{N}-\text{CH}_{7-11}\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right]^+$
(Q)	<i>Tetrabutylammonium</i> (Eastman Organic Chemicals, No. 7377, as bromide) $[\text{N}-(\text{---}(\text{CH}_2)_3\text{CH}_3)_4]^+$
(Q)	<i>Tetra-<i>n</i>-heptylammonium</i> (Eastman Organic Chemicals, No. 7630, as iodide) $[\text{N}-(\text{---}(\text{CH}_2)_6\text{CH}_3)_4]^+$
	<i>Acids</i>
(H ₂ P)	<i>MBP</i> , mono- <i>n</i> -butylphosphoric acid (Victor Chemical Corp., Monsanto Chemical Co.) $\begin{array}{c} \text{O} \\ \\ (\text{HO})_2-\text{P}-\text{O}-(\text{CH}_2)_3\text{CH}_3 \end{array}$
(H ₂ P)	<i>M2EHPA</i> , mono-2-ethylhexylphosphoric acid (Victor Chemical Co.) $\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ \text{O} \\ \\ (\text{HO})_2-\text{P}-\text{O}-\text{CH}_2\text{CH}(\text{CH}_2)_3\text{CH}_3 \end{array}$
(H ₂ P)	<i>DDPA</i> , monododecylphosphoric acid ("Dowsol 12," Dow Chemical Co.) $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2 \\ \\ \text{O} \\ \\ (\text{HO})_2-\text{P}-\text{O}-\text{CH} \end{array}$
(H ₂ P)	<i>TDPA</i> , monotetradecylphosphoric acid (Virginia-Carolina Chem. Corp.) $\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ (\text{CH}_2)_2\text{CH}(\text{CH}_2)_3\text{CH}_3 \\ \\ \text{O} \\ \\ (\text{HO})_2-\text{P}-\text{O}-\text{CH} \end{array}$
(H ₂ P)	<i>HDPA</i> , monoheptadecylphosphoric acid ("Dowsol 17," Dow Chemical Co.) $\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ (\text{CH}_2)_2\text{CH}(\text{CH}_2)_5\text{CH}_3 \\ \\ \text{O} \\ \\ (\text{HO})_2-\text{P}-\text{O}-\text{CH} \end{array}$
(H ₂ P)	<i>Mono(<i>p</i>-octylphenyl)phosphoric acid</i> (Victor Chemical Co.) $\begin{array}{c} \text{O} \\ \\ (\text{HO})_2-\text{P}-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)_2 \end{array}$
(HP)	<i>DBP</i> , di- <i>n</i> -butylphosphoric acid (Victor Chemical Co., Monsanto Chemical Co.) $\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{P}-[\text{---}\text{O}-(\text{CH}_2)_3\text{CH}_3]_2 \end{array}$

BOOK REVIEW

Systematic Qualitative Analysis: An Introduction. G. A. MORRISON. Butterworth and Co. (Publishers) Ltd., London, 1961. pp. ix + 198. 25s.

THOUGH stated to be only an introduction, this book includes fifteen of the less common metals in an orderly concise scheme of semimicro qualitative inorganic analysis which can also be easily adapted for use in a more elementary form.

After a consideration of the factors involved in the formation of a precipitate (dissociation constants, buffered solutions and solubility constants), and of apparatus and techniques (an apparatus is shown which prepares H_2S in acetone when needed) there follows a full treatment of preliminary tests including a 10-page reference table showing the solubility of compounds of the more common metals in hot and cold water and in dilute and concentrated acids. One doubts, however, whether the latter is of much use at this stage of the analysis.

The theory of group separations is fully discussed, with useful tables of solubility products and pH conditions. The separation of cations follows one of the classical procedures, the alkaline earth metals being precipitated as carbonates (5th Group), although it is well known that significant losses of these ions occur in earlier groups. In an alternative procedure for separating strontium from calcium by the addition of potassium chromate in ammonia solution, the addition of ethanol to effect complete separation is omitted. Many will disagree with the author regarding the use of "spot tests", the only ones included being tests for Ag, Ni and Mg. In a treatise at this level one would wish for the inclusion of the more reliable spot reagents, especially for those cations, *e.g.* Sr, for which there is a dearth of other suitable confirmatory tests.

Running nomenclature diagrams are given for naming a precipitate or solution at any stage within a group separation. Those replace the usual tabular forms, but would appear to add to the difficulties in the interpretation of the instruction manual and in the writing up of the analysis.

Anions are identified by a number of separate investigations on different portions of the stock solution, and difficultly soluble substances are subjected to fusion, first with sodium carbonate and afterwards, if necessary, with sodium hydroxide.

The book, which is attractively produced, is a suitable "bench" handbook, and as it also contains basic theoretical principles, will be much welcomed by those who require a shorter text of advanced analysis.

W. F. JONES

Separation of the Heavy Metals. ANIL K. DE. Pergamon Press, Ltd., London, Paris, New York, 1961. pp. 308. 60s.

In the last two decades, a large amount of work has been done on the separation of the heavy metals using modern techniques and a large volume of literature on the subject has been published in many different journals. It is pleasing to see a book which gathers together much of this material into a handy-sized volume.

The book deals with the liquid-liquid extraction and ion-exchange methods for the separation of the metals in the range $Z = 37-102$; the "intermediate heavy metals" have been included to cover most of the metals which are of some importance in the nuclear energy programmes. Some of the analytical techniques used to evaluate the separation techniques are given in a separate section, whilst a further section illustrates the roles of the techniques in some of the radiochemical separations used for processing spent reactor fuels.

The stated objective of the book is that of "bringing together and co-ordinating the enormous amount of literature made available during the last ten years" but the author only attempts "to include in this book a complete survey of the literature up to the middle of 1958." However some reviews, which appeared before 1958, are not included and since the author refers to two papers published in 1960, it seems that it should have been possible at least to list the titles of the many papers published in 1958-60.

The presentation of the theoretical aspects of liquid-liquid extraction is well done but the general description of the types of extraction is not so good; part of one of the diagrams is inverted, with the solvent boiler at the top of the diagram and a reflux condenser at the bottom, the author seems to have difficulty in deciding which of the apparatus shown has a fritted disc or a "small orifice" and some

diagrams are awkwardly placed with respect to their descriptions, necessitating much page turning for reference from text to diagram.

The presentation of the corresponding part for ion-exchange is better but still has inadequate descriptions for some diagrams.

For each of the 30 or so metals listed, several methods of solvent extraction are described, but it becomes increasingly apparent that insufficient attention has been given to standardisation of the presentation. The percentage extraction (%E), is used in some methods, and an extraction coefficient (E, which is not defined in the theoretical section) is used in others; in yet further cases the amounts extracted are not denoted at all.

In some extraction methods the procedure for the determination of the metal is given, but in general no details are given correlating the "separated state" of the metal and the state used in its determination. In the case of indium, more comprehensive details for the extraction with oxine, including a list of interfering elements, are to be found in the analytical section than in the appropriate separation section. Tellurium is not mentioned in one of the three sections (liquid-liquid extraction.).

The best part of the book is the section concerned with radiochemical separations. In a brief but useful survey of existing methods, the author deals with such topics as the separation of radio-isotopes from target materials and the analysis of radioactive dusts.

In the lengthy appendix, which includes a comprehensive list of the characteristics of readily available ion-exchange materials and the physical constants of some organic solvents and chelating agents, the lack of correlation is again noticed: *n*-butyl phosphate is listed as such only in the appendix; in all extraction procedures it is called tri-butyl phosphate or TBP; the constants for dioxan—not listed in the extractions—are given, but those for some solvents such as tri-octylamine, used in some of the separations, are not given.

It would seem that in the promised future editions, due attention should be paid to these errors and to the correction of others such as "from such system," "procedures of heavy metals," "Gross Lanthanides have been separated," a comma at the end of a sentence; and to spelling mistakes such as University (in the dedication), tungstan, volune, chunk (chuck) and the compound H_4O_2 .

The uncommon type face and the brilliant white paper combine at first sight to give an impression of slightly blurred and uneven printing.

To summarise—this is excellent material somewhat spoiled by poor correlation and presentation of the various sections, but I look forward to a revised edition of this book, free from irritating errors.

L. S. BARK

Az analitikai Kémia módszereinek kialakulása (The Development of Methods of Analytical Chemistry). FERENC SZABADVÁRY. Akadémia Kiadó, Budapest, 1960. 418 pp. 100 Hungarian forint. In Hungarian.

This is the first work in the literature which deals with the history of analytical chemistry from ancient days up to the present time. The development of analytical chemistry is treated chronologically up to the end of the eighteenth century; separate chapters deal with the analytical works of ancient (1) and medieval (2) times, as well as of iatrochemistry (3), the phlogiston age (4), and from Lavoisier to Berzelius (5), while the works and life of Berzelius (6) conclude the first part of the book. In the following chapters the development of various branches of analytical chemistry is described separately; there are presented the further development of qualitative and gravimetric analysis (7), titrimetric analysis (8), organic analysis (9), electrogravimetry (10), optical methods (11), electrometric analysis (13) and other methods (14); in chapter 12 the development of theoretical analytical chemistry is presented. Subject and author indexes are also included.

The material has been collected mainly from original contemporary papers, and more than one thousand references are to be found. The book contains a number of citations from original texts. One hundred figures, mostly facsimiles, are reproduced in the book. If one merely looks through the illustrations, it is possible to get a good insight into the history of analytical chemistry. Analytical chemists of today will turn with interest to the pictures of the first gasometric device of Cavendish, the laboratory equipment of Lavoisier, the first atomic weights table of Berzelius, the title page of Fresenius' *Zeitschrift für analytische Chemie* which was the first journal of analytical chemistry (1862); the first spectroscope of Bunsen and Kirchoff, etc. There are a number of portraits of old and new analytical chemists. Short biographies of more than eight hundred scientists are presented, the most important being included in the text and references given for the others. Some details of the work of living analysts are mentioned.

The author is an analytical chemist himself and has published several original papers. He plans to publish the book in English and German, so that this very interesting text should soon be available to almost all analytical chemists in the world.

GYULA SVEHLA

Chemical Indicators. É. BÁNYAI. Műszaki Könyvkiadó, Budapest, 1961. 361 pp. 31 Hungarian forint. In Hungarian.

THIS book, dealing with every type of chemical indicator, is divided into five chapters: a short historical introduction, acid-base indicators, redox indicators, precipitation indicators and complexometric indicators.

In the introductory part of each chapter the theory of the titrations is discussed *e.g.* acid-base reactions, some problems concerning oxidation-reduction, solubility and complex equilibria. Many examples in the text assist the reader to learn and apply the theory.

In the chapter on acid-base indicators, colour change, fluorescent, luminescent and other types of acid-base indicator are treated. A detailed review of their mechanism is given and the relevant data and physico-chemical constants for the most important indicators are summarised. This chapter also includes titration curves, indicator corrections, colorimetric measurement of pH, and many practical problems.

In the chapter on redox indicators, after the treatment of redox equilibria the author deals with colour-change redox indicators, the oxidation mechanism of redox indicators, the effect of pH, some problems of colour change, the rH exponent, *etc.* A very detailed table, with the most recent references, presents the physico-chemical constants of redox indicators, the change in oxidation potentials with change in pH, *etc.* The author also deals with the end-point detection of redox reactions in alkaline media and with chemiluminescent indicators.

Under the heading of precipitation indicators the mechanism of adsorption indicators is discussed, the recent theory of Schulek and Pungor being mentioned. An interesting part of this chapter is the use of redox and fluorescent adsorption indicators.

In the final chapter the author, on the basis of the most recent literature, discusses the mechanism of metal indicators, and the sensitivity, possibilities and limits of use of metal indicators. The application of luminescent and redox indicators for the end-point detection of chelometric titrations is mentioned. A table, showing all the important characteristics of metal indicators, is included.

The book will be useful for all who have problems concerning indicators. The theoretical part is so extensive that a very considerable knowledge of analytical chemistry can be acquired from it.

E. KÖRÖS

NOTICES

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

UNITED KINGDOM

Wednesday 28 March 1962: Annual General Meeting followed by **Short Lectures: Polarographic Society**. Physics Department, Imperial College of Science and Technology, Prince Consort Road, London, S.W. 7. 2.30 p.m.

Wednesday 4 April 1962: Meeting for reading of Original Papers: Society for Analytical Chemistry Burlington House, London, W.1. 7.00 p.m.

Thursday 5 April 1962: Analytical Research: Dr. J. HASLAM: Royal Institute of Chemistry, Mid-Southern Counties Section and Portsmouth and District Chemical Society. College of Technology, Portsmouth. 7.00 p.m.

Thursday 5 April 1962: The Determination of Boron: Dr. H. J. CLULEY and Dr. R. H. BIDDULPH: Society for Analytical Chemistry, Midlands Section. Wolverhampton and Staffordshire College of Technology, Wulfruna Street, Wolverhampton, 7.00 p.m.

Friday 6 April 1962: The Assessment of Psychostimulants: Discussion to be opened by Dr. M. W. PARKES: Society for Analytical Chemistry, North of England Section and Biological Methods Group. Nag's Head Hotel, Lloyd Street, Manchester. 7.15 p.m.

Monday-Friday 9-13 April 1962: Feigl Anniversary Symposium: Society for Analytical Chemistry, Midlands Section, under the patronage of I.U.P.A.C. University, Edgbaston, Birmingham 15 (see also *Talanta*, 1962, 9, 185).

The following additions and minor alterations to the scientific programme have been made:

V. ANGER (Vienna, Austria)

Bedeutung des Chemismus von organischen Farbreaktionen für bei analytische Forschung.

Detection of Chemicals in Feeds.

A. BONDI (Jerusalem, Israel)

Tetrazolium Salts in Quantitative Colorimetric Analysis.

C. A. JOHNSON (Boots Pure Drug Co., Nottingham, U.K.)

Monday-Friday 9-13 April 1962: Sixth Congress of the International Society for Fat Research: Society of Chemical Industry, Oils and Fats Group. Imperial College of Science and Technology, Physics Building, Prince Consort Road, London, S.W.7.

The provisional list of papers to be presented includes:

Analytical Techniques

U. GLOOR (Basle)

Quantitative Determination of Ubiquinones in Biological Material.

A. HAUTFENNE (Brussels)

The Estimation of Peroxides by Use of the Leucobase of 2:6-Dichlorophenol-indophenol.

K. DE JONG (Vlaardingen)

Location of Double Bonds with Osmium Tetroxide.

G. JURRIENS (Vlaardingen)

Separation of Lipids with Poly-ethylene.

H. K. MANGOLD and L. J. MORRIS (Austin)

Utilisation of Modern Techniques in Studies of Unusual Seed Oils.

R. MARCUSE (Gothenburg)

Separation of Fatty Acid Carbonylic Derivatives by Thin Layer Chromatography.

M. NAUDET (Marseille)

The Location of Double Bonds in Unsaturated Fatty Acids.

B. DE VRIES (Vlaardingen)

Quantitative Separation of Cis- and Trans-Isomers by means of Complexes with Silver Ions.

Spectroscopic Methods

D. CHAPMAN (Cambridge)

High Resolution Nuclear Magnetic Resonance of Isomeric Glycerides.

C. Y. HOPKINS and H. J. BERNSTEIN (Ottawa)

Proton Magnetic Resonance and Fatty Acid Structure.

L. J. MORRIS (London)

Near Infrared Characteristics and Relative Polarities of Long-chain Hydroxy Compounds in relation to their Structures.

- L. A. O'NEILL and S. M. RYBICKA (Teddington) *Some Applications of Chromatographic and Spectroscopic Techniques in Drying Oil Chemistry.*
 J. ZAJIC (Prague) *Application of Infrared Spectrophotometry to the Saccharose Esters.*

Physical Methods and Properties

- E. FEDELI and A. ARPINO (Milan) *Determination of Molecular Weights by Isothermal Distillation Technique—Applications in the Field of Rats.*
 C. PAQUOT, R. PERRON and Mme. J. PETIT (Bellevue) *Application of Differential Thermal Analysis to the Study of Lipids—II: Ternary Mixtures of 1-Mono-, 1:3- Di- and Tristearins.*
 J. W. SELBY (Leatherhead) *A Comparison of the Dilatometric and Calorimetric Methods for Determining the Solid Phase in Shortenings.*

Registration forms and further particulars may be obtained from Drs. F. BRADLEY and H. JASPERSON, Joint Hon. Secretaries, Vith Congress of the International Society for Fat Research, 14, Belgrave Square, London, S.W.1, England.

The Annual General Meeting of the Scottish Section of the Society for Analytical Chemistry was held on Friday 26 January 1962 at the Grosvenor Restaurant, Gordon Street, Glasgow. The Chairman, Mr. A. F. WILLIAMS, presided.

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

Chairman: Mr. A. F. WILLIAMS

Vice-Chairman: Dr. R. A. CHALMERS

Hon. Secretary and Treasurer: Mr. J. BROOKS, Research and Development Department, I.C.I. Ltd., Nobel Division, Stevenston, Ayrshire.

UNITED STATES OF AMERICA

Thursday 15 March 1962: **An Automatic Approach to the Microdetermination of Carbon and Hydrogen:** Dr. H. F. HABER: *Metropolitan Microchemical Society.* (see also *Talanta*, 1962, 9, 186).

Tuesday 3 April 1962: **Atomic Absorption Spectroscopy:** Mr. DAVID MANNING and Mr. WALTER SLAVIN: *Society for Applied Chemistry, New York Section.* Statler-Hilton Hotel, New York, N.Y. 8.00 p.m.

Wednesday–Friday 13–15 June 1962: **Analytical Automation and Data Processing:** *Annual Summer Symposium of Division of Analytical Chemistry, American Chemical Society and Analytical Chemistry.* College Park, Maryland (see also *Talanta*, 1962, 9, 186).

The following minor alterations to the scientific programme have been made:

H. FREUND

Graduate Instruction Involving Continuous Automation Systems.

A. SAVITZKY and M. J. E. GOLAY

Some Numerical Operations on Analytical Data.

R. E. WAINERDI, D. GIBBONS and L. E. FITE

Automation of Radioactivation Analytical Method, including Computer Data Processing.

W. J. BLAEDEL and G. P. HICKS

Automatic Enzyme Procedures.

The Officers for the current year of the *Division of Analytical Chemistry, American Chemical Society* are:

Chairman: Mr. JOHN MITCHELL, JR.

Chairman-elect: Dr. L. B. ROGERS

Secretary-Treasurer: Dr. DONALD H. WILKINS, General Electric Research Laboratory, Schenectady, N.Y.

PAPERS RECEIVED

- Ultraviolet spectrophotometric determination of scandium with Tiron:** HIROSHI HAMAGUCHI, NAOKI ONUMA, ROKURO KURODA and RYUITIRO SUGISITA. (1 January 1962).
- Stepwise determination of cadmium, mercury and tellurium:** K. L. CHENG. (1 January 1962)
- Ion exchange in mixed solvents: Adsorption behaviour of uranium and thorium on strong base anion-exchange resins from mineral acid-alcohol media: Separation methods for uranium and thorium:** J. KORKISCH and G. E. JANAUER. (1 January 1962).
- A polarographic study of dissolved oxygen—II:** V. S. GRIFFITHS and M. I. JACKMAN. (8 January 1962).
- The determination of the oxidation states of tracer uranium, neptunium and plutonium in aqueous media:** S. C. FOTI and E. C. FREILING. (8 January 1962).
- The application of an improved steam distillation apparatus to the determination of fluorine in rocks and minerals:** C. O. INGAMILLS. (12 January 1962).
- The determination of nitrite ion in the presence of large quantities of azide ion:** H. F. COMBS and E. L. GROVE. (13 January 1962).
- Semimicro iodometric determination of thallium^{III} by an amperometric method with two polarisable electrodes:** RITA BHATNAGAR, M. L. BHATNAGAR and N. K. MATHUR. (15 January 1962).
- Phase titrations—I: Binary systems involving carbon tetrachloride and binary systems involving carbon disulphide:** D. W. ROGERS and ROBERT KOLEJ. (17 January 1961).
- The effect of some anions on the spectrophotometric absorption of bis (di-n-octylethylenediamine) Cu^{II} complexes in Hexone:** D. BETTERIDGE and T. S. WEST. (18 January 1962).
- The continuous determination of uranium in impure solutions by gamma spectrometry:** M. R. HAYES and A. P. SEYFANG. (22 January 1962).
- Spot test for 2- and 4-valent sulphur in organic compounds based on reduction with Raney alloy:** FRITZ FEIGL and DORA HAGUENAUER-CASTRO. (25 January 1962).
- Spot test for bivalent sulphur based on pyrolysis with mercuric cyanide:** FRITZ FEIGL and E. LIBERGOTT. (25 January 1962).



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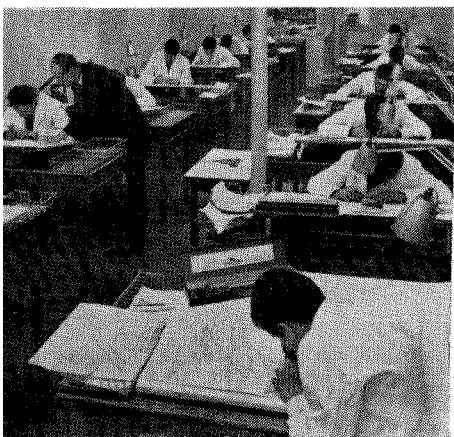
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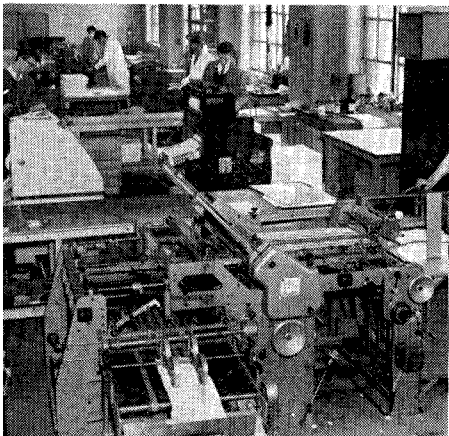
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