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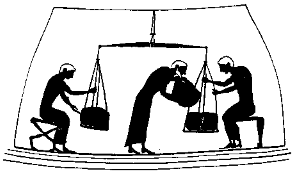

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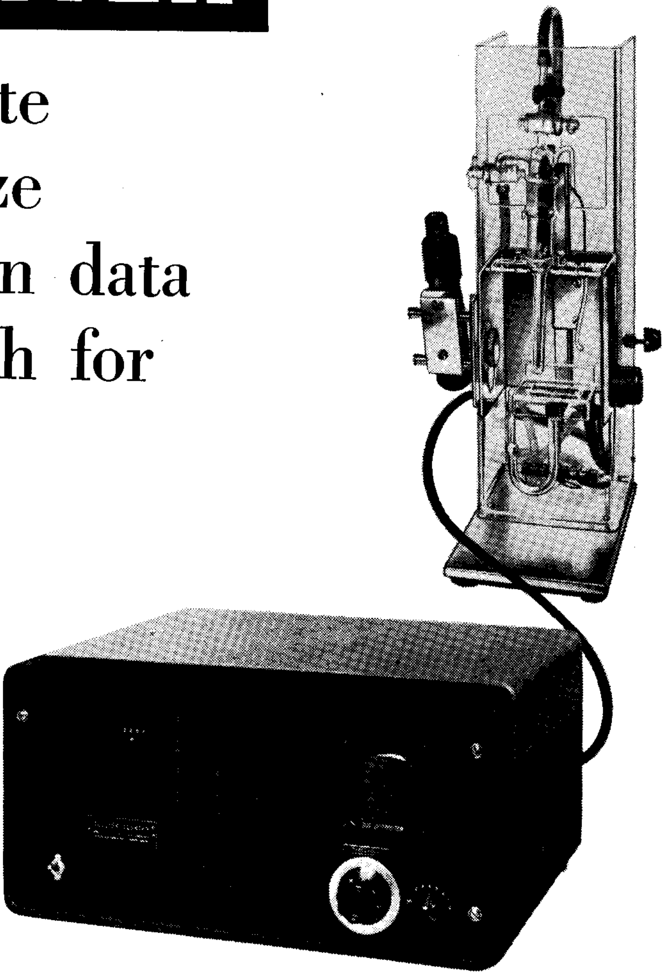

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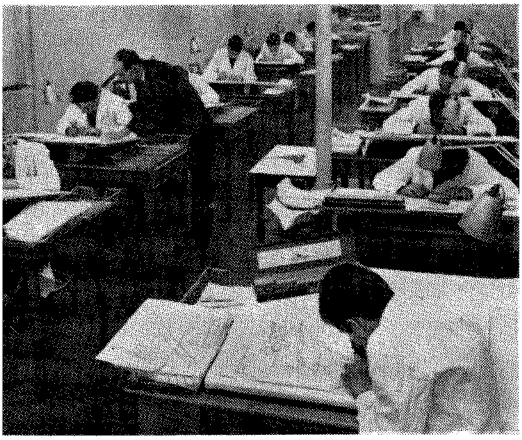
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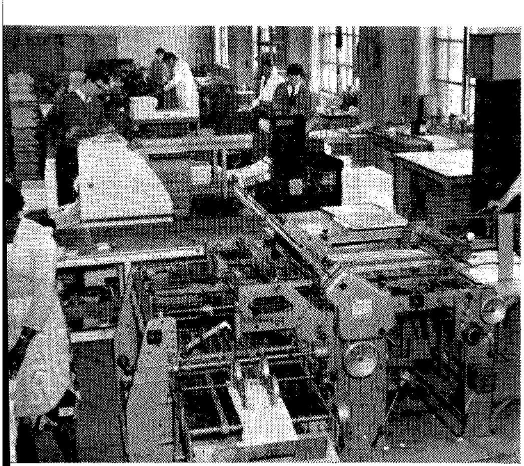
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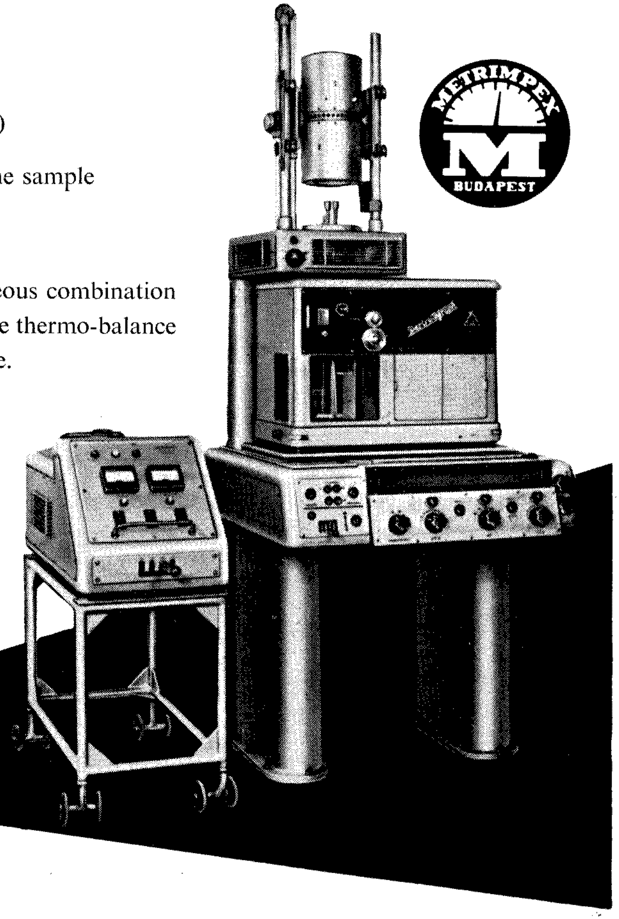

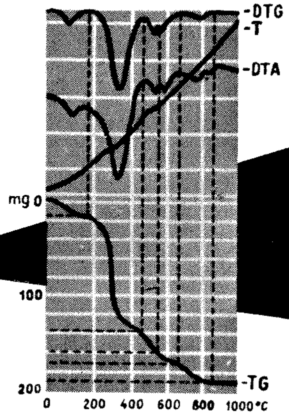
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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—IV

THE CHLORAMINE-T-IODIDE REACTION

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Summary—A study has been made of the oxidation by chloramine-T of iodide to free iodine and to monopositive iodine ion over a wide range of conditions. For the oxidation to free iodine, sulphuric or acetic acid media are suitable, and a concentration of 1·0*M* is recommended. Hydrochloric acid is very much less suitable. The reverse titration (the addition of iodide to acidified chloramine-T) is subject to considerable negative errors and is not recommended. Titration in neutral solution, buffered or unbuffered, is impracticable. Bromide to a maximum concentration of 0·01*M* may be present, particularly in sulphuric acid media, without causing error, and arsenic^{III} and iodide in mixture can be successively titrated.

Oxidation to iodine monochloride is quantitative only over the range of hydrochloric acid concentration of 3·0 to 4·0*M*, and is better conducted with carbon tetrachloride as a visual indicator than by the potentiometric method.

THE status of chloramine-T as a titrimetric reagent has been assessed,[1] methods of standardising reagent solutions have been critically examined,[1] the reaction between chloramine-T and arsenic^{III} has been thoroughly studied,[2] and the performance of a number of indicators in chloramine-T titrimetry has been fully investigated.[3] Next in fundamental importance to the reaction with arsenic^{III} is the reaction of chloramine-T with iodide and iodine. This reaction is basic to (*a*) the standardisation of chloramine-T, both against iodate through thiosulphate and against arsenic^{III} in bicarbonate buffer, (*b*) reactions in buffer media of pH 4–10 in which the presence of iodide is essential before any reaction can occur or the end-point be located, iodine being either a reaction intermediate or purely a catalyst, (*c*) reactions wherein an aliquot of chloramine-T is used to liberate a known quantity of free iodine which is then used in the determination, and (*d*) Andrews-type reactions in which iodine monochloride is used as a reaction intermediate in strong hydrochloric acid solutions, and which depend essentially on the oxidation of iodide or iodine to monopositive iodine ion.

It is necessary, therefore, to establish the quantitativeness of the oxidation by chloramine-T of iodide to free iodine and to iodine monochloride before assessing the validity of determinations involving these reactions. A wide range of conditions has therefore been examined.

Previous work is neither extensive nor very informative. Iodide has been titrated potentiometrically in hydrochloric[4,5] and in sulphuric acid[5] to iodine, and Tomicek and Suchanla[4] report a suitable hydrochloric acid concentration to be 0·35*M*. No sulphuric acid concentration has been specified, though Afanas'ev[6] reported that the reverse titration was satisfactory in 0·5*M* sulphuric acid, with which we are not in entire agreement. Iodide has also been titrated[7] in "dilute" hydrochloric acid in the presence of cyanide to iodine monocyanide using starch as indicator, and in "strong" hydrochloric acid to iodine monochloride using carbon tetrachloride as indicator.

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In an earlier paper[1] it was shown that in using chloramine-T to liberate a known amount of iodine, certain minimal requirements in the amount of both acid and iodide employed must be met. In the absence of an excess of free acid, buffer solutions are essential to prevent the pH running so high that the oxidation of iodide ceases, hypoiodite is formed, and both iodine and hypoiodite oxidise thiosulphate to sulphate giving early end-points. At the same time, it was pointed out that although chloramine-T in hydrochloric acid media, with or without the addition of bromide, could oxidise thiosulphate to sulphate, the reaction was not quantitative, suffered from the incidence of side reactions including the formation of tetrathionate, and was not analytically useful. Claims to the contrary have been made[8] and renewed,[9] but the figures adduced in support[9] are in reasonable agreement with our own, *i.e.*, that the reaction shows a deficiency of about 2% from strict stoichiometry. Although the reproducibility is fair, and the eight-fold multiplication of equivalence may be considered as an eight-fold division of the error, we do not find cause to alter our statement because the stoichiometry and precision do not fall within the limit of ±0·04% of the oxidation to tetrathionate under the proper conditions.

EXPERIMENTAL

Apparatus and reagents

These have mostly been described before,[1-3] additional reagents being specified below.

Potassium iodide solution, 0·1*M*: Prepared by direct weighing of AnalaR potassium iodide dried for 2 hr at 150° and solution in de-oxygenated water. The solution was standardised by titration in 4·0*M* hydrochloric acid with primary standard potassium iodate,[1] using the potentiometric method and the visual indicators amaranth and carbon tetrachloride to locate the end-point. The results for the factor of the iodide solution were: potentiometric 0·994; amaranth 0·9943, 0·9943; carbon tetrachloride 0·994, 0·994.

Carbon tetrachloride: AnalaR.

Procedure

The concentrations specified are referred to the equivalence point volume of the titration solution, which was arranged to be 200 ml. Andrews titrations with visual indicators were conducted in titration bottles. Before the addition of the iodide solution, all solutions were freed from oxygen by the passage of a rapid stream of carbon dioxide from Drikold for 20 min, and wash water was similarly treated before use. The titration procedure has already been outlined.[1,2] The results shown in the table for potentiometric titrations refer to the particular curves shown in the figures, but replicate determinations were actually made and found to agree within the experimental error in each case.

RESULTS AND DISCUSSION

1. *Oxidation of iodide to free iodine*

The colour of free iodine precludes the use of visual indicators, and the potentials attained are not sufficiently high to permit the use of chemiluminescent indicators such as siloxene, so electrometric methods must perforce be used to locate the end-point. A straightforward classical potentiometric study has been made, using media which had been de-oxygenated by the passage of carbon dioxide in order to avoid direct or induced oxidation of iodide by molecular oxygen. Passage of carbon dioxide was continued during the titration: any loss of iodine by volatilisation is unimportant—indeed it is an advantage, though this could be fully realised only by complete removal of the iodine.

(a) *Direct titration in acid medium.* Titration in sulphuric acid at concentrations between 0·05*M* and 2·0*M* and in acetic acid between 1·0*M* and 2·0*M* gives excellent results as shown in Fig. 1 and Table 1. A concentration of 1·0*M* for either acid is recommended. Hydrochloric acid is much less satisfactory at a concentration of 0·1*M* to 0·5*M*, while in 1·0*M* acid the potential rise through the end-point is considerably diminished by the partial setting up of the iodine/iodine monochloride redox system,

TABLE I. TITRATION OF IODIDE AT A CONCENTRATION OF 0·01*M* WITH 0·05*M* CHLORAMINE-T UNDER VARIOUS CONDITIONS

Fig.	Curve	Acid	Concn., *M*	Titre, *ml*		Error	
				Calc.	Found	*ml*	%
Direct titration in acid solution:							
1	1	Hydrochloric	0·1	19·98	20·00	+0·02	+0·1
	2		0·5		20·00	+0·02	+0·1
	3		1·0		20·00	+0·02	+0·1
	4	Sulphuric	0·05	19·98	20·01	+0·03	+0·15
	5		0·5		20·01	+0·03	+0·15
	6		1·0		20·005	+0·025	+0·1
	7		2·0		20·00	+0·02	+0·1
	8	Acetic	1·0	19·98	20·00	+0·02	+0·1
	9		2·0		20·01	+0·03	+0·15
Direct titration in acid solution in the presence of 0·01*M* bromide (no distinct inflection in 0·1*M* bromide):							
2	1	Sulphuric	0·5	19·98	20·00	+0·02	+0·1
	2	Hydrochloric	0·25		20·00	+0·02	+0·1
Direct titration in acid solution in the presence of 0·00125 mole of arsenic^{III}:							
2	5	Sulphuric	1·0	45·18	45·16	−0·02	−0·05
	6	Hydrochloric	1·0		45·20	+0·02	+0·05
Reverse titration in acid solution:							
2	7	Sulphuric	0·5	20·02	19·91	−0·11	−0·55
	8		1·0		19·91	−0·11	−0·55
Direct titration to ICl, potentiometric:							
3	1	Hydrochloric	1·0	39·94	39·85	−0·09	−0·23
	2		2·0		39·88	−0·06	−0·15
	3		3·0		39·91	−0·03	−0·08
	4		4·0		39·95	+0·01	+0·03
	5		5·0		40·08	+0·14	+0·35
Direct titration to ICl, carbon tetrachloride as indicator:							
—	—	Hydrochloric	1·0	39·94	39·90	−0·04	−0·1
			2·0		39·91	−0·03	−0·08
			3·0		39·92	−0·02	−0·05
			4·0		39·93	−0·01	−0·03
			5·0		39·93	−0·01	−0·03

and the end-point becomes difficult to locate. No such effect can occur in sulphuric or acetic acids and the potential rise through the end-point is consequently very much greater and sharper. Attempts to increase the size of the potential break at the end-point by removing iodine from solution by extraction into a globule of carbon tetrachloride added to the titration solution[10] met with limited success. Equilibration of potentials was rapid in all cases.

(b) *Direct titration in unbuffered and buffered neutral solution.* In view of instructions[11] and recommendations[12,13] to use chloramine-T as a titrant in "neutral" unbuffered solutions in conflict with the present findings that chloramine-T is inactive in the absence of added halide,[1,2] that at pH values above 4 the reaction is dependent on the presence specifically of iodide[2] and that arsenic^{III} cannot be titrated in neutral unbuffered media whether iodide be present or not,[1] an investigation was made of the behaviour of chloramine-T under such conditions. If the reagent is capable of reaction in these circumstances, then it should certainly oxidise iodide. The matter is additionally important in respect to reactions of chloramine-T in the presence of iodide of appropriate concentration in media of pH values up to 10.[2]

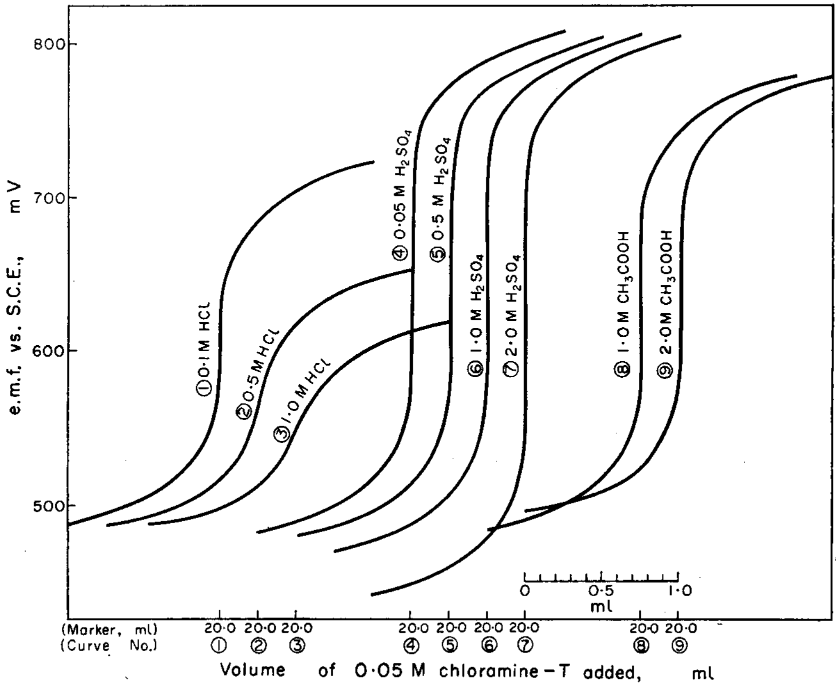

FIG. 1.

In a plain unbuffered aqueous medium, the solution turned yellow after the addition of 1 ml of chloramine-T. Thereafter the colour did not deepen, nor did the potential change by more than a few mV even after the addition of a 15% excess of oxidant. The pH of the solution was then 9·8, which agrees well with previous findings[2] as to the pH at which reaction ceases, and with the amount of hydrogen ion consumed by 1 ml of oxidant. Reaction in this medium is therefore impracticable.

In a phosphate buffer of pH 7·0, iodine was readily liberated, the potentials in the early part of the titration being similar to those recorded in 1·0*M* acetic acid. Over the interval ±5% round the equivalence point, however, there was no potential break, merely a slow drift of 25 mV. The determination of iodide at pH 7 is therefore impracticable even in a buffer medium.

Titrations in the reverse sense were no more successful in either medium. The addition of iodide to an aliquot of chloramine-T produced a yellow colour with the first ml, but this colour practically disappeared within 1 min, and further additions gave no more than the faintest colour. It is possible at the pH of the solution that iodine either hydrolyses to hypoiodite which then disproportionates, or is oxidised by chloramine-T to iodate, and that the products do not then react with iodide, but the exact explanation is difficult to establish.

This bears additionally on the mechanism of the reaction at pH values up to 10 in the presence of iodide. It has been shown[2] that above pH 6, chloramine-T will oxidise arsenic^{III} only in the presence of iodide. This reaction may be sequential, *i.e.*, chloramine-T first oxidises iodide to iodine, then iodine oxidises arsenic^{III} to arsenic^{V}, in which case the iodine is a reaction intermediate. Alternatively, iodide, or an oxidation product thereof, such as iodine, iodate or an intermediate species, may be a catalyst for the direct reaction between chloramine-T and arsenic^{III}. It is unlikely that the reaction is a heterogeneous chemisorption catalysis since the only solid phase present is represented by the vessel and the electrodes: the concentration of dichloramine is less than micromolar[1] and this species is completely soluble under these conditions. The distinction between a chemical catalyst and a reaction intermediate is purely one of quantity, the former being effective in very small concentration. Where a buffer is available to supply hydrogen ion for reaction, iodine is plentifully liberated, and so may be regarded as a reaction intermediate, but at the upper pH limit of the reaction, or when no buffer is available, only small amounts of iodine are liberated, and the requirement in iodide concentration increases, so iodide could be regarded as a reaction intermediate and iodine as a catalyst. On the whole it appears most satisfactory to regard iodide as a reaction intermediate.

(c) *Direct titration in acid media in the presence of bromide.* Curves 1 to 4 in Fig. 2 illustrate the effect of bromide on the titration. Although the equilibration speed was satisfactory, the addition of bromide is not helpful. The inflections were completely suppressed at a bromide concentration of $0{\cdot}1M$, but appeared when the bromide concentration was reduced to $0{\cdot}01M$. In hydrochloric acid the flattening is not marked compared with bromide-free media, but the end-point potential change in sulphuric acid is very much decreased, although a sulphuric acid medium yields better curves than a hydrochloric acid medium. Iodide can therefore be determined in the presence of bromide of equal initial concentration, provided this does not exceed $0{\cdot}01M$.

(d) *Direct titration in acid media in the presence of arsenic*^{III}. Titration of a mixture of known quantities of arsenic^{III} and iodide solutions in $1{\cdot}0M$ hydrochloric or sulphuric acids gave curves 5 and 6 in Fig. 2. The end-points were in satisfactory agreement with the theoretical value for the sum of the two reductants. The potentials, surprisingly, accord with the oxidation of iodide as the potential-determining reaction in the end-point region and not, as might have been expected in strong acid media, with the oxidation of arsenic^{III} (*cf.* curves 3 and 6, Fig. 1). The same results were obtained by adding excess chloramine-T to an aliquot of iodide, followed by an aliquot of arsenic^{III} solution (larger than was equivalent to the iodide) and finally titrating with chloramine T. Sulphuric acid again provides much the better medium.

Since arsenic^{III} in bicarbonate buffer in the presence of iodide at a concentration below $0{\cdot}05M$ can be accurately titrated with chloramine-T either visually[1] or potentiometrically,[2] it is evident that by combining this titration with titration after acidification with, preferably, sulphuric acid, arsenic^{III} and iodide can be successively determined in one solution. Furthermore, the determination of iodide can be accompanied by the standardisation of the titrant by the addition of an aliquot of standard arsenic^{III} solution in the same way.

(e) *Reverse titration in acid media.* To test Afanas'ev's claim[6] in respect to the titration of chloramine-T in 0·5*M* sulphuric acid with iodide, aliquots of chloramine-T solution which had been de-oxygenated with nitrogen were added to the required acid solution previously outgassed with carbon dioxide, and titrated with iodide. The titration curves are satisfactory as shown in Fig. 2 at acid concentrations of 0·5*M* and 1·0*M*, but at an acid concentration of 0·05*M* the reaction was too slow to be followed. Dichloramine-T was precipitated on the addition of chloramine-T to the acid medium, and slowly dissolved as the reaction proceeded. Through the interval of 1·0 ml before the equivalence point, the potential after each increment of iodide fell swiftly and recovered slowly. Though the curves are satisfactory, the end-points are about 0·4% early, the error being independent of time and acid concentration and not therefore caused by loss of oxidant. Nor is the error caused by induced oxidation of iodide because it would then be positive. This sense of titration cannot therefore be regarded as satisfactory.

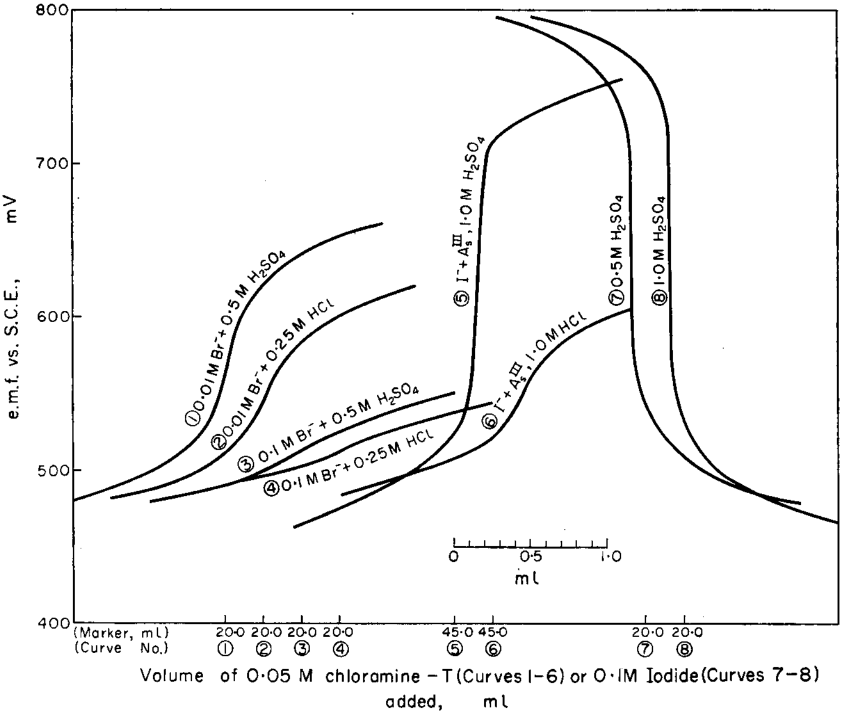

Fig. 2.

2. *Oxidation to monopositive iodine*

In Andrews-type reactions, *i.e.*, those in which monopositive iodine is formed by oxidation and stabilised by combination with chloride ion as iodine monochloride, it is convenient to provide the stabilisation by means of hydrochloric acid. A lower limit to the required hydrochloric acid concentration is set by dissociation of the iodine monochloride in falling chloride concentration and hydrolysis of the I^+ ions so formed in falling hydrogen ion concentration. The two are interrelated and it is possible to conduct such titrations at low hydrogen ion concentrations in the presence of high chloride ion concentrations (or cyanide or bromide) and *vice versa.* An upper limit to the hydrochloric acid concentration may be set by the effect of hydrogen ion on the potential of the reductant system, combined with the katagenic effect of chloride ion on the monopositive iodine potential. The present examination was restricted to hydrochloric acid media, and the concentrations varied over a wide range. In the fully oxidised solution, the iodine colour is replaced by the pale yellow of iodine monochloride and it becomes possible to use visual indicators as well as potentiometric methods to locate the end-point.

(a) *Potentiometric titrations.* Curves for potentiometric titrations in 1·0*M* to 5·0*M* hydrochloric acid are shown in Fig. 3, and the results are given in Table I.

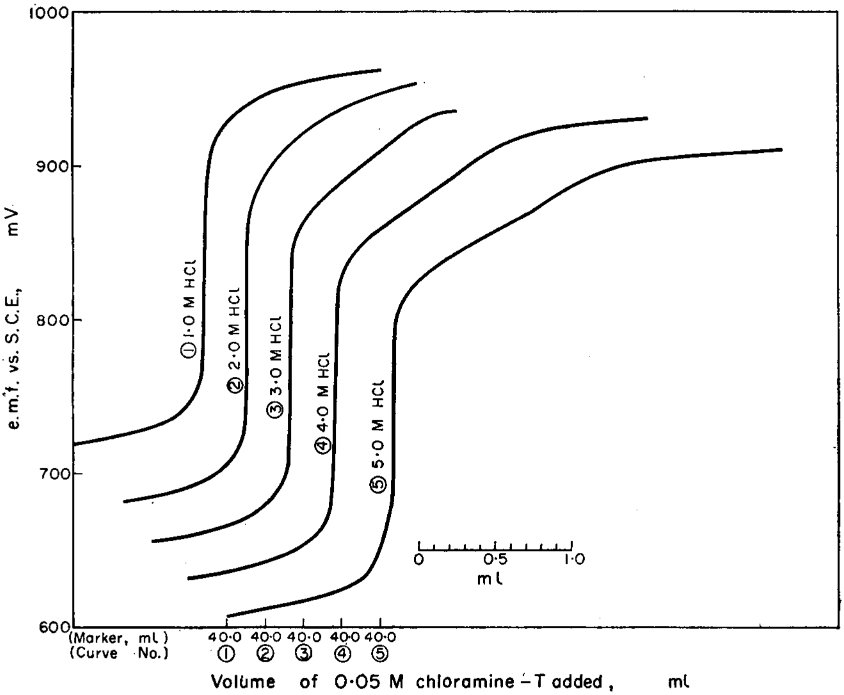

Fig. 3.

Although the potentials reached equilibrium quickly and the end-points are sharp, the curves are a little ragged. The results are good in the range 3–4*M* acid, but the end-points are premature in more dilute acid and late in more concentrated acid. In fact the consumption of oxidant increases progressively with increasing acid concentration, and it is correct over only a narrow range. This steady increase is not caused by an impurity in the hydrochloric acid, as will be shown later: there is a trace of titratable substance in this reagent, but its nature is such that the inflection lies at very much higher potentials than those here recorded.

(b) *Titration with carbon tetrachloride as visual indicator.* Carbon tetrachloride is not the most convenient indicator; chloroform, with a lower partition coefficient permits faster reaction at the end-point; but with due allowance in longer time of shaking carbon tetrachloride gives rather more accurate results in Andrews titrations, and was used in this work. The end-points in 1·0*M* to 5·0*M* hydrochloric acid were all quite sharp and satisfactory, as the results show. Once again there is an increase in consumption of oxidant with increasing acid concentration, though only 0·1% compared with 0·5% by the potentiometric method. It is difficult to account for this discrepancy. For the best results, the concentration of hydrochloric acid should be 3·0*M* to 4·0*M*, and the end-point detection with carbon tetrachloride is preferred.

These determinations correspond to a quantity of 20 ml of 0·1*M* iodine monochloride, and although the errors sharply restrict the hydrochloric acid concentration range in the determination of iodide, these errors are greatly reduced when much smaller quantities of iodine monochloride are used as a reaction intermediate in other determinations, and should fall within the experimental error over the range 2·0*M* to 4·0*M* hydrochloric acid for 2 to 5 ml of 0·1*M* iodine monochloride.

Zusammenfassung—Die Oxydation von Jodid zu Jod und monopositivem Jodion mit Chloramin-T wurde über einen breiten Bereich wechselnder Bedingungen studiert. Zur Oxydation zu freiem Jod wird Schwefelsäure und Essigsäure in einer Konzentration von 1,0 m als bestes Medium empfohlen. Salzsäure ist viel weniger gut geeignet. Die umgekehrte Titration (d.h. Zugabe von Jodid zur angesäuerten Chloramin-T-Lösung) gibt negative Fehler und ist nicht geeignet. Titration in neutralem Medium (gepuffert oder ungepuffert) ist abzuraten. Bromid bis zu einer maximalen Konzentration von 0,01 m verursacht in schwefelsäurem Medium keine Störung. Arsen(III) und Jodid können in einer Mischung nacheinander titriert werden.

Oxydation zu Jodmonochlorid verläuft nur in 3·0–4·0 m Salzsäure quantitativ. Die Titration wird besser mit Kohlenstoff-tetrachlorid unter visueller Extraktionsindication vollzogen als potentiometrisch.

Resumé—Les auteurs ont étudié l'oxydation par la chloramine-T de l'iodure en iode libre et en ion positif monovalant dans de nombreuses conditions. Pour l'oxydation en iode libre, les milieux acide sulfurique ou acétique conviennent, une concentration 1,0 M est recommandée. L'acide chlorhydrique convient beaucoup moins bien. Le titrage inverse (addition d'iodure à la chloramine-T acidifiée) est sujet à des erreurs par défaut considérables et n'est pas recommandé. Le titrage en solution neutre, temponnée ou non, est irréalisable. Du bromure de concentration maximale 0,01 M peut être présent, en particulier en milieu acide sulfurique, sans causer d'erreur. De l'arsenic (III) et de l'iodure mélangés peuvent être dosés successivement.

L'oxydation en monochlorure d'iode est quantitative seulement dans le domaine de concentration d'acide chlorhydrique 3–4 M; elle est mieux réalisée avec le tétrachlorure de carbone comme indicateur visuel que par la méthode potentiométrique.

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UNTERSUCHUNG DER KATIONENSORPTION AUS KOMPLEXANMEDIUM—II*

CHROMATOGRAPHISCHE TRENNUNG DES CALCIUMS UND STRONTIUMS

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Zusammenfassung—Es wurde die Trennung des Calciums von Strontium auf chromatographischem Wege ausgearbeitet. Die vorstehenden zunächst an Kationenaustauscher adsorbierten Kationen lassen sich mittels einer 0,02–0,05 m Lösung von 1·2-Diaminocyclohexan-N.N.N'.N'-tetraessigsäure (DCyTE) in 0,4 m Ammoniumacetat (pH 5,1) stufenweise nacheinander auswaschen. Unter diesen Bedingungen wird zunächst Calcium und erst nach dem Durchgang von etwa 400 ml der 0,05 m Waschlösung auch Strontium ausgewaschen. Mit Hilfe dieser Methode wurden Calcium und Strontium in den verschiedensten Konzentrationverhältnissen voneinander getrennt; so wurden z.B. 1000 μg Strontium von 200 mg Calcium (d.h. im Verhältnis von 1:200) mit einem Fehler von ±1% getrennt.

Die schwierige Trennung der Erdalkalien mittels klassischer analytischer Methoden wurde bisher nicht zufriedenstellend gelöst. Die genaue und verlässliche Bestimmung von Strontium in überschüssigem Calcium stellt ein wichtiges Hilfsmittel der Bestimmung des absoluten Alters von Gesteinen und der genauen Klassifizierung einiger Mineralarten. Hand in Hand mit der Entwicklung der Kerntechnik hat auch die analytische Chemie des Strontiums und Bariums gewaltig an Bedeutung zugenommen. Zur erfolgreichen Lösung aller diesen Fragen wurden vor allem schnelle und verlässliche Trennmethoden für die einzelnen Glieder der Erdalkalireihe gesucht. Als besonders vorteilhaft erwies sich die Ionenaustausch-Technik und zwar die chromatographische Trennung von an Kationenaustauschern adsorbierten Metallionen mit verschiedenen Auswaschmitteln. Zur Trennung von Erdalkalien wurden ausser Mineralsäuren hauptsächlich einige organische Oxysäuren wie Wein-, Citronen-, Milch-, α-Hydroxyisobuttersäure u. ä. vorgeschlagen. Ein sehr wirksames Trennmittel für solche Chromatographie stellt auch die Äthylendiamintetraessigsäure—ÄDTE—dar. Die letztere wird entweder als Auswaschmittel verwendet oder werden die Erdalkalien aus ÄDTE-Medium bei verschiedenem pH ausgewaschen.

Die grundlegende Arbeit über die Trennung des Strontiums und Bariums stellt die Untersuchung von Bovy und Duyckaerts[1] dar, in der die Beziehung zwischen dem Verteilungskoeffizient und den Komplexbildungskonstanten der entsprechenden Chelate abgeleitet wird. Mit Hilfe ähnlicher Chromatographie gelang es auch Fouarge und Fuger,[2] Calcium, Strontium, Barium und Radium voneinander abzutrennen. Die Sorbierbarkeit der Erdalkalien aus ÄDTE-Medium in Abhängigkeit vom pH-Wert untersuchten auch Taketatsu[3] bzw. Nikolskij und Trofimov.[4]

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* Part I—see ref. 16.

Mit der chromatographischen Trennung des Calciums und Strontiums mit ÄDTE-Lösung befasste sich Myers[5]; die gleichzeitige Trennung von Calcium, Strontium, Barium und Radium mit Hilfe der gleichen Technik wurde von Duyckaerts und Lejeune[6] beschrieben. Zur chromatographischen Trennung einiger Metalle bei der Analyse des ausgebrannten Kernmaterials wurde ÄDTE bei verschiedenen pH-Werten von Honda[7] verwendet. Einen oft untersuchten Gegenstand stellen auch die Arbeiten über die selektive Sorption von Metallen aus ÄDTE-Medium, wie z.B. die Trennung des Strontiums von überschüssigem Calcium[8,9] oder die Trennung des Radiums von überschüssigem Barium[10]. Die gleiche Technik wurde auch zur Bestimmung von Strontium, evtl. Barium und Radium in Boden[11], Trinkwasser[12] oder biologischem Material[13] herangezogen.

Zur Trennung der Erdalkalien erwiesen sich auch Anionenaustauscher im ÄDTE-Cyclus brauchbar.[14] In dieser Weise wurden durch Auswaschen mit gepufferten ÄDTE-Lösungen Calcium und Strontium voneinander getrannt.[15] In der vorangehenden Arbeit[16] zeigten wir, dass ein besseres Auswaschmittel als ÄDTE die 1.2-Diaminocyclohexan-N.N.N'.N'-tetraessigsäure, DCyTE, die bisher nur zur selektiven Trennung des Mangans[17] von den Erdalkalien verwendet wurde, darstellt. Die Sorptionskurven der Erdalkalien aus DCyTE-Medium weisen in der pH-Abhängigkeit grössere Unterschiede als die Sorptionskurven der entsprechenden ÄDTE-Komplexe auf. Dadurch ist die Voraussetzung einer besseren Trennung der Erdalkalien, insbesondere des Calciums und Strontiums und zwar auch in extremen Konzentrationsverhältnissen, gegeben.

VERSUCHSTEIL

Verwendete Apparate und Reagenzien

Die Bestimmung von Strontium und Calcium erfolgte durch Aufnahme des Molekularbandspektrums mit Hilfe des Flammenphotometers Zeiss III unter Anwendung des Li-Filters mit maximaler Durchlässigkeit von 665–687 mμ im Falle des Strontiums und eines Filters mit maximaler Durchlässigkeit von 620–630 mμ im Falle des Calciums. Die Lösung wurde in Luft-Acetylen-Flamme bei 0,4 at und 40 mm Wassersäule angeregt.

Sämtliche pH-Messungen wurden mit Hilfe des Titrimeters TTT-1 der Firma Radiometr, Kopenhagen, Dänemark, durchgeführt. Um dem Auslaugen von Kationen aus Glas vorzubeugen, wurde das Abdampfen und die Oxydation von Komplexanen in Quarzgefässen durchgeführt. Die 1m Lösung von Ammoniumacetat wurde durch Neutralisieren von 60 g Eisessig in 500 ml destilliertem Wasser mit verdünntem Ammoniak (1:1) bis zum pH 5,1 und durch anschliessendes Auffüllen zu 1 Liter hergestellt.

Die Komplexbildner—die Äthylendiamintetraessigsäure und die 1.2-Diaminocyclohexan-N.N.N.'N'-tetraessigsäure wurden durch mehrmaliges Umfällen aus 10% iger Salzsäure, Auswaschen mit Wasser und Trocknen bei 50°C gereinigt. Ihre 0,02m bzw 0,05m Lösungen wurden durch Neutralisieren der wässrigen Suspension mit verdünntem Ammoniak (1:1) bereitet.

Die Standartlösungen der Erdalkalien wurden aus spektral reinen Ca- bzw. Sr-Präparaten hergestellt. Die letzteren wurden durch Reinigung[18] der handelsüblichen pro Analysi Präparate gewonnen. Ammoniumhydroxyd wurde durch Sättigen von deionisiertem Wasser mit Ammoniakgas bereitet.

Es wurde an einem stark sauren Kationenaustauscher, Amberlit IR-120, im Ammoniakcyclus gearbeitet. Die Korngrösse des Ionenaustauschers bzw. die Grösse der Kolonne siehe[16]. Zum Studium der Sorption aus Komplexanmedium wurden Füllungen von 25 ml verwendet.

ERGEBNISSE

Wir untersuchten zunächst gesondert das Verhalten von Calcium und Strontium bei dem Auswaschen mit DCyTE bei verschiedenen pH-Werten. Die Auswaschlösungen wurden so hergestellt, dass sie 0,02 bzw. 0,05 m an DCyTE und 0,4 m an

Ammoniumacetat waren; der gewünschte pH-Wert wurde mit Essigsäure bzw. mit Ammoniak unter potentiometrischer Kontrolle eingestellt.

Die Calcium- bzw. Strontiumstandartlösungen wurden aus einem kleinen Volumen am Ionenaustauscher adsorbiert und die Kolonne wurde jeweils mit 50 ml Wasser ausgewaschen. Hierauf wurde mit dem Auswaschen begonnen; bei einer Geschwindigkeit der Auswaschlösung von 1–1,5 ml. min^{-1}. cm^{-2} wurden Fraktionen von 25 ml aufgefangen. Diese Fraktionen wurden durch Abdampfen zur Trockne mit 20 ml konz. Salpetersäure mineralisiert, in 3 ml konz. Salzsäure aufgenommen, im 25 ml Messkolben aufgefüllt und ihr Gehalt an Strontium bzw. Calcium flammenphotometrisch ermittelt. Die Ergebnisse dieser Bestimmungen sind in Abbildung 1 wiedergegeben. Das Auswaschen des Strontiums wurde bei pH 5,1 bis zur 20. Fraktion verfolgt. Spuren von Strontium erscheinen erst in der 16. Fraktion. Das Auswaschen von Strontium bei diesem pH-Wert ist sehr langsam. Wenn alles Strontium ausgewaschen werden soll, ist es nötig, mit 0,02 m DCyTE bzw. 0.02 m ÄDTE oberhalb pH 6,6 auszuwaschen.

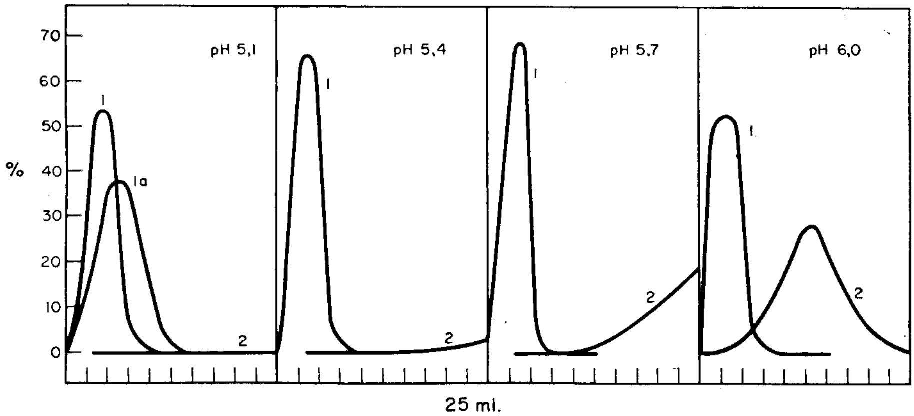

Abb. 1. Auswaschen von Calcium (Kurven 1, la) und Strontium (Kurven 2) mit 0,02 m DCyTE Lösung in Abhängigkeit vom pH-Wert.

Amberlite IR-120, NH_4, 0,15–0,30 mm, 1 cm^2 × 25 ml. Auswaschgeschwindigkeit 1,5 ml. min^{-1} cm^{-2}. Analysiert wurden Fraktionen zu 25 ml. Ordinate: ausgewaschene Prozente des Metallions. Ca — 20 mg (1a–40 mg) Sr — 22 mg.

Aus Abbildung 1 ist ersichtlich, dass der pH-Wert von 5,1 eine Grenze darstellt, bei der sich Calcium von Strontium und wie im weiteren festgestellt wurde auch von Barium verlässlich trennen lässt. Die Bildung der Calcium-DCyTE-Komplexe verläuft verhältnismässig schnell, so dass sich z.B. 100 mg Calcium mit 125 ml 0,05 m DCyTE quantitattiv auswaschen lassen. Das Strontium erscheint bei diesem pH-Wert erst in der 16. Fraktion, d.h. nach dem Durchlaufen von 375 ml Waschlösung. Zwischen den Grenzen der beiden Banden liegt also ein Volumen von wenigstens 175–200 ml Waschlösung, was zur scharfen Abtrennung vollkommen ausreicht. Eine noch schärfere Trennung erreicht man durch Anwendung von feiner gekörntem Ionenaustauscher. Dies hat jedoch auf der anderen Seite eine Abnahme der Durchlaufgeschwindigkeit zur Folge. Da bei der Komplexbildung beträchtliche Mengen Wasserstoffionen frei werden, muss zur Einhaltung des pH-Wertes der Puffer in 0,4 molaren Konzentration verwendet werden.

Auf Grund der obigen Erfahrungen wurde die Trennung von Calcium und Strontium in synthetischen Proben durchgeführt. Nach der Sorption am Ionenaustauscher wurde die Kolonne mit 50 ml Wasser ausgewaschen und hierauf Calcium mit 100 ml 0,02 m DCyTE-Lösung von pH 5,1 und anschliessend Strontium mit der gleichen Lösung von pH 7,2 bei konstanter Geschwindigkeit von 1,5 ml. min^{-1}. cm^{-2} eluiert. Die erhaltenen Fraktionen wurden mit Salpetersäure mineralisiert und ihr Gehalt flammenphotometrisch ermittelt. Die Messergebnisse (Tabelle 1) wurden mit Werten der unter den gleichen Bedingungen gemessenen Standartlösungen verglichen. Die Bestimmungsfehler, im Durchschnitt von ±3% rel. sind eher auf Fehler der flammenphotometrischen Bestimmung als auf Fehler der Trennug zurückzuführen.

TAB. I. CHROMATOGRAPHISCHE TRENNUNG VON CALCIUM UND STRONTIUM MIT 0,02 m DCyTE BEI pH 5,1 Sr = 3,94 mg

Probe	Ca, *mg*		Δ%	Ca:Sr
	gegeben	gefunden		
1	0,39	0,39	—	1:10
2	0,98	0,98	—	1:4
3	1,97	1,90	−3,5	1:2
4	2,95	3,10	5,1	1:1,3
5	3,93	3,93	—	1:1
6	5,11	5,20	1,7	1,3:1
7	6,29	6,20	−1,4	1,6:1
8	7,47	7,38	−1,2	1,9:1
1–8	3,94	3,94 ± 0,05	±1,3	Sr-Bestimmung

DIE BESTIMMUNG VON STRONTIUM IN ÜBERSCHÜSSIGEM CALCIUM

Die verhältnismässig grossen Unterschiede der Calcium-bzw. Strontium-DCyTE-Komplexe bei pH 5,1 wurden auch zur Trennung von einem grossen Überschuss des Calciums von wenig Strontium ausgenutzt. Die Metalle wurden aus 80–100 ml Lösung, die neben 200 mg Calcium noch verschieden grosse Mengen Strontium enthielt, am Ionenaustauscher adsorbiert. Nach dem Auswaschen der Säule mit 50 ml Wasser und 20 ml 0,4 m Ammoniumacetat (pH 5,1) wurde Calcium mit 200 ml 0,05 m DCyTE im gleichen Puffer ausgewaschen. Der Ionenaustauscher wurde mit 30–50 ml destilliertem Wasser ausgewaschen und das Strontium wurde dann mit 10 ml 0,05 m ÄDTE und 20 ml Schwarzenbachschem Puffer[16] eluiert. Die Säule wurde mit Wasser in Quarzgefässe so ausgewaschen, dass das Volumen des Eluiermittels und der Waschflüssigkeit kleiner als 100 ml war. Nach dem Einengen auf etwa 30 ml wurde die Mineralisierung mit 20 ml destillierter konzentrierter Salpetersäure durchgeführt. Die unter stürmischer Gasentwicklung verlaufende Oxydation wurde durch Zusatz von weiteren 20 ml konzentrierter Säure beendet. Hierauf wurde die Lösung zur Trockne abgedampft, mit 1 ml konzentrierter Salzsäure zweimal befeuchtet und erneut zur Trockne abgedampft. Der Abdampfrückstand wurde mit 2–4 ml konzentrierter Salzsäure versetzt, die ausgeschiedenen Salze wurden in destilliertem Wasser gelöst und die entstandene Lösung wurde dann in einen 25–50 ml fassenden Messkolben übergeführt. Der Strontiumgehalt wurde flammenphotometrisch ermittelt. Die Standartlösungen wurden in analoger Weise, d.h. durch Oxydation mit Salpetersäure bei Gegenwart von ÄDTE und Schwarzenbachschem Puffer bereitet.

Aus den in Tabelle 2 angeführten Ergebnissen geht hervor, dass eine verlässliche Trennung von Strontium bis zum Verhältnis von Calcium zu Strontium 2,000: 1 bei absolutem Gehalt an Strontium von 100 μg möglich ist. Die Hauptfehlerquelle bilden Verunreinigungen aus Salpetersäure, die zur Mineralisierung verwender wird, und daher vor der Verwendung umdestilliert werden muss. Bei sorgfältiger Arbeit ist die Calciummenge in der Strontiumfraktion kleiner als 0,1 mg, d.h. weniger als 0,05 % Ca von den ursprünglichen 200 mg.

Tab. II. Bestimmung kleiner Mengen Strontium in überschüssigem Calcium
Ca = 200 mg

Sr, *mg*		Differenz %
gegeben	gefunden	
5,00	4,93	−1,4
5,00	5,05	1,0
4,00	4,02	0,5
3,00	3,02	0,7
2,00	1,98	−1,0
1,00	1,01	1,0
0,75	0,75	0,0
0,50	$0,50_8$	1,6
0,20	$0,20_8$	4,0
0,10	0,11	10,0

Gleichzeitig mit Calcium wird auch Magnesium ausgewaschen. Mit DCyTE in 0,4 m Acetatpuffer (pH 5,1) wird Magnesium viel besser als mit ÄDTE ausgewaschen.[16] Die gleichzeitige Anwesenheit weiterer Metallionen wie z.B. von Eisen, Mangan, Aluminium, Titan, Blei, Zink, Kupfer, Uran, Nickel, Kobalt und von vielen anderen stört die Trennung nicht, da die genannten Metallionen mit DCyTE bei pH 5,1 sehr feste Anionenkomplexe liefern, die gleichzeitig aus der Säule mit Calcium ausgewaschen werden.

Die vorgeschlagene Trennung des Calciums von Strontium wurde bei der Bestimmung dieser Elemente in natürlichem Material und in Mineralwasser verwendet.[18] Die gleiche Methodik ist auch zur Isolierung von Strontium 90 aus verschiedenem Material anwendbar.

Summary—The separation of calcium from strontium has been carried out chromatographically. The cations after sorption on a cation-exchanger, are eluted stepwise by means of a 0·02–0·05*M* solution of 1,2-diaminocyclohexane-N,N,N',N'-tetra-acetic acid (DCyTE) in 0·4*M* ammonium acetate at pH 5·1. Under these conditions calcium is first eluted, and after about 400 ml, strontium. By means of this method 1 mg of strontium can be separated from 200 mg of calcium (*i.e.*, a ratio of 1:200) with an error of 1%.

Résumé—La séparation du calcium et du strontium a été réalisée par chromatographie. Les cations après fixation sur un échangeur de cations, sont élués graduellement au moyen d'une solution 0,02–0,05 M d'acide 1,2-diamine-cyclohexane N N N' N' tétracétique (D Cy T E) dans l'acétate d'ammonium 0,4 M à pH 5,1. Dans ces conditions, le calcium est élué en premier, et ensuite le strontium après passage d'environ 400 ml de solution. Par cette méthode on peut séparer 1 mg de strontium de 200 mg de calcium (c'est-à-dire un rapport de 1/200) avec une erreur de 1%.

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THE SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF SILVER

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Summary—Pyrogallol red may be used as a reagent for the spectrophotometric determination of silver ions in dilute solution. The reagent forms a yellow complex, $[Ag_2(C_{19}H_8O_8S)]^{2-}$, the colour of which is stable for at least 24 hr. Optical density measurements at 390 mμ show that at pH 7–7·5 Beer's law is obeyed over the range up to 85 μg of Ag^+. The colour system is unaffected by normal laboratory variations in temperature or lighting conditions and no special purification of reagents is necessary. None of the common anions interferes except the halides. Most cations interfere, but this is readily prevented by the addition of an amount of EDTA equivalent to the total molar concentration of the other metal ions. This total can readily be determined by a simple titration process on a separate aliquot of solution without separating the silver ions. The method appears to be more reproducible than the standard dithizone method.

Bromopyrogallol red may be used similarly with measurements made at *ca.* 440 mμ.

THERE is a dearth of satisfactory spectrophotometric methods for the determination of silver ions in very dilute (*ca.* $10^{-6}M$) solutions. The most commonly used reagents are *p*-dimethylaminobenzalrhodanine and dithizone.[1] The former is fairly selective in its action, but is troublesome in many respects. It reacts with silver in acidic media to give a coloured complex or a precipitate which is usually measured spectrophotometrically at *ca.* 470 mμ. Different authors recommend a variety of different conditions resulting in the formation either of a precipitate with considerable colour or alternatively of little precipitate and little colour. The colour system is very susceptible to changes in acidity and it is our experience that unaccountable results are not infrequent.

Silver dithizonate is normally extracted into carbon tetrachloride from acid solution and its absorption in the extract is measured at 460 mμ. For trace amounts of silver, however, the undue susceptibility of the reagent solution to photodecomposition, oxidation to diphenylthiocarbadiazone and the influence of changes in temperature combine to cause non–reproducibility from day to day.

Catalytic methods offer high sensitivity, but demand rigid control of experimental conditions, and are generally very susceptible to interference from other ions.

Bearing these limitations in mind and as a result of it being necessary for us to find a more reliable method for following the behaviour of traces of silver ions in extraction experiments, we have undertaken an examination of the colour systems formed by silver ions with eighteen metallochromic reagents including Solochrome Black T, *o*-Cresolphthalein complexan, P.A.N., P.A.R., Catechol violet, Glycine thymol blue, Pyrogallol red, Bromopyrogallol red, *etc.* As a result of this examination, it was concluded that the two last mentioned dyestuffs were alone worthy of detailed examination. This paper describes the application of both reagents to the determination of silver in aqueous solution. A later paper will discuss the application of one of them to the direct colorimetry in organic media of silver extracted by a selective new extraction system.[2]

The preparation of Pyrogallol red, (*cf.* Fig. I) was first reported in 1898 by Sohon,[3]

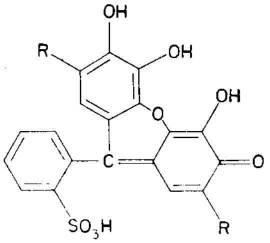

FIG. 1.—Pyrogallol red, R = H.
Bromopyrogallol red, R = Br.

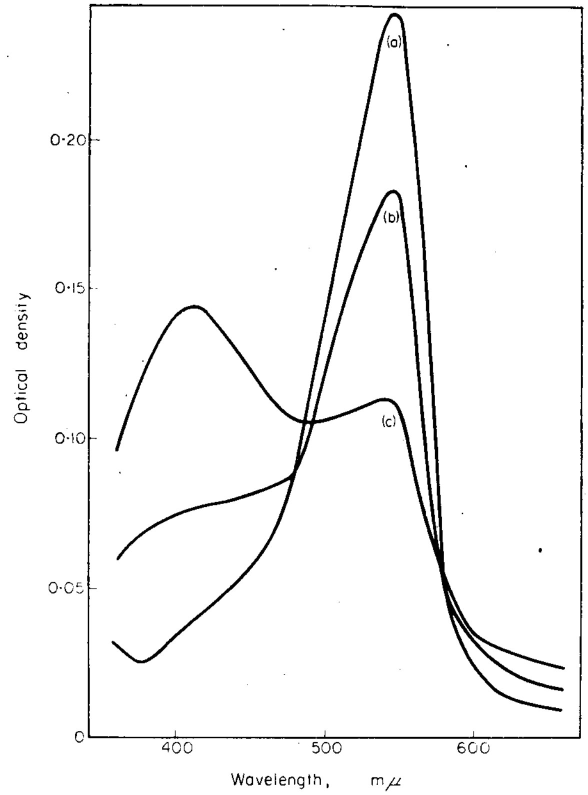

FIG. 2.—Silver-Pyrogallol red colour system
(*a*) 10 ml of $10^{-4}M$ Pyrogallol red buffered at pH 7 and diluted to 100 ml.
(*b*) As (*a*), but plus 10 ml of $10^{-4}M$ $AgNO_3$. Measured after 30 min.
(*c*) As (*a*), but plus 20 ml of $10^{-4}M$ $AgNO_3$. Measured after 30 min.

who obtained it by condensation of *o*-sulphobenzoic anhydride with pyrogallol. The dye and its dibromo-derivative, are now available commercially as a result of their use by Suk, Malat and Jenickova[4] as complexometric indicators for the ethylenediamine-tetra-acetate titration of several metal ions, including Bi, Ni, Co, Pb, Cd, Mg, Mn^{II}, Ce^{III} and the rare earths under a variety of pH conditions. Several other ions form coloured products, *e.g.*, Cu^{II} and Ag, though these cannot be utilised for indicator purposes. Both reagents have been advocated by Vodák and Leminger[5] as spot-test reagents for the detection of silver ions, but the test is subject to interference from practically all cations except those of the alkali metals. Both dyes are slightly soluble in ethanol, but insoluble in other organic solvents. In dilute aqueous solution they exhibit an orange-yellow colour in mineral acid solution, claret-red in near-neutral solution and violet in alkaline media. Pyrogallol red unlike its dibrominated derivative is markedly unstable in solutions of high pH, though otherwise quite stable.

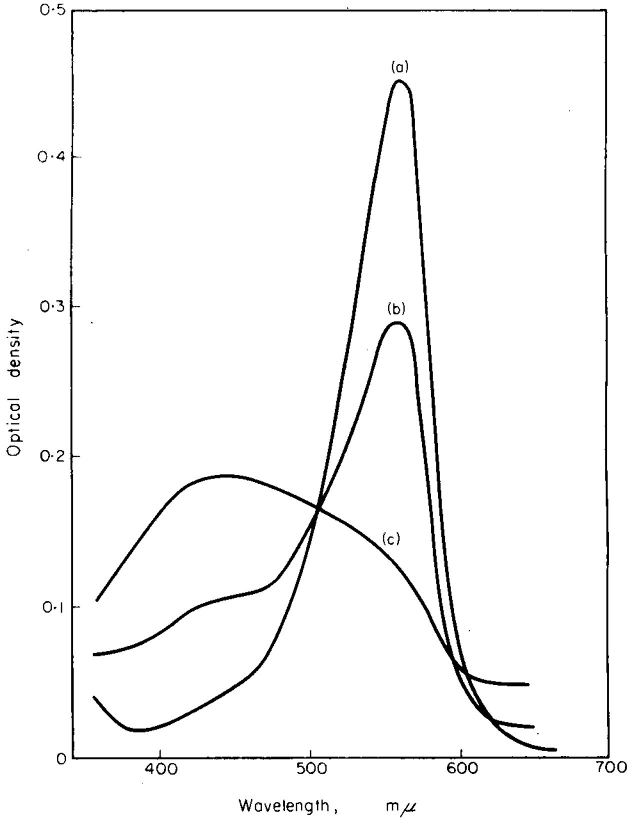

FIG. 3.—Silver-Bromopyrogallol colour red system
(*a*) 10 ml of $10^{-4}M$ Bromopyrogallol red at pH 7 diluted to 100 ml.
(*b*) As (*a*) but plus 10 ml of $10^{-4}M$ $AgNO_3$. Measured after 30 min.
(*c*) As (*a*) but plus 20 ml of $10^{-4}M$ $AgNO_3$. Measured after 30 min.

It was found in preliminary experiments that both reagents reacted best with silver around pH 7, when the claret-red colour of the reagent underwent a change to a less intensely absorbing greenish-yellow coloured solution together with a slight colloidal suspension (especially apparent at high concentrations of silver). Figs. 2 and 3 were obtained with a Unicam SP 600 spectrophotometer (10-mm path) using (*a*) 10 ml of the appropriate reagent in 10^{-4} *M* solution in 50% v/v aqueous ethanol; (*b*) with the addition of an equimolar amount of silver ion; and (*c*) a two-molar ratio of silver ion. In each case the solution was buffered with 20% sodium acetate to pH ≈ 7 and diluted to 100 ml. In each case, it will be observed that the addition of silver decreases and practically eliminates the band absorption *ca.* 550 mμ and builds up another band absorbing *ca.* 410–420 mμ. The results represented by Figs. 2 and 3 were obtained after a reaction time of 30 min. Subsequently it was found that longer standing caused increased optical densities at the silver peaks *ca.* 410 mμ and decreased absorption at the reagent peaks *ca.* 550 mμ. Further experiments established that the optimum conditions were obtained after 1·5 hr standing time and that for maximum colour formation it was desirable not to dilute the solutions to 100 ml till this time had elapsed. The "blank" solutions were quite stable, and it was found that the absorption at the silver peaks exhibited maximum stability; the absorption *ca.* 400 mμ remained unchanged for several days.

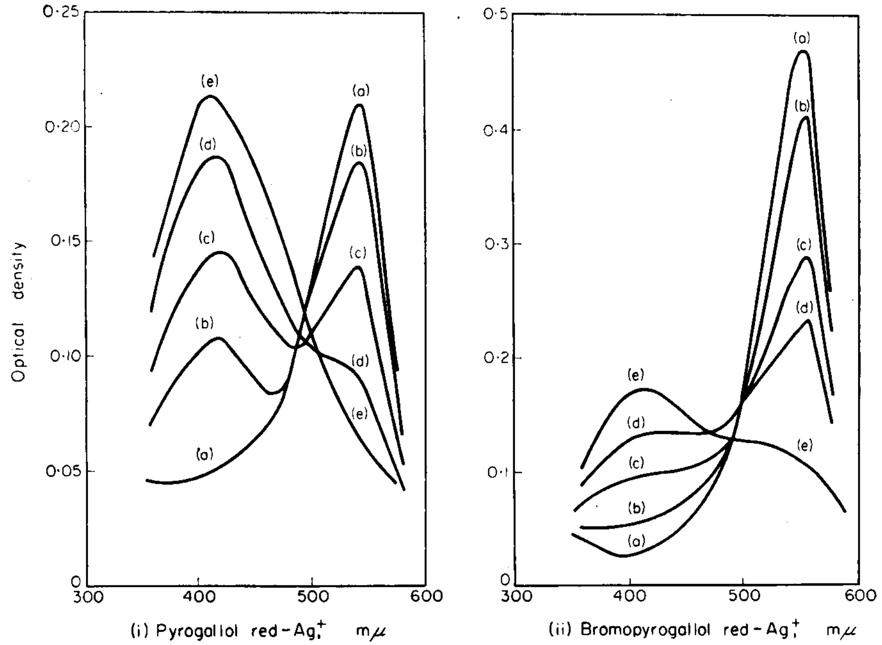

FIG. 4.—Comparison of Pyrogallol red and Bromopyrogallol red under optimum conditions Standard time of development 90 min *before* dilution.

(*a*) 10 ml of reagent.
(*b*) 10 ml of reagent +5 ml of $10^{-4}M$ $AgNO_3$.
(*c*) 10 ml of reagent +10 ml of $10^{-4}M$ $AgNO_3$.
(*d*) 10 ml of reagent +15 ml of $10^{-4}M$ $AgNO_3$.
(*e*) 10 ml of reagent +20 ml of $10^{-4}M$ $AgNO_3$.

An attempt was now made to establish which reagent was to be preferred for the determination of silver and to ascertain whether it was best to measure the decrease in absorption of the reagent bands *ca.* 550 mμ or the silver bands *ca.* 400 mμ. The best pH range for Pyrogallol red was found to be 7–7·5 and for Bromopyrogallol red the best value was 7·5. Using these optimum conditions, varying amounts of $10^{-4}M$ silver nitrate were added to constant amounts of the two reagents and the results obtained (*cf.* Fig. 4) show that at the most stable peak, *ca.* 400 mμ, the Pyrogallol red reagent is the more sensitive. In addition, a 2:1 complex [$(Ag)_2$ Pyrogallol red] or [$(Ag)_2$ Bromopyrogallol red] is suggested by the observation that ratios of silver to reagent greater than two cause no further increase in the optical density of the solution.

A continuous variations plot with 10^{-4} M Pyrogallol red and silver nitrate solutions at 390 mμ* (*cf.* Fig. 5) shows a clear indication of a 2:1 silver-reagent complex.

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* 390 mμ represents the wavelength of maximum separation between the absorption curves for the reagent and its silver complex.

Similar results were obtained with Bromopyrogallol red when measurements were made at 440 mμ.

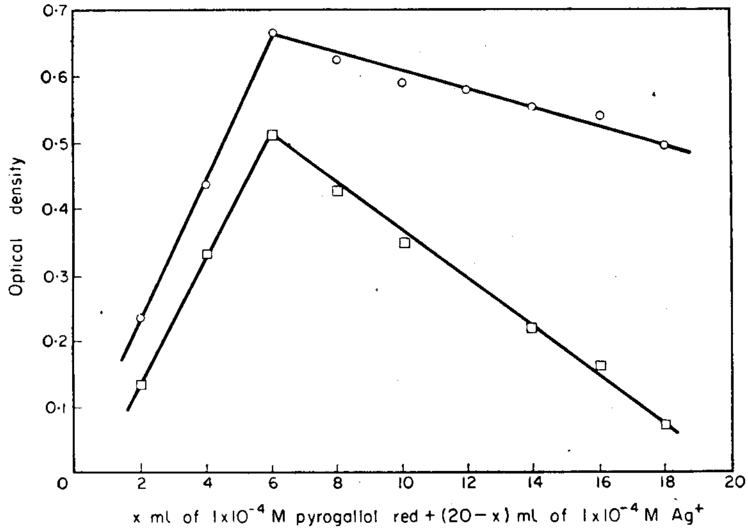

FIG. 5.—Job Plot of Silver—Pyrogallol red system (390 mμ)
(*a*) Experimentally obtained curve.
(*b*) Curve corrected for reagent background.
Point of maximum absorbance, Ag/reagent = 2·2/1

A calibration curve was next obtained by the procedure recommended under *Experimental.* It is represented by a straight line passing through the origin. Beer's law is obeyed up to 85 μg of silver. The interference of a selected range of cations *viz.*, Hg^{II}, Cu^{II}, Al, Zn, Pb, Mg, Ca, Ba, was examined, and not unexpectedly, all were found to interfere by reacting with the reagent. All these complexes are broken down by EDTA, but though silver only forms a weak complex (Log $K \approx 10^{-7}$) with the complexan it is also partially attacked; masking by the addition of excess of EDTA is therefore not possible. Similar attempts to utilise weak complexans such as iminodiacetic acid and anthranilic acid diacetic acid also failed, though they caused much less interference with the silver-Pyrogallol red colour system. The most successful method of overcoming the interferences was to add an amount of EDTA equivalent to the molar concentration of these foreign cations. This amount can readily be established in most instances by a process of pretitration on an aliquot sample of the solution. Silver does not interfere with EDTA titrations at pH < 7 and in the titration of calcium and magnesium it can readily be masked by cyanide ion. Only with aluminium was difficulty experienced, because of the lack of an indicator sufficiently reliable at low dilutions. The use of a suitable indicator or other means of detecting the end-point would probably eliminate its interference in the same way. The interference of copper cannot be overcome in this manner because of the colour of the Cu^{II}-EDTA complex and the stability of the Cu-Pyrogallol red compound. Table I shows the interference of ten-fold molar ratios of these cations and the removal of such interference by the addition of the requisite amount of EDTA, this latter value having been obtained by direct complexometric titration of the foreign ion in the presence of the silver without separation. It will be seen that in most of these

TABLE I. MASKING OF INTERFERING IONS*

Cation nitrate, *ca.* $10^{-3}M$.	Titration system		Colour change	Amount of $10^{-3}M$ EDTA, *ml*	Solutions	Optical density, 4-cm cuvettes, 390 mμ
	Indicator	Buffer				
Hg^{II}	Xylenol Orange[6]	Pyridine, pH 6	Claret → yellow (good)	0·94	(a) Ag only	0·111
					(b) Ag + ion	0·172
					(c) EDTA added	0·111
Pb	Xylenol Orange[6]	Acetate, pH 5	Claret → yellow (good)	0·95	(a)	0·132
					(b) As above	0·046
					(c)	0·133
Zn	Xylenol Orange[6]	Acetate, pH 5	Purple → yellow (fair)	1·06	(a)	0·118
					(b) As above	0·148
					(c)	0·118
Ca	Acid Alizarin Black SN[7]	NaOH, pH 12 + 5% KCN	Claret → blue (good)	0·93	(a)	0·126
					(b) As above	0·133
					(c)	0·129
Cu^{II}	*o*-Dianisidine-tetra-acetic acid[8]	Acetate, pH 6	Fluorescent (fair)	1·06	(a)	0·135
					(b) As above	0·025
					(c)	0·109
Al	Chrome Azurol S[9]	Acetate, pH 4 80°	Violet → orange-red (poor)	0·82	(a)	0·126
					(b) As above	0·008
					(c)	0·073
Mg	Solochrome Black 6B[10]	Ammonia, pH 10 + 5% KCN	Claret → blue (fair)	1·08	(a)	0·126
					(b) As above	0·130
					(c)	0·128

* The amount of silver taken in these experiments was *ca.* 30–40 μg. In each case a ten-fold molar ratio of the interfering cation was added.

experiments the interference has been completely eliminated. The interference of other cations, most of which could also be complexed preferentially with EDTA as described, was not examined further, though it is logical to assume that moderate amounts of coloured ions such as nickel, cobalt and chromium^{III} would still interfere in the same way as copper^{II}.

As with cations, the interference of only a selected range of anions was examined. These were nitrate, sulphate, chloride, phosphate, perchlorate and acetate. Only chloride was found to interfere.* It was noticeable, however, that the presence of the anions speeded up colour formation. Thus a thousand-fold excess of nitrate ion, relative to the molar concentration of silver ion, caused a reduction of the necessary standing time from 90 to 30 min. Such large excesses of anion, however, caused slightly low recoveries, and promoted instability of the colour. It was noticeable, also, that a moderate excess of nitrate ion (*ca.* ten-fold) was beneficial, in that it eliminated the opalescence of the solution which had hitherto been present. Consequently the addition of an excess of nitrate ion is recommended as a standard procedure.

DISCUSSION

The proposed method for the determination of silver is considered to be essentially simpler than the standard dithizone and *p*-dimethylaminobenzalrhodanine procedures which have hitherto been used almost exclusively for the determination of trace amounts of silver. There is no danger of precipitation and no necessity for critical adjustment of acidity as with *p*-dimethylaminobenzalrhodanine, nor is it essential to extract and control closely conditions such as temperature, purity of reagents, absence of strong daylight (or fluorescent light), as with dithizone. The calibration curve can be reproduced precisely from day to day, and the silver-Pyrogallol red complex, once formed, maintains an unchanged optical density for several days. Consequently, there is a wider latitude of experimental conditions than with the standard methods for silver. The stability of the silver complex is well illustrated by its resistance to break down by chloride ion. Thus, *once the silver complex has been formed* the addition of an amount of chloride ion theoretically sufficient to precipitate all the silver in it causes no diminution in the intensity of the colour. No shielding of the solution from laboratory light sources or normal day-light is required.

TABLE II. ANALYSIS OF UNKNOWN SOLUTIONS FOR SILVER BY THE PYROGALLOL RED PROCEDURE

Ag^+ supplied, μg	Ag^+ found, μg	Error, %
28·30	31·3	+9·6
42·07	41·3	−1·9
29·99	29·9	−0·3
12·30	13·8	+10·9
47·30	47·0	−0·6
57·40	53·7	−6·9
73·10	71·0	−3·0

Against these attractive features relative to conventional reagents, the Pyrogallol red method is subject to more cationic interference. However, these interferences can in most cases be readily overcome by the addition of an amount of EDTA equivalent

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* Chloride interferes by slowing down colour formation.

to the total molar concentration of the foreign ions *e.g.*, Ca, Mg, Zn, Pb, Hg^{II}. The necessary amount is readily determined by complexometric titration, since silver does not interfere with complexometric titrations in acid solution, and is readily masked in alkaline media. None of the common anions interferes except chloride.

Finally, the results of the analyses of a series of unknowns are given in Table II. Precision data were obtained by multiple analyses of a series of solutions containing 32·4 μg of silver ion. These gave an average deviation of 1·3 μg Ag (standard deviation ± 1·8 μg).

EXPERIMENTAL

Reagents

Silver nitrate, $10^{-4}M$: Prepared by dilution of standard $0{\cdot}1M$ silver nitrate solution.

Pyrogallol red, $10^{-4}M$: 10·5 mg of Pyrogallol red (B.D.H. Ltd.) dissolved in 125 ml of absolute ethanol and diluted to 250 ml with distilled water.

Sodium acetate, 20%: 20 g of AnalaR sodium acetate trihydrate dissolved in water and diluted to 100 ml.

Sodium nitrate ca. $10^{-3}M$: 85 g of AnalaR sodium nitrate dissolved and made up to 1 litre with distilled water.

Apparatus

Unicam S.P. 600 Spectrophotometer: Operated from stabilised 12V transformer; 1- and 4-cm cuvettes.

Method

(*a*) *Preparation of calibration curve.* Pipette 1-ml to 10-ml aliquots of $10^{-4}M$ silver nitrate solution into 100-ml standard flasks, add 1 ml of $10^{-3}M$ sodium nitrate and enough distilled water to give a constant volume (*i.e.*, 11 ml). Finally add 0·5 ml of 20% sodium acetate to give a final pH of 7–7·5 and 5 ml of $10^{-4}M$ Pyrogallol red reagent. Do not dilute the solutions at this stage, but allow the colour system to develop for 90 min. Then dilute the contents of each flask to 100 ml and measure the optical density of each solution in a 4-cm cuvette at 390 mμ against a standard containing all the reagents but no silver. Provided that the dilution is carried out after 90 min, the absorption measurements may be made either immediately or after the lapse of several hr.

The graph of optical density against the amount of silver taken is a straight line from 10 to 85 μg of Ag and passes through the origin.

$$1 \text{ ml of } 10^{-4}M \text{ AgNO}_3 \equiv 10{\cdot}8\ \mu\text{g Ag}.$$

(*b*) *Determinations.* Take an aliquot of the unknown silver solution containing <85 μg of Ag^+ (in 10 ml) in a 100-ml flask, add the necessary amount of EDTA solution (*vide infra*) followed by 1 ml of $10^{-3}M$ sodium nitrate solution and sufficient distilled water to make the volume up to 11 ml. Finally, into this solution, pipette 0·5 ml of 20% sodium acetate and 5 ml of $10^{-4}M$ Pyrogallol red solution. Allow the contents to stand for 90 min *without further dilution.* Lastly dilute the contents to 100 ml and measure the absorbance of the solution against a reagent blank containing no silver, but carried throughout the above processes.

(*c*) *Amount of complexan required.* If the silver solution contains ions which react with Pyrogallol red, take a 5-ml or 10-ml aliquot of this solution in a conical flask, add a small amount of the necessary buffer and indicator (*cf.* Table I), and titrate with an EDTA solution of suitable molarity till the end-point is reached. Note the volume of EDTA required per ml of test solution.

Note: Silver does not react with the great majority of metallochromic indicators which function in solutions of low pH, and its chelate with EDTA is too weak to cause high results. If, however, the ions *e.g.*, Mg, Ca, must be titrated in alkaline solution, then both the indicator and the EDTA should be protected, through the addition of potassium cyanide as a masking agent, against attack by silver ions. This allows the total of (EDTA) titratable ions to be determined.

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Zusammenfassung—Pyrogallolrot kann als Regans zur photometrischen Bestimmung von Silber verwendet werden. Das Reagens formt mit Silber einen gelben Komplex der Zusammensetzung $[Ag_2(C_{19}H_8O_8S)]^{2-}$. Die Farbe ist für wenigstens 24 Stunden beständig. Absorptionsmessung bei 390 mμ zeigten, dass im pH-Bereich 7–7·5 Beer's Gesetz bis hinauf zu 85 μg Silber erfüllt ist. Die Farbe ist unbeeinflusst durch Änderungen in Temperatur und Beleuchtung, wie sie normalerweise im Laboratorium auftreten; keine besondere Reinigung des Reagenses ist nötig. Von den gewöhnlichen Anionen stören lediglich die Halide. Die meisten Kationen stören, doch kann das leicht ausgeschaltet werden, durch Zugabe von ÄDTA in einem zu der anwesenden Kationenmenge äquivalenten Betrag. Diese Menge kann leicht mittels einer seperaten Titration in einem Aliquot der Probe ermittelt werden, ohne vom Silber zu trennen. Die Methode scheint besser reproduzierbar zu sein, als die üblicherweise angewandte Dithizonmethode. Brompyrogallolrot kann in gleicher Weise verwendet werden nur ist die Messung bei etwa 440 mμ durchzuführen.

Résumé—Le rouge de pyrogallol peut être utilisé comme réactif pour le dosage spectrophotométrique des ions argent en solution diluée. Le réactif forme un complexe jaune $[Ag_2(C_{19}H_8O_8S)]^{2-}$ dont la couleur est stable pendant au moins 24 h. Les mesures de la densité optique à 390 mμ montrent que, à pH 7–7,5, la loi de Beer est suivie dans le domaine allant jusqu'à 85 μg d'ions Ag^+. La couleur n'est pas modifiée par les variations normales de température ou d'éclairage du laboratoire, et il n'est pas nécessaire de purifier spécialement les réactifs. Aucun des anions communs ne gêne, sauf les halogénures. La plupart des cations gênent, mais cette interférence est facilement évitée par l'addition d'une quantité d'EDTA équivalente à la concentration molaire totale des autres ions métalliques. Ce total peut être facilement déterminé par un simple titrage sur une portion de la solution sans séparer les ions argent. Cette méthode se présente comme plus reproductible que la méthode standard à la dithizone. Le rouge de bromopyrogallol peut être utilisé de manière analogue, les mesures étant faites à environ 440 mμ.

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PHOTOMETRIC TITRATIONS—III

THE CONSECUTIVE TITRATION OF CALCIUM AND MAGNESIUM

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Summary—The photometric titration of calcium in ammonia-ammonium chloride buffer, pH 10, is studied. Ethyleneglycol-bis(aminoethyl)-tetra-acetic acid is used as titrant and murexide as indicator. This method permits the direct titration of calcium in presence of up to a hundred-fold amount of magnesium. The determination of magnesium can immediately follow in the same solution to a photometric end-point using EDTA as titrant and Eriochrome Black T as indicator. Interferences and their exclusion are discussed.

INTRODUCTION

THE "classical" complexometric determination of calcium and magnesium is based on the use of two aliquots. In the first aliquot calcium is titrated at a very high pH where magnesium is precipitated as the hydroxide. In the second aliquot the sum of the two metals is determined at pH 10. The magnesium content is calculated by difference. This procedure is a significant improvement over the methods available before the introduction of complexometric titrations. However, certain disadvantages and limitations persist and many papers have been published describing attempts to overcome them.

The method of masking magnesium by hydroxide precipitation has some disadvantages. The precipitate will include calcium, thus causing an error which will become intolerably high when a certain Mg:Ca ratio is exceeded. This error may be effectively reduced by adding the complexing agent (EDTA) in excess over the amount of calcium present and then precipitating the magnesium and back-titrating the excess of EDTA in an aliquot of the clear supernate.[1] However, this procedure should be classified strictly as a separation and not as masking. Lott and Cheng[2] were able to decrease the co-precipitation of calcium considerably by the addition of polyvinyl alcohol. Burg and Conaghan[3] reported the same effect with acetylacetone.

Another problem caused by the hydroxide precipitation is the adsorption of the indicator; this was studied in detail by Belcher and coworkers.[4] Here, also, the addition of polyvinyl alcohol or acetylacetone serves as an effective remedy.[2,3]

Despite these improvements, the precipitate still was considered a potential source of trouble and its exclusion seemed desirable. Tichomorova and Simackova[5] performed the titration of calcium at a high pH and avoided the magnesium precipitation by addition of tartrate. For high concentrations of magnesium, considerable amounts of tartrate are necessary for a complete prevention of the precipitation. When applying this method, and using EDTA as the titrant, the present authors found high results for calcium, which is in agreement with Burg and Conaghan,[3] and indicates that some of the magnesium is co-titrated.

When EGTA [ethyleneglycol-bis(aminoethyl)-tetra-acetic acid] was introduced as a titrant for calcium the situation was greatly improved, since the titration was performed at a pH where magnesium remains in solution without the addition of a masking agent. The logarithms of the stability constants of the calcium and magnesium EGTA complexes are 11.0 and 5.2 respectively.[6] This difference is sufficient for the selective titration of calcium in the presence of magnesium. Excellent results have been obtained employing a potentiometric end-point with the mercury drop electrode on the macro[7] as well as on the ultramicro scale.[8] An indirect end-point using the zinc-Zincon system was developed, which permitted a visual titration.[9,10] Unfortunately, this indicator system is very sensitive to changes in the ammonia concentration thus causing difficulties in its application to practical analyses. Both methods are somewhat restricted because certain important masking agents, in particular cyanide, cannot be used.

Burg and Conaghan[3] proposed a combination of the old and new methods. These investigators titrated calcium at a high pH with EGTA (using Calcon as the indicator) in the presence of tartrate to prevent the precipitation of magnesium. No magnesium was co-titrated under these conditions because of the low stability constant of its EGTA complex. Unfortunately, it was impossible to proceed with an EDTA titration of magnesium (using Erio-T as the indicator) after lowering the pH, because the end-point was very sluggish. Therefore, they titrated the sum of calcium and magnesium in another aliquot and again found the magnesium by difference. The use of aliquots is inconvenient, and presents a serious difficulty when only a small volume of the sample is available. Another difficulty occurs in adjusting the pH to a value as high as 13 when a composite sample is to be analysed and ammonium salts have been introduced during any previous analytical operations. These salts would have to be removed before the calcium titration.

The present authors have attempted, therefore, to find a way to titrate calcium in the presence of magnesium at a lower pH. The pH should be in a range where magnesium is not precipitated, thus avoiding errors arising from occlusion, adsorption or the addition of a masking agent. Furthermore, the magnesium should be titrated in the same solution immediately following the calcium determination after only a change of indicator and titrant.

A method based on a visual end-point detection did not seem feasible for theoretical reasons; hence, attention was directed towards a photometric titration. An indicator unusable in a visual titration because of a sluggish end-point might be used in a photometric titration. Furthermore, the second colour transition in the presence of the first indicator will be more readily detected by the phototitrator than by the observer's eye.

Preliminary experiments showed that of all the indicators investigated murexide was the only one which gave a useful colour change with calcium at pH 10. The colour transition at the end-point at pH 10 was insufficient for a visual indication, but gave well developed titration curves when a phototitrator was used. Murexide has frequently been used in photometric titrations of calcium at higher pH values before the introduction of better indicators.[11,12] To the best of the authors' knowledge, murexide has never been used at pH 10.

The absorption spectra of murexide and the calcium-murexide complex at pH 10 are shown in the lower part of Fig. 1 by curves I and II. Subtracting the two curves gives what may be called the Δ-curve, A, in the upper part of Fig. 1. The Δ-curve shows that the largest difference in the absorbance at the end-point occurs at 490 mμ.

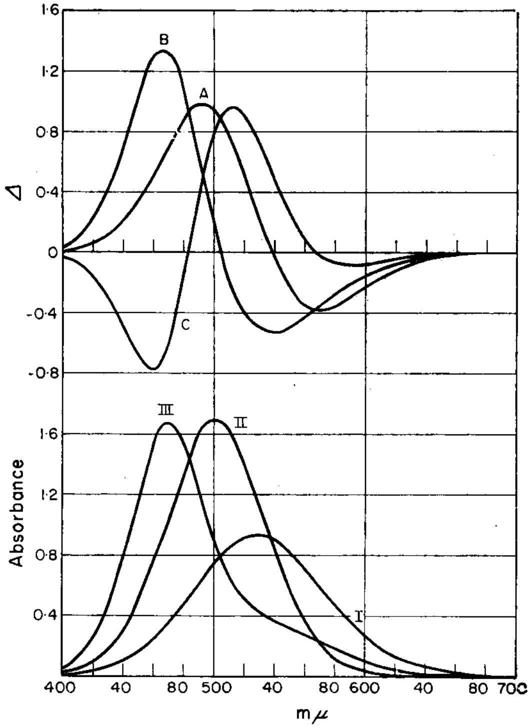

FIG. 1.—Lower part: Spectral curves of I: murexide, II: calcium-murexide complex, III: magnesium-murexide complex. The total concentration of murexide in all three samples was identical. pH 10.
Upper part. A, Δ-curve II minus I (from lower part): B, Δ-curve III minus I (from lower part): C, Δ-curve A minus B (from upper part).

At pH 10, the formation of the magnesium-murexide complex must also be considered. The colour of this rather weak complex is yellow. Its absorption spectrum is shown as curve III in Fig. 1. Therefore, with high magnesium concentrations the colour change will not be to that of free murexide but to the yellow of the magnesium complex. With the phototitrator the situation is a fortunate one, in that at about 505 mμ absorbance curves of the magnesium-murexide complex and the free murexide show an isosbestic point. At this wavelength the response of the phototitrator is independent of the "colour-change" *i.e.*, whether it proceeds to that of murexide or its magnesium complex. This fact is also evident from the Δ-curve, B, which is obtained by subtracting the absorbance curve of the free murexide from the curve of the magnesium-murexide complex. The optimum wavelength for the titration, 505 mμ, can also readily be read from curve C, which is obtained by subtracting curve B from curve A (upper part of Fig. 1.)

Despite the fact that the magnesium-murexide complex is weak, a large excess of magnesium might cause a shift of the equilibrium

$$\text{Ca–Mu} + \text{Mg} \rightleftharpoons \text{Mg–Mu} + \text{Ca} \qquad (1)$$

(omitting charges for simplicity) towards the right to an extent that no useful endpoint could be obtained. However, experiments have shown that even with a ratio of

$Mg:Ca = 100:1$, the break in the titration curve is still sufficiently pronounced to permit a sound extrapolation towards the end-point.

The maximum in the Δ-curve for Erio T and its magnesium complex is at approximately 620 mμ.[6] Murexide does not absorb appreciably at this wavelength, hence there will be no interference when magnesium is titrated after finishing the calcium determination. Preliminary experiments have shown that there is no interference from a small excess of EGTA when magnesium is titrated with EDTA. This excess results from the calcium titration, since some points beyond the end-point are necessary in order to provide an appropriate basis for the extrapolation. Thus the EDTA titration of magnesium can be performed in the same solution immediately following the determination of calcium.

EXPERIMENTAL

Apparatus

All titrations were carried out with the phototitrator described in a previous paper of this series.[13] Rectangular cells with light paths of 1·5 and 3 cm and a capacity of 100–200 ml were used. The absorbance curves were made with a Cary Model 14 Recording Spectrophotometer.

Reagents

Solutions of the metal ions were prepared from appropriate salts. EGTA and EDTA solutions were prepared by dispersing the acids in de-ionised water and adding enough sodium hydroxide to achieve complete dissolution. The solutions were standardised according to well-established chelometric procedures. The indicators murexide and Eriochrome Black T were ground with sodium chloride to a fine powder. All materials used were of reagent grade quality.

Procedure

Exactly measured volumes of the metal ion solutions were pipetted into the titration cell and when necessary were approximately neutralised with sodium hydroxide. Between 5 and 10 ml of buffer (pH 10) were added, and the solution was diluted to about 150 ml. The cell was positioned in the phototitrator and the 508-mμ interference filter was inserted into the filter holder. With this solution as reference 100% transmittance was set on the galvanometer. A spatula tip of ascorbic acid was added to prevent air oxidation of the indicators. Murexide indicator powder was added, and the calcium was titrated with EGTA. The transmittance was recorded and plotted on semi-log graph paper. After the calcium end-point was found, the 622-mμ filter was inserted and Erio T indicator was added. The transmittance was adjusted to about 95% (instead of 100% to provide room for changes through dilution) and the magnesium was titrated with EDTA. The end-points were found at the intersection of the straight lines drawn through the recorded points.

RESULTS AND DISCUSSION

Typical curves are presented in Fig. 2 for the determination of calcium and magnesium alone and for the titration of calcium in the presence of various amounts of magnesium. The end-points in cases of high Mg: Ca ratios can be located better when the curves are replotted in terms of absorbance on linear graph paper with a suitable scale.

Table I shows the very satisfactory precision.

Those metal ions which interfere with the visual titrations of calcium and magnesium of course also interfere with the photometric titration. The same methods of masking can be used successfully with the exception of masking by precipitation. Potassium cyanide was used to mask Co, Ni, Cu, Zn, Cd and Hg. Aluminium was masked by the addition of triethanolamine. Iron was converted into the ferrocyanide complex.[14] When tartrate ion is involved during a masking procedure, care should be taken to avoid too great an excess of it. In the presence of unduly large amounts of tartrate

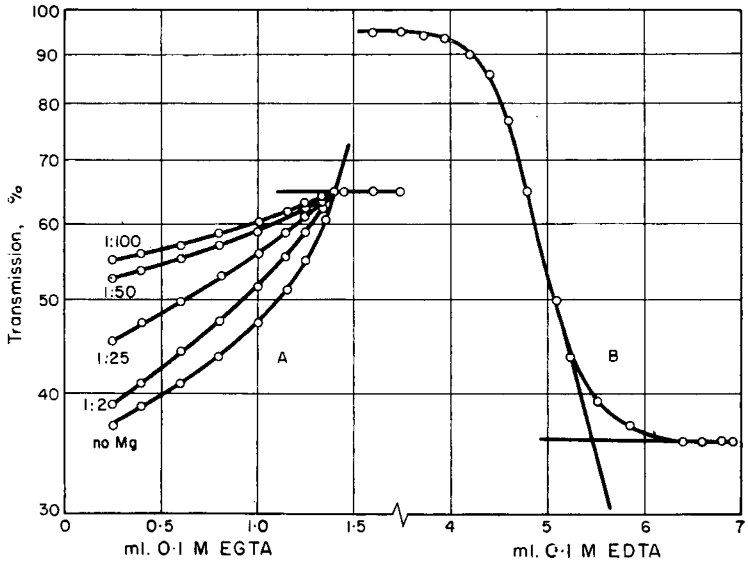

FIG. 2.—Typical titration curves.

A: Calcium titrated with EGTA at pH 10 using murexide as indicator at various ratios of Ca:Mg. 508 mμ.

B: Magnesium titrated with EDTA at pH 10 using Eriochrome Black T as indicator. 622 mμ.

TABLE I. REPRESENTATIVE RESULTS FOR THE TITRATION OF CALCIUM AND MAGNESIUM

$CaCl_2$, 0·1M		Mg: Ca ratio	$Mg(NO_3)_2$,0·1M	
Taken, ml	Found, ml		Taken, ml	Found, ml
2·95	2·96	—	none	
5·23	5·22	—	none	
9·45	9·50	—	none	
none		—	2·65	2·68
none		—	3·66	3·61
none		—	4·38	4·41
3·60	3·65	1·7:1	6·02	6·02
4·29	4·29	0·7:1	3·07	3·06
6·43	6·42	0·15:1	0·94	0·98
1·13	1·15	22:1	25	not determined
1·24	1·17	40:1	50	not determined
1·00	1·04	100:1	100	not determined
1·51	1·55	132:1	100 (0·2M Mg)	not determined

a drift of the galvanometer pointer was observed for which, at the present time no satisfactory explanation can be given.

It is essential to protect both indicators from air oxidation (which manifests itself *via* a drift of the galvanometer) by maintaining a sufficient concentration of ascorbic acid in the titration solution. If the titration is extended over a longer period of time, further additions of ascorbic acid during the titration are recommended.

It is of advantage to keep the solutions reasonably free of carbon dioxide, otherwise a precipitate of calcium carbonate may form. This precipitate will disappear during the course of the titration. It is, however, important to proceed very slowly especially near the end-point, because the dissolution is a slow process. No false results are obtained when working with slightly turbid solutions when the rate of titration is reduced appropriately.

The new method was practically evaluated by the analysis of an NBS sample "Burned Magnesite No. 104". The sample was dissolved in hydrochloric acid and filtered into a volumetric flask. An aliquot of the solution was taken, the iron and aluminium masked with cyanide and triethanolamine. A turbidity which occurred during the process was filtered off, and the calcium was titrated with EGTA in the manner described above.

A determination in triplicate gave the following values: 3·34, 3·29 and 3·52%. The average, 3·38%, compares favourably with the certified value of 3·35% of CaO.

Acknowledgement—This work was performed under a grant from the National Science Foundation. Permission to use their Cary Model 14 Spectrophotometer was given by the Coca-Cola Co., Atlanta, Ga., U.S.A. The National Bureau of Standards provided the magnesite sample. These aids are gratefully acknowledged.

Zusammenfassung—Die photometrische Titration von Calcium in Ammoniak-Ammoniumchlorid-Puffer pH 10 wird beschrieben. Äthylenglycol- bis(aminoäthyl) tetraessigsäure ist das Titrationsmittel und Murexid der Indicator. Die Methode gestattet die direkte Bestimmung von Calcium in Gegenwart von bis zur hundertfachen Menge Magnesium. Die Bestimmung des Magnesiums kann unmittelbar angeschlossen werden, wobei mit ÄDTE titriert wird und Eriochromschwarz T als Indicator dient. Störungen werden untersucht und über ihre Ausschaltung wird berichtet.

Résumé—Les auteurs ont étudié le dosage photométrique du calcium en tampon ammoniaque-chlorure d'ammonium à pH 10. L'acide éthylène glycolbis (aminoéthyl) tétracétique est utilisé comme agent titrant et la murexide comme indicateur. Cette méthode permet le titrage direct du calcium en présence de plus de cent fois plus de magnésium. Le dosage du magnésium peut suivre immédiatement dans la même solution le point équivalent étant déterminé par photométrie en utilisant l'EDTA comme agent titrant et le noir ériochrome T comme indicateur. Les interférences et leur élimination sont discutées.

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DETERMINATION OF ALKALI SULPHIDES BY DIRECT TITRATION

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Summary—A new titrimetric method has been developed for the determination of sulphides with cadmium acetate standard solutions and dead-stop indication. The determination must be carried out in a medium buffered by sodium acetate. The determination is not interfered with by sulphur oxides, nitrites, but it is affected by hydroxide and cyanide ions.

THE simple and rapid iodometric method cannot be applied to the determination of the sulphide content of sodium sulphide, because sodium sulphide is decomposed into various sulphur acids through time; the presence of these interferes with the determination. The determination is sometimes made by precipitating the sulphide with cadmium acetate, and titrating the sulphide precipitate iodometrically after filtration.[1] When the necessary precautions are taken, the method is fairly accurate, but lengthy.

It was necessary therefore to develop a rapid direct titration method.

The method was developed on the basis of the property of sulphide of forming very insoluble precipitates with many cations. For precipitation-titration investigations silver and cadmium ions were selected; the end-points were determined potentiometrically. Employing sulphide solutions of high purity, the titration can be carried out with either cation and a sudden potential change of 1000 or 300 mV respectively, can be measured at the end-point.

For the results obtained with various standard solutions, a constant deviation of 1–2% (corresponding to the solubility product) can be maintained.

Should sulphur acids (sulphite, thiosulphate) or chloride be present in addition to sulphide, the determination can be made only with cadmium standard solution, since the silver ions will react with sulphur acids and chloride.

It has also been investigated whether the end-point of the titration with cadmium may be indicated by the very elegant dead-stop method. On the basis of the promising initial results, a dead-stop indication method for the determination of sulphide with cadmium acetate standard solution was developed.

EXPERIMENTAL

Standard solution

Dissolve 26·65 g of cadmium acetate, $Cd(CH_3COO)_2 \cdot 2H_2O$, and 5 g of concentrated acetic acid in 1000 ml. The cadmium acetate solution is standardised, by the present method against a sulphide solution, the concentration of which has been determined.

The concentration of the sulphide solution is determined by precipitating the sulphide by excess cadmium acetate, filtering, transferring the cadmium sulphide precipitate together with the filter paper to a hydrochloric acid—iodine standard solution, and titrating the excess iodine by thiosulphate standard solution. The sulphide concentration is calculated from the iodine consumption.

Procedure

Transfer 20 ml (20–50 mg of S) from the approximately neutral solution under investigation to a beaker, dilute by boiled distilled water to *ca.* 50 ml, and add approximately 1 g of crystallised sodium acetate. Employing a galvanometer of 1·5–4·0 × 10^{-8} A sensitivity for 50–100 mV potential, titrate the solution with a 0·1*M* cadmium acetate standard solution, using dead-stop indication. During titration, the current intensity decreases continuously, but increases suddenly at the end-point.

The accuracy of the method is ±0·2%. Results of measurements are shown in Table I.

TABLE I.

No.	Weight of sample, *mg* of S^{--}	Weight found, *mg* of S^{--}	Deviation	
			mg	%
1	29·70	29·67	−0·03	−0·1
2		29·65	−0·05	−0·2
3	26·00	25·98	−0·01	−0·1
4		25·97	−0·03	−0·1
5	31·20	31·26	+0·06	+0·2
6	52·0	51·97	−0·03	−0·1
7		52·04	+0·04	+0·1

DISCUSSION

At the beginning of the titration, the galvanometer needle must be near the end of the scale, since the current intensity decreases continuously during titration, but shows a sudden increase only at the end-point (Fig. 1.) This increase in intensity is, however, only transitory, since it decreases again upon addition of excess standard solution. It is probable that the increase in intensity of the current is brought about by the system consisting of dissolved cadmium sulphide and cadmium acetate. The dissociation of the cadmium sulphide is slowly suppressed by the excess cadmium acetate, resulting in gradual decrease of the intensity.

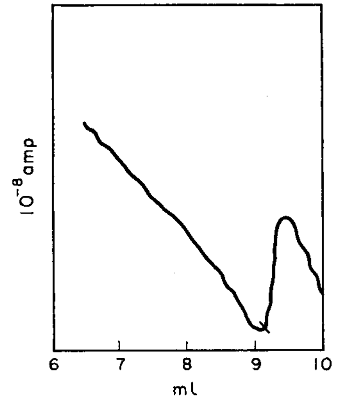

Fig 1. Titration curve of sulphide ion

The determination can only be carried out below pH 7, because at higher pH values there is no sudden change at the equivalence-point. The reason for this is the reaction of hydroxyl ions with cadmium, which occurs to a greater extent when the hydroxyl is bound to ammonium ion. In neutral and acidic media, ammonium ion does not interfere with the reaction.

In strongly acidic medium, loss of sulphide from the solution is considerable. Taking into account the above considerations, a sodium acetate medium ensuring a pH of *ca.* 6–6·4 was selected for the measurement.

The determination is interfered with by hydroxyl and cyanide. No trouble is caused by sulphur acids, nitrite, chloride, *etc.*

Acknowledgement—I take this opportunity to express my thanks to my co-worker, Mrs. Rozsa B Doszpod for her help in carrying out the measurements.

Zusammenfassung—Eine neue, titrimetrische Methode zur Bestimmung von Sulfid mittels Cadmiumazetatlösung und "dead stop"-Endpunkt wurde ausgearbeitet. Die Titration muss in einem mit Natriumazetat gepufferten Medium durchgeführt werden. Die Bestimmung wird nicht beeinflusst durch die Anwesenheit von Schwefeldioxyd oder Nitrit, wird jedoch durch Hydroxyd- und Cyanionen gestört.

Résumé—L'auteur a mis au point une nouvelle méthode titrimétrique de dosage des sulfures par une solution étalon d'acétate de cadmium et détermination du point équivalent par dead stop. Le dosage peut être réalisé en milieu tamponné par de l'acétate de sodium. Les oxydes de soufre ou les nitrites ne gènent pas le dosage, mais les ions hydroxyle et cyanure le pertubent.

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5-AMINO-2-BENZIMIDAZOLETHIOL AS AN ANALYTICAL REAGENT—I

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

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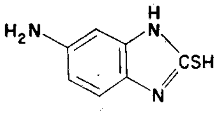
Summary—The orange coloured complex formed by palladium^{II} with 5-amino-2-benzimidazolethiol in the pH range 2–4 forms the basis of a very sensitive colorimetric method for the determination of trace amounts of the metal. The complex shows maximum absorption at 390 mμ, where the reagent has negligible absorption, and it obeys Beer's law from 1 to 8 ppm of palladium^{II}, the optimum range being 2–7 ppm where the percentage relative error per 1% absolute photometric error is 2·95. The sensitivity of the reaction is 0·008 μg/cm^2. Most of the common cations and anions are without effect on the complex. The interferences of some of the platinum metals are avoided by developing the complex in the cold and using EDTA (disodium salt) as a masking agent. A composition study by the molar ratio method shows that at pH 3·42 the solution contains both 1:1 and 1:2 complexes, the dissociation constant of the latter being $1{\cdot}32 \times 10^{-11}$. However, above pH 5·5 incipient precipitation of the orange-red palladium complex occurs, and the precipitation is quantitative above pH 10. The analysis of this precipitate shows a ratio of 1:2 between the metal and the reagent.

INTRODUCTION

5-Amino-2-benzimidazolethiol (I) has been found to be a sensitive reagent for the spectrophotometric determination of palladium in aqueous solution. Since no mention of the use of the reagent in analytical processes is found in the literature, a systematic study of its reactions with noble and common metals has been undertaken. This showed that with the exception of iron the reagent was almost unreactive towards common metals. It reacts, however, with some platinum metals and silver, but under controlled conditions it is highly selective for palladium^{II}. The orange coloured palladium complex is soluble below pH 5.5 and shows maximum absorption at 390–400 mμ where the reagent absorption is negligible. The reagent precipitates palladium quantitatively above pH 10, suggesting the possibility of its use as a gravimetric reagent.



I

EXPERIMENTAL

Apparatus

Wavelength-transmittance curves of the complex were obtained with a Beckman DK1 recording Spectrophotometer, and absorbances of other solutions were measured with a Beckman DU Spectrophotometer. In all cases, 1·00-cm silica cells were used.

A Beckman model G pH meter was employed for all pH determinations.

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Reagents

Standard palladium solution: A standard solution of palladium was prepared by dissolving 1 g of palladous chloride in hot water containing 10 ml of concentrated HCl and diluting to 500 ml. This solution was standardised gravimetrically by the α-picolinic acid method.[1]

5-Amino-2-benzimidazolethiol solution: A 0·5 % solution of the reagent was prepared by suspending 0·5 g of the recrystallised reagent (m.p. 245°, Eastman Organic Chemicals Department, U.S.A.) in 100 ml of water, and dissolving by the dropwise addition of 6*N* acetic acid and stirring.

Buffer solutions: Buffer solutions of pH range 3·42–5·89 were prepared by mixing 0·2*N* acetic acid with 0·2*N* sodium acetate in different proportions.[2]

Other reagents: Solutions of other platinum metals and common ions were prepared as described in a previous paper.[3]

Reactions of 5-amino-2-benzimidazolethiol with cations

Simple qualitative tests of the reagent with diverse metal ions were carried out in weak acid medium (pH 2–5) both in the cold and hot solutions. It was found that the reagent does not react with common ions like Zn^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2}, As^{+3}, Cu^{+2}, Cr^{+3}, Al^{+3}, Co^{+2} or Ni^{+2}. With Fe^{+3} it gives a yellow precipitate. The reactions of the reagent with noble and platinum metals are listed in Table I.

TABLE I.

Metal	Taken as	Reaction in cold solution	Reaction in hot solution
Os^{VIII}	OsO_4	Purple colour but no precipitate	As in cold solution
Pt^{IV}	H_2PtCl_6	Yellow colour but no precipitate	As in cold solution
Rh^{III}	$RhCl_3$	No change	Orange colour
Ru^{III}	$RuCl_3$	No change	As in cold solution
Pd^{II}	$PdCl_2$	Intense orange colour	As in cold solution
Ir^{IV}	Na_2IrCl_6	No change	As in cold solution
Au^{III}	$AuCl_3$	No change	As in cold solution
Ag^{I}	$AgNO_3$	No change	White precipitate

Colorimetric determination of palladium with 5-amino-2-benzimidazolethiol

Recommended procedure: Five ml of 0·5% reagent solution were added to the palladium^{II} solution taken in a 25-ml volumetric flask, and the volume was made up with buffer solution of pH 3·42. After allowing to stand for 35 min at room temperature, the absorbance was measured against a reagent blank prepared identically without palladium.

RESULTS AND DISCUSSION

Spectral curve

The wavelength-transmittance curve of the complex (Fig. 1) shows that the maximum absorption takes place in the region 390–400 mμ, where the reagent has negligible absorption.

Effects of pH, reagent concentration and time

Between pH 2 and 4 the absorbance of the complex remains constant at 390 mμ. At lower or higher pH values the absorbance increases slightly.

For 4 ppm of palladium, 5 ml of 0.5% reagent are necessary for full development of the colour. Greater amounts of reagent do not increase the absorbance if the measurements are carried out against a reagent blank at 390 mμ.

The colour begins to develop instantaneously at room temperature when the reagent is added to a palladium solution at pH 2–4, and a constant absorbance value is obtained after standing for 35 minutes and measuring at 390 mμ. The colour is stable for 24 hours.

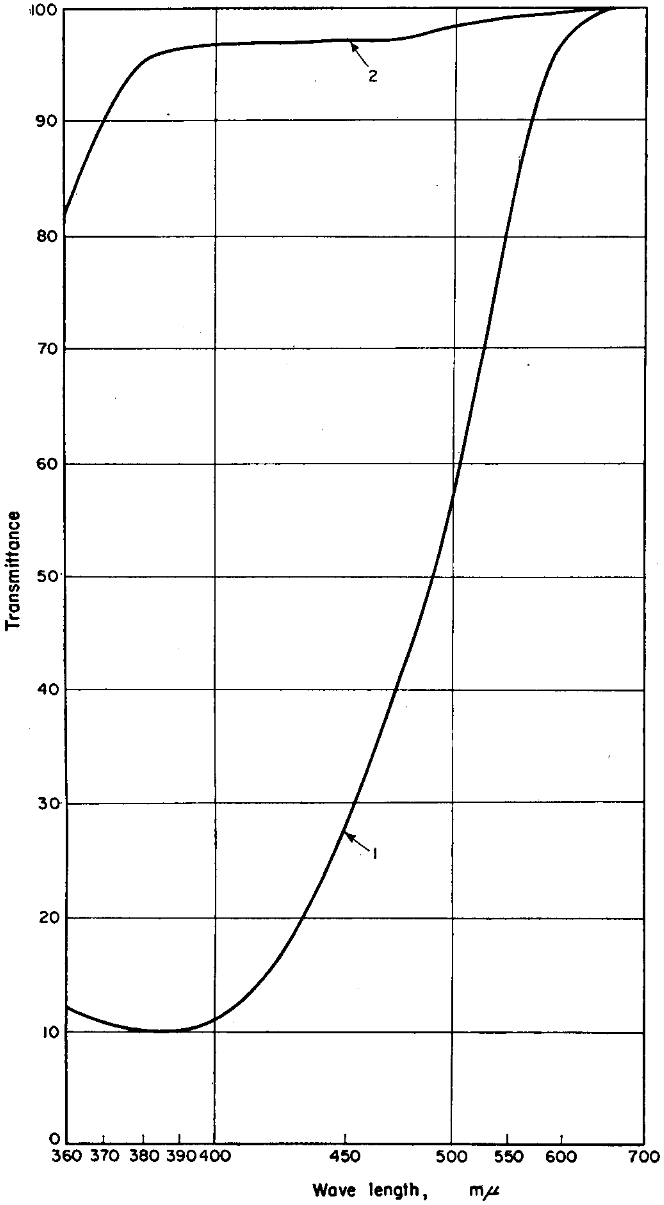

FIG. 1.—Wavelength-transmittance curves of 5-amino-2-benzimidazolethiol and its palladium^{II} complex at pH 3·42.
Curve 1: 8 ppm of palladium^{II} +5 ml of 0·5 % reagent solution.
Curve 2: 5 ml of 0·5 % reagent solution diluted to 25 ml with buffer, pH 3·42

Beer's law, optimum range and accuracy

The colour complex obeys Beer's law for a palladium^{II} concentration of 1 to 8 ppm (Fig. 2). Ringbom's[4] curve (Fig. 3), as obtained by plotting percentage absorptancy (*i.e.* 100 − % transmittance) versus log concentration, shows that the optimum concentration range is between 2 and 7 ppm where the percentage relative error per 1 % absolute photometric error, as evaluated by Ayres' equation,[5] is 2·95.

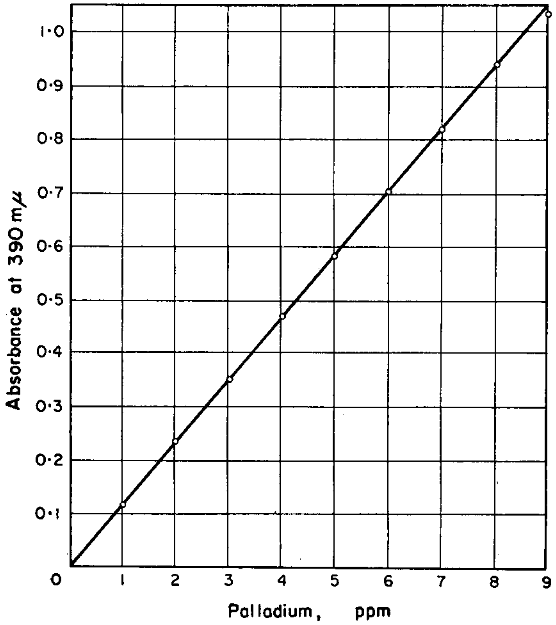

FIG. 2.—Beer's law plot for the palladium^{II} complex at pH 3·42.

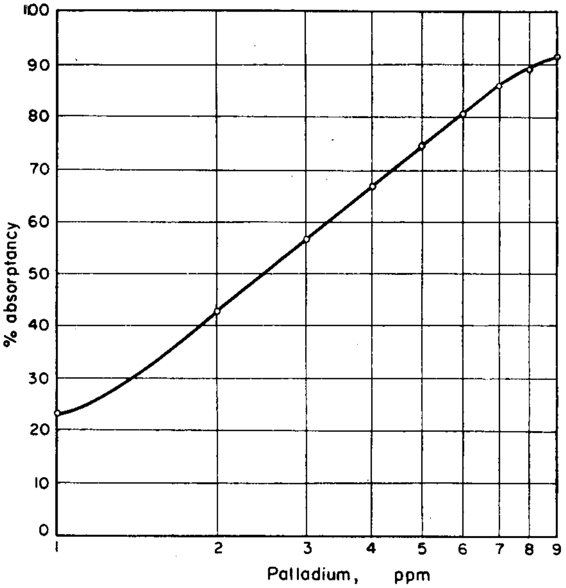

FIG. 3.—Calibration curve for palladium^{II} complex at 390 mμ, pH 3·42.

Sensitivity

Sandell's[6] spectrophotometric sensitivity, as calculated from Beer's law data, is 0·008 $\mu g/cm^2$, and the molecular extinction coefficient is $5{\cdot}46 \times 10^4$. This is calculated from the equation: Molecular extinction coefficient $= \frac{M}{S}$ where M = mol. wt. in g. of the 1:2 complex, S = Sandell's sensitivity.[6]

Effect of diverse ions

The effect of diverse ions on the complex was studied by adding different amounts of the ionic species to the palladium$^{\mathrm{II}}$ solution and then developing the colour exactly as outlined under *Recommended Procedure.* An increase or decrease of 0·005 unit in the absorbance value was considered to be an interference. It was found that the disodium salt of ethylenediaminetetra-acetic acid (EDTA) could increase the tolerance limits of a number of ions. The tolerance limits of various ions for 4 ppm of palladium$^{\mathrm{II}}$, with and without EDTA (disodium salt), are given in Table II.

TABLE II.

Ion	EDTA (disodium salt) added, *ppm*	Maximum amount of ion tolerated, *ppm*	Ion	EDTA (disodium salt) added, *ppm*	Maximum amount of ion tolerated, *ppm*
Ru^{+3}	—	4	Zn^{+2}	—	16
Ru^{+3}	32	12	Zn^{+2}	32	32
Rh^{+3}	—	8	Cd^{+2}	—	40
Ir^{+3}	—	8	As^{+3}	—	40
Ir^{+3}	32	16	Pb^{+2}	—	40
Au^{+3}	—	8	Mn^{+2}	—	16
Cu^{+2}	—	4	Mn^{+2}	32	32
Cu^{+2}	32	8	UO_2^{+2}	—	64
Ni^{+2}	—	8	MoO_4^{-2}	—	40
Ni^{+2}	32	16	WO_4^{-2}	—	40
Co^{+2}	—	40	Th^{+4}	—	40
Al^{+3}	—	40	Zr^{+4}	—	40
Cr^{+3}	—	32	Cl^{-1}	—	>200
NO_3^{-1}	—	>200	SO_4^{-2}	—	>200

Platinum$^{\mathrm{IV}}$ interferes even in the presence of EDTA (disodium salt). Osmium should be separated from palladium as osmic acid by nitric acid distillation[6] in order to avoid its interference.

Composition study of the palladium complex

The composition of the complex in solution was studied by the molar ratio method of Yoe and Jones.[7] For this method, solutions were prepared at pH 3·42 in such a way that the palladium$^{\mathrm{II}}$ concentration remained constant but the ratio of the moles of reagent to the moles of palladium varied from 0·25 to 4·0. The absorbances of these solutions were measured at 390 mμ against a water blank. The results, as represented in Fig. 4, show two breaks corresponding to 1:1 and 1:2 complex-formation between the metal and the reagent. Evidently at the lower reagent concentration a 1:1 complex is formed and this changes to a 1:2 complex when the reagent is in excess.

The palladium-reagent complex was found to be precipitated above pH 5·5, but the precipitation was quantitative only above pH 10. The palladium complex precipitated both at pH 6 and at pH 10 was filtered through a sintered-glass crucible, washed thoroughly with hot water and dried at 110°. An accurately weighed amount of each dried portion was then decomposed by wet digestion with nitric acid-perchloric acid mixture and the palladium was determined by the α-picolinic acid method.[1]

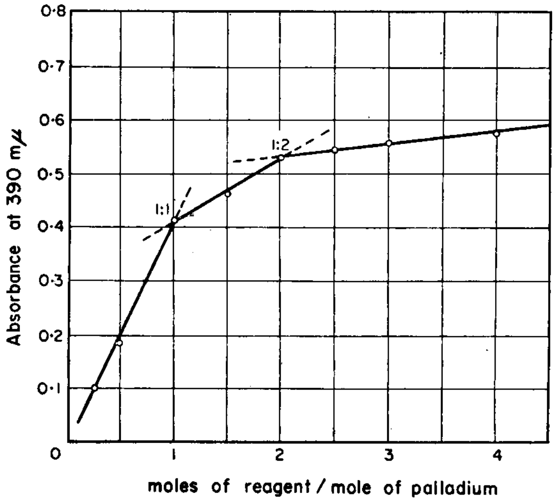

FIG. 4.—Determination of the ratio of palladium to reagent by molar ratio method. Palladium^{II} concn. = 6·78 × $10^{-5}M$; reagent concn. varied.

The complex was found to have the composition $Pd(C_7H_7N_3S)_2$ (% Pd calc., 24·41; found 24·39 at pH 6, 24·40 at pH 10).

Dissociation constant

From the absorption data of Fig. 4, the dissociation constant of the 1:2 palladium complex in solution was calculated by employing the equations $K = (\alpha C)(n\alpha C)^n/C(1 - \alpha)$ and $\alpha = (E_m - E_s)/E_m$ of Harvey and Manning[8] and the value was found to be $1{\cdot}32 \times 10^{-11}$ at room temperature.

Comparison of 5-amino-2-benzimidazolethiol with other colorimetric organic reagents for palladium

Table III illustrates the organic reagents that are available for the colorimetric determination of palladium in the optimum concentration range of 0·5 to 10·0 ppm. Though some of these reagents are fairly sensitive in developing a colour, almost all suffer from non-specificity for palladium, so that in all cases prior separation of palladium is essential. The advantage of using 5-amino-2-benzimidazolethiol is that it does not react with common metals, and under controlled conditions it can be made highly selective for palladium. It also compares favourably with other reagents in sensitivity and in the concentration range of palladium with low percentage relative error.

TABLE III.

Reagent	Wavelength for maximum absorption, *mμ*	Optimum concn. range, *ppm*	Interferences	Reference
p-Nitrosodiphenylamine	510–525	0·5 to 3·0	Ag, Au, and large amounts of Pt metals	9, 10
1-Nitroso-2-naphthol	420	0·5 to 5·0	Ni, Fe, Co	11
2-Nitroso-1-naphthol	370	1·0 to 5·0	EDTA masks the interferences of Cu, Cr, Ni, Co, Fe. No interference from other Pt metals	12
α-Furildioxime	420	1·2 to 4·8	Ru, Rh, Ir, Pt, Au,	13
3-Hydroxy-1-*p*-sulphonato-phenyl-3-phenyltriazine	413	0·2 to 6·0	Can tolerate very small amounts of Fe^{III}, Rh, Ir and Pt	14
Bismuthiol I	400–410	0·8 to 8·0 (Beer's law range)	Pt, Au, Cu, Cr, Fe, Hg, Ag, Tl, U	15
Bismuthiol II	410–430	0·8 to 8·0 (Beer's law range)	Pt, Au, Cu, Cr, Fe, Hg, Ag, Tl, U	16
Phenyl-1-pyridyl ketoxime	410, 340	2·0 to 10·0	Au, phosphate, cyanide. EDTA masks interferences of a number of ions	17
Quinoxaline-2,3-dithiol	548	0·4 to 3·0	Pt, Os, Fe^{III}, Co, Ni	18
Thiomalic acid	350	1·1 to 2·6	Ni, Co do not interfere. Fe, Cu, Ru, Os, Au	19
N,N′-Bis(3-dimethylamino propyl)dithiooxamide	427	1·6 to 5·7	Relatively high concn. of Pt, Rh, Ir, Au, Co, Ni, can be tolerated	20
5-Amino-2-benzimidazolethiol	390	2·0 to 7·0	Rh, Ir, Au, Ni, Co and other common metals do not interfere. Larger amounts of Ru, Ir, Cu, Ni, Zn, Mn can be tolerated by using EDTA as a masking agent	Present work

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Zusammenfassung—Palladium(II) gibt mit 5-Amino-2-benzimidazolthiol im pH-Bereich 2–4 eine orange Färbung, was zur sehr empfindlichen Bestimmung von Spurenmengen herangezogen werden kann. Der gefärbte Komplex zeigt ein Absorptionsmaximum bei 390 mμ, wo das Reagens eine zu vernachlässigende Absorption aufweist. Beer's Gesetz wird für Mengen von 1–8 ppm erfüllt, der optimale Bereich ist 2–7 ppm, wobei der relative Fehler 2·95 beträgt (für einen absoluten photometrischen Fehler von 1 %). Störungen durch einige Platinmetall kann vermieden werden, indem die Farbe in der Kälte entwickelt und ÄDTE als Maskierungsmittel zugesetzt wird. Die Empfindlichkeit der Reaktion ist 0·008 μg/cm^2. Bei pH 3·42 lassen sich ein 1:1 und ein 1:2 Komplex nachweisen. Die Dissoziationskonstante des letzteren beträgt $1{\cdot}32 \times 10^{-11}$. Bei pH 5·5 beginnt der orangegelbe

Komplex auszufallen. Die Fällung ist bei pH 10 quantitativ. Der Niederschlag zeigt eine Zusammensetzung Pd:Reagens = 1:2.

Résumé—La couleur orangée formée par le palladium et le 5-amino-2-benzimidazolethiol dans un domaine de pH 2–4 est à la base d'une méthode colorimétrique très sensible de dosage de traces du métal. Le complexe coloré a un maximum d'absorption à 390 mμ, longueur d'onde à laquelle le réactif a une absorption négligeable; il suit la loi de Beer de 1 à 8 p.p.m. de palladium (II), le domaine de concentration le meilleur étant 2–7 p.p.m., pour lequel l'erreur relative, pour une erreur photométrique absolue de 1 %, est de 2,95 %. La sensibilité de la réaction est 0,008 μg/cm^2. La plupart des anions et des cations communs sont sans effet sur le complexe coloré. Les interférences des métaux de la mine du platine sont évitées en formant le complexe à froid et en utilisant l'EDTA (sel disodique) comme agent complexant. Les études de la composition du complexe par la méthode du rapport molaire montrent que, à pH 3,42, la solution contient les complexes 1/1 et 1/2, la constante de dissociation de ce dernier étant $1{,}32 . 10^{-11}$. Cependant, à pH supérieur à 5,5, la précipitation du complexe rouge orange palladium-réactif commence; elle devient complètement quantitative à pH supérieur à 10. L'analyse du précipité montre un rapport métal/réactif de 1/2.

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SPECTROPHOTOMETRIC AND POTENTIOMETRIC STUDIES ON THE COMPOSITION OF IRON COMPLEXES OF POTASSIUM MOLYBDO- AND MOLYBDICYANIDE

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Summary—Iron^{III} forms a soluble complex with potassium molybdocyanide. An instantaneous blue colour is produced when ferric chloride is added to a solution of potassium molybdocyanide. The composition of the complex was determined by the method of continuous variation and by the slope ratio method, which indicated the existence of the complex $KFe^{III}Mo^{IV}(CN)_8$. The formation constant of the complex was found to be $1 \cdot 37 \times 10^4$ and the free energy of formation works out to be $-5 \cdot 57$ Kcals at 20°. Ferric sulphate also gives a blue complex with potassium molybdicyanide. Its composition has been studied potentiometrically using the $Mo(CN)_8{}^{4-} \rightleftharpoons Mo(CN)_8{}^{3-} + e^-$ couple at a bright platinum electrode; it was found to be $K\,Fe^{II}Mo^{V}\,(CN)_8$.

SOLUBLE complexes of heavy metal molybdocyanides are not reported in the literature. We, for the first time, obtained a Cr^{III} complex of this type by the interaction of chromium^{III} chloride and potassium molybdocyanide, and assigned the formula $KCr^{III}Mo^{IV}\,(CN)_8$ to the red compound[1,2] thus obtained. Other soluble complexes of this series were obtained by the interaction of Fe^{III} with potassium molybdocyanide and Fe^{II} with potassium molybdocyanide. This communication deals with the composition of these complexes as indicated by physico-chemical methods of examination.

Preliminary experiments on the interaction of iron^{III} chloride and iron^{II} sulphate with potassium molybdocyanide and potassium molybdicyanide respectively gave evidence of similar type of colour changes. Thus it was observed that with excess of iron^{III} or iron^{II} ions, a blue solution was obtained, but with excess of molybdo- or molybdicyanide a greenish-blue solution is obtained. Since the reaction appeared to be analogous to that observed in the formation of "iron blues", it was thought worthwhile to elucidate the nature and composition of the complex or complexes formed, using various physico-chemical methods.

The composition of the complex formed by the interaction of ferric chloride and potassium molybdocyanide could not be studied satisfactorily by conductometric, potentiometric or amperometric titration methods. Interestingly enough this complex was found to be reducible at the dropping mercury electrode, giving a typical polarographic wave, but the polarographic method[3] could not be successfully employed either in view of the fact that the complex became unstable on coming in contact with the mercury drops (a slight turbidity, followed by precipitation in the polarographic cell, was observed). The spectrophotometric method was, however, found useful in determining the composition and stability of the complex. This method was also tried for investigating the complex formed by the interaction of ferric sulphate and potassium molybdicyanide, but reliable information could not be obtained since $K_3Mo(CN)_8$ was appreciably decomposed by the light from the tungsten lamp of the spectrophotometer. Several electrometric methods were then tried and it was found that very satisfactory results could be realised by a potentiometric method, using a $Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{3-} + e^-$ couple at a bright platinum electrode.

EXPERIMENTAL

Reagents

Ferric chloride (AnalaR) and *ferrous sulphate* (recrystallised three times) were dissolved in doubly distilled water and the strengths of the solutions were determined by the usual methods. *Potassium molybdocyanide* was prepared by the method recommended by Fieser[4] and the strength of the solution was determined by titrating potentiometrically against $KMnO_4$ solution. Kolthoff's method[5] was used for obtaining *potassium molybdicyanide.* The strength of the solution was also determined potentiometrically using potassium ferrocyanide.

Apparatus

A Beckman DU spectrophotometer with 1-cm Corex cells and a tungsten lamp as the light source was used for optical density measurements.

PROCEDURES

In order to determine the number of complexes formed by the interaction of ferric chloride and potassium molybdocyanide, the method of Vosburgh and Cooper[6] was followed. The reactants were mixed in different proportions and the optical density was measured at different wavelengths ranging from 360 mμ to 1000 mμ. All the mixtures gave a maximum at 840 mμ showing thereby the formation of only one complex (Fig. 1).

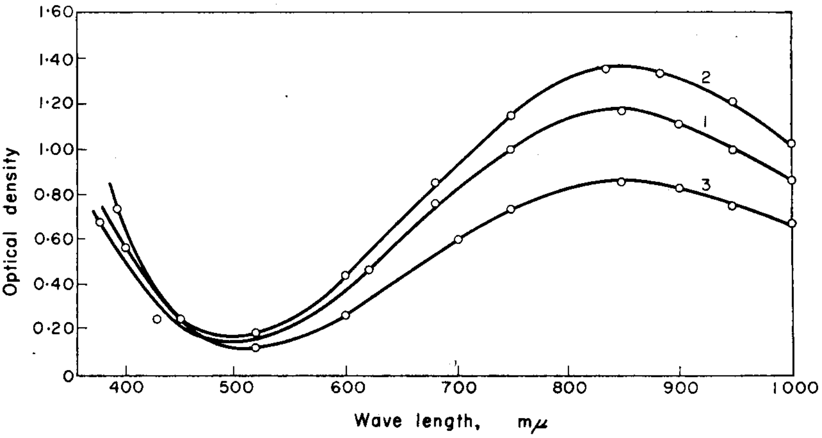

FIG. 1.—$FeCl_3$ and $K_4Mo(CN)_8$ mixed in the proportions (1) 2:1, (2) 1:1, and (3) 1:2. Concentration of the reactants, $3{\cdot}3 \times 10^{-3}M$.

Job's method[7] of continuous variation was followed for determining the composition of ferric molybdocyanide. Solutions of ferric chloride and potassium molybdocyanide of three different concentrations, *viz.*, $4 \times 10^{-3}M$, $2 \times 10^{-3}M$ and $1{\cdot}25 \times 10^{-3}M$, were mixed according to the method of continuous variation, and O.D. was measured at 840 mμ after 10 min of mixing. Ferric chloride and potassium molybdocyanide at these concentrations had a negligibly small absorption at 840 mμ. The optical densities of the solutions were plotted against the ratio $[Fe^{3+}]/[Fe^{3+}] + [Mo(CN)_8^{4-}]$. The results are depicted in Fig. 2.

The results were further confirmed by the slope ratio method.[8] Two sets of experiments were performed. In the first set the concentration of potassium molybdocyanide was kept constant and that of ferric chloride was varied; in the other set the mixing was done in the reverse order. The results are given in Fig. 3. The slope was determined over the straight line portion of the curve.

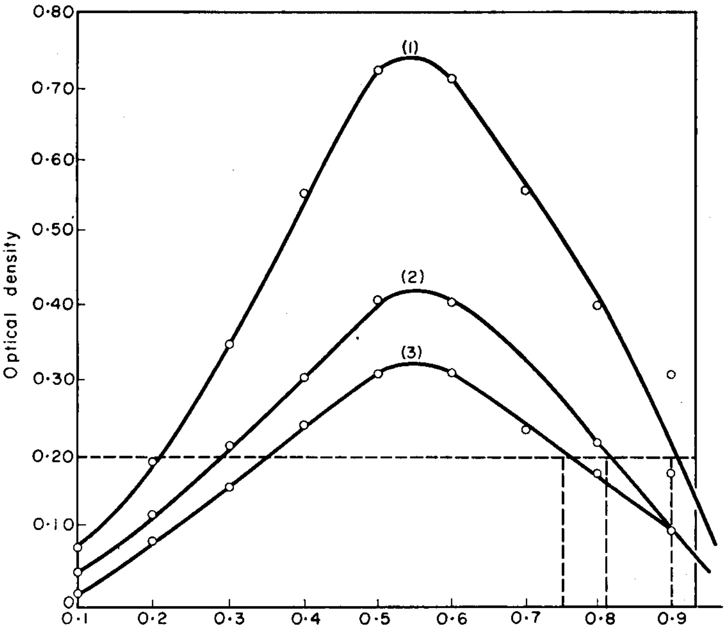

FIG. 2.
The ratio $Fe^{3+}/Fe^{3+} + Mo(CN)_8^{3-}$. Concentrations of the reactants, (1) 4 × $10^{-3}M$, (2) 2 × $10^{-3}M$ and (3) 1·25 × $10^{-3}M$.

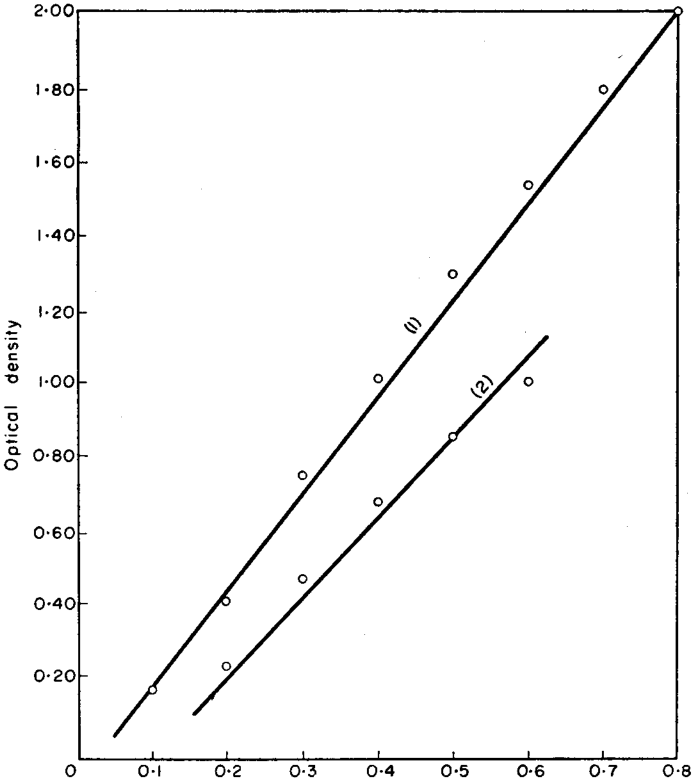

FIG. 3.
Slope ratio method.
(1) Concentration of $K_4Mo(CN)_8$ constant, 1·66 × $10^{-3}M$. Concentration of $FeCl_3$ varied, 2 × $10^{-2}M$.
(2) Concentration of $FeCl_3$ constant, 1·66 × $10^{-3}M$.
Concentration of $K_4Mo(CN)_8$ varied, 2 × $10^{-2}M$.

Potentiometric titrations between ferrous sulphate and potassium molybdicyanide were carried out using a Tinsley Vernier potentiometer (type 33873); the indicator electrode [$Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{3-} + e^-$ couple] was obtained by dipping a bright platinum electrode in the solution of potassium molybdicyanide containing a little potassium molybdocyanide. The titrations at three different concentrations of molybdicyanide solution, *viz.*, 0·03*M*, 0·02*M* and 0·02*M*, were performed for determining the composition of ferrous molybdicyanide. In the cell fitted with the indicator electrode and the saturated calomel electrode, 10 ml of the molybdicyanide solution were taken and ferrous sulphate (0·1*M*) was added from the burette. The curves are shown in Fig. 4. Reverse titrations with ferrous sulphate in the cell were not successful. The experiments were performed in a dark room and the vessels were wrapped with black paper to avoid the decomposition of potassium molybdicyanide by light.

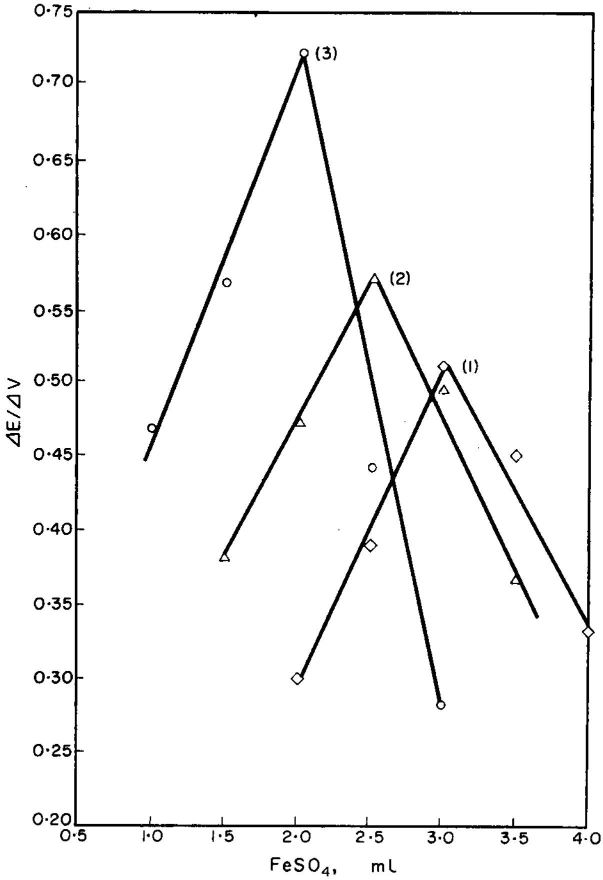

FIG. 4.—Determination of end-point in potentiometric titration. 10 ml of $K_3Mo(CN)_8$ of concentration (1) 0·03*M*, (2) 0·025*M*, and (3) 0·020*M* versus 0·1*M* $FeSO_4$.

DISCUSSION

Several authors, including Davidson,[9] have extensively investigated the nature of the reaction between ferrous chloride and potassium ferrocyanide and the composition of the complex. When iron^{III} ions are added to an equimolecular quantity of ferrocyanide ions, a redox equilibrium sets in with the result that the iron^{III} ions are almost completely reduced to iron^{II} ions by the ferrocyanide ions, which, in turn, are simultaneously oxidised to ferricyanide ions. The possibility of such a redox equilibrium, existing in the case of the ferric chloride-potassium molybdocyanide reaction appears to be remote, since the equilibrium constant value,

$$K298 = \frac{[Fe^{3+}][Mo(CN)_8{}^{4-}]}{[Fe^{2+}][Mo(CN)_8{}^{3-}]} = 10{\cdot}4,$$

$$(Fe^{2+} \rightleftharpoons Fe^{3+} + e,\ E_0 = -0{\cdot}76;$$
$$Mo(CN)_8{}^{4-} \rightleftharpoons Mo(CN)_8{}^{3-} + e,\ E_0 = -0{\cdot}82)$$

is quite low when compared to the ferric chloride-potassium ferrocyanide reaction ($K298 = 1{\cdot}215 \times 10^5$). Thus on theoretical grounds it could be inferred that the complexes formed by the interaction of ferric chloride and potassium molybdocyanide, and between ferrous sulphate and potassium molybdicyanide, could not be one and the same and unlike "iron blues" would have different compositions.

The combining ratio of 1:1 for Fe^{3+} to $Mo(CN)_8{}^{4-}$ is obtained both by the continuous variation and slope ratio methods (Figs. 2 and 3) for the interaction of ferric chloride and potassium molybdicyanide. The composition of the complex would, therefore, be represented by the formula $KFe^{III}Mo^{IV}(CN)_8$, according to the reaction,

$$FeCl_3 + K_4Mo(CN)_8 \rightarrow KFe^{III}Mo^{IV}(CN)_8 + 3\ KCl.$$

The formation constant of the complex was determined by the method followed by Mukherji and Dey[10] for the reaction

$$mA + nB \rightleftharpoons AmBn,$$

where $m/n = 1$ or $m = 1$ or $m = n = 1$

The formation constant is

$$K = \frac{x}{(a - x)(b - x)},$$

where x is the concentration of the complex, and a and b are the initial concentration of ferric chloride and potassium molybdocyanide respectively. Taking two concentrations a_1 and a_2 and b_1 and b_2 of the reactants giving the same optical density. (that is the same value of x),

$$K = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)}$$

or

$$x = \frac{a_1b_1 - a_2b_2}{(a_1 + b_1) - (a_2 + b_2)}.$$

Knowing the value of x from the above equation, K is calculated from different values of a and b. Taking two concentrations of Fe^{3+} and $Mo(CN)_8{}^{4-}$ at the optical density 0·20 (Fig. 2), and the value of x from the above equation as $2{\cdot}19 \times 10^{-4}M$, the value of K was found to be $1{\cdot}37 \times 10^4$.

The free energy of formation of the complex was calculated with the help of the expression

$$\Delta F^\circ = -RT \ln k,$$

where ΔF° is the standard free energy change, R, the gas constant and T, the absolute temperature. The free energy of formation of ferric molybdocyanide complex works out to be $-5{\cdot}75$ kcals. at 20°.

Potentiometric titrations carried out at different concentrations of potassium molybdicyanide with ferrous sulphate give the combining ratio of Fe^{2+} to $Mo(CN)_8{}^{3-}$

as 1:1, indicating the formation of the complex $KFe^{II}Mo^{V}(CN)_8$, according to the reaction,

$$FeSO_4 + K_3Mo(CN)_8 \rightarrow KFe^{II}Mo^{V}(CN)_8 + K_2SO_4.$$

This method, in addition to providing information regarding the composition of the iron^{II} molybdicyanide complex, has demonstrated the utility of a new electrode (the $Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{3-} + e^-$ system at bright platinum) for investigating the reaction between heavy metal ions and potassium molybdo- and molybdicyanide. This electrode could be used successfully for studying the precipitation reaction between potassium molybdocyanide and Ni^{II}, Co^{II}, or Cu^{II}.

Zusammenfassung—Auf Zugabe von Eisen(III)-ionen zu einer Lösung von Kalium-Molybdocyanid bildet sich augenblicklich ein blauer, wasserlöslicher Komplex. Die Zusammensetzung des Komplexes wurde auf grund eines Job-Diagrammes und nach der Methode der Neigungsverhältnisse als folgende ermittelt: KFe(III)Mo(IV)(CN)$_8$. Die Bildungskonstante beträgt $1{\cdot}37 \times 10^4$. Die freie Bildungsenergie wurde zu $-5{\cdot}57$ Cal bei 20°C berechnet. Ferrisulfat gibt auch mit Molybdicyanid einen blauen Komplex. Seine Zusammensetzung wurde durch Potentialmessungen an Gleichgewicht $Mo(CN)_8^{-4} \rightleftharpoons Mo(CN)_8^{-3} + e^-$ an einer blanken Platinelektrode ermittelt, und ist KFe(III)Mo(V)(CN)$_8$.

Résumé—Par addition de fer(III) à une solution de molybdo-cyanure de potassium, il se forme instantanément un complexe bleu soluble. La composition du complexe a été déterminée par la méthode des variations continues et par la méthode du rapport des pentes; ces méthodes montrent l'existence du complexe $KFe^{(III)}Mo^{(IV)}(CN)_8$. La constante de formation du complexe est 1,37 . 10^4 et l'énergie libre de formation calculée est −5,57 kcal. à 20°. Le sulfate de fer(II) donne aussi un complexe bleu avec le molybdo-cyanure de potassium. Sa composition a été étudiée par potentiométrie à une électrode de platine poli, utilisant le système oxydo-réducteur:

$$Mo(CN)_8^{4-} \rightleftharpoons Mo(CN)_8^{3-} + e$$

Les auteurs ont trouvé la formule suivante pour le complexe: $KFe^{(II)}Mo^{(V)}(CN)_8$.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—VII*

DETERMINATION OF COPPER AND IRON

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Summary—A simple complexometric determination of iron in the presence of copper has been devised. It is based upon the masking of copper with thiourea. Simultaneous reduction of iron is prevented by the addition of ammonium fluoride. The determination of iron is carried out in an indirect manner, *viz.* by back titration of an added excess of EDTA with lead nitrate using Xylenol Orange as indicator. The same procedure is employed in determining the sum of iron and copper, but without the previous masking of copper. The possibilities of determination of these two elements in the presence of others are discussed.

In view of the considerable difference between the stability constants of EDTA complexes with iron^{III} and copper^{II} (pK_{FeY} 25·1; pK_{CuY} 18·8) one could anticipate the possibility of direct consecutive determinations of the two elements. That this is actually possible has been demonstrated by potentiometric[1] as well as spectrophotometric[2] titrations of mixtures of iron and copper. In the field of visual titrations, however, no suitable procedure has so far been found. Such a method is possible only by the selective masking of copper. The masking agents hitherto used for copper in an acidic medium (thiosulphate, thiourea, thioglycollic acid), the action of which consists in reducing copper^{II} to copper^{I}, also react with iron^{III} ion, thus rendering this determination impossible. Preliminary experiments with the above mentioned substances have shown thiourea to be the most suitable reagent. Once copper has been masked by thiourea in a weakly acidic medium it no longer reacts with an added excess of EDTA—the solution remains colourless. The presence of iron gives rise to a brown coloration or even to a precipitate which, however, readily dissolves on the addition of EDTA; the solution is then yellow in colour because of the formation of an iron-EDTA complex. By back titration of an added excess of EDTA with lead nitrate using Xylenol Orange as indicator somewhat low results were obtained. At higher concentrations of iron, the indicator changes were blurred, which was probably caused by displacement of the iron^{II} present and by blocking of the indicator. This drawback can easily be eliminated by preventing the reaction of iron with thiourea by means of another complexing agent—in our case by the addition of ammonium fluoride. The colourless fluoride complex of iron^{III} is virtually inactive towards thiourea. The masking of copper by thiourea also has the advantage that a quite colourless copper^{I} complex is formed. The above method can be applied to the determination of iron even at high concentrations of copper.

EXPERIMENTAL

Reagents

0·05*M* solutions of $FeCl_3$, $CuSO_4$, $Pb(NO_3)_2$ and EDTA were prepared from reagent grade chemicals. Their concentrations were controlled by suitable complexometric methods. Other

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* Part VI—Rudolf Přibil and Vladimír Veselý, *Talanta*, 1961, **8**, 565.

reagents were 20% thiourea, 1*M* ammonium fluoride and 0·5% Xylenol Orange solutions, and solid hexamethylenetetramine.

1. *Determination of iron in the presence of copper*

To the slightly acid solution add ammonium fluoride in excess. The blue-greenish coloration of the solution changes to pure blue. The solution of thiourea is then slowly added till discoloration of the solution occurs, plus 2 ml in excess, followed by the addition of an excess of EDTA solution. The mixture turns to yellow because of the formation of an iron-EDTA complex. The pH is adjusted to 5–5·5 with hexamethylenetetramine and the solution titrated with lead nitrate solution until the indicator changes from yellow to violet. The results of these titrations are listed in Table 1.

TABLE I—DETERMINATION OF IRON AND COPPER
(1 ml of 0·05*M* EDTA ≡ 2·7925 mg of Fe or 3·177 mg of Cu)

Taken, *mg*		Found, *mg*		Remarks
Fe	Cu	Fe	Cu	
2·83	32·40	2·84	32·28	
28·34	16·21	28·34	16·05	
2·83	16·21	2·82	16·30	
56·68	16·21	56·80	16·12	
2·83	162·10	2·95	162·24	During the titration a white precipitate appears but does not disturb the end-point.
14·18	64·84	14·26	64·62	
141·77	3·24	141·72	4·35	The end-point is less sharp (after screening of Cu) because of the slight blocking of Xylenol Orange 105 ml of EDTA used.
141·77	162·10	141· 68	162·41	

A closer investigation of the reaction of the FeF_6^{3-} complex with thiourea has revealed that microgram amounts of $iron^{II}$ are formed (slightly positive reaction with phenanthroline). The concentration of the $iron^{II}$ ions is so low, however, that it does not affect the results ($pK_{KeY} = 13{\cdot}9$) and, what is very important, the colour change of the indicator. As one sees from Table I, quite reliable results are obtained in determining 3–100 mg of iron and 3–150 mg of copper in 150 ml of solution.

2. *Determination of copper in the presence of iron*

The literature describes several complexometric methods for this determination. All are based upon the masking of iron by means of ammonium fluoride in a very weakly acidic medium followed by direct titration of copper with EDTA using a suitable indicator. Theis[3] recommends Chromazurol S and pH 6–6·5. Wehber,[4] in titrations of copper using Variamine Blue B as indicator (pH 5·5), presents a case of masking 170 mg of iron by the addition of 1·2 g of ammonium fluoride. Lassner[5] also utilises ammonium fluoride in the determination of copper in the presence of iron and nickel.

In view of the fact that copper can be titrated directly with EDTA using Xylenol Orange as indicator and trace amounts of phenanthroline as "catalyst",[6] this method has also been tried in the presence of iron masked by ammonium fluoride. However, the experiments met with complete failure. This can be simply explained as caused by the fluoride complex, FeF_6^{3-}, being "sufficiently" dissociated to react with such a sensitive indicator as Xylenol Orange. Because of the blocking of the indicator the titration of copper cannot be carried out at all. Our experience is that the masking of iron with ammonium fluoride is never quite reliable. A much better method we consider to be the differential determination, *i.e.* one aliquot is used for the determination of iron according to the procedure described above, and another for the determination of the sum of the iron and copper using the same method, except that no fluoride and thiourea are added. The results for copper are also given in Table I.

DISCUSSION

The described determination of iron and copper is very simple and affords reliable results over considerable concentration ranges of the two components (3–100 mg of iron and 3–150 mg of copper in 150 ml of solution). The applicability of a back titration with lead nitrate as titrant and Xylenol Orange as indicator, characterised by one of the most contrasting changes in colour at the end-point, can very easily be extended to analyses of mixtures containing more components. Thus an Fe-Al-Cu system can, in principle, be analysed in such a way that one aliquot is used to determine the sum of all the three elements, another to determine the sum of iron and copper after previous masking of aluminium with fluoride, and a third to determine iron after masking aluminium and copper with ammonium fluoride and thiourea respectively. Other combinations, encountered chiefly in analyses of special alloys, are the subject of further study and will be referred to elsewhere.

Zusammenfassung—Eine einfache Methode zur komplexometrischen Bestimmung von Eisen in Gegenwart von Kupfer wurde ausgearbeitet. Kupfer wird mit Thioharnstoff maskiert. Gleichzeitige Reduktion des Ferrieisens wird durch Zusatz von Ammoniumfluorid verhindert. Die Bestimmung des Eisens erfolgt indirekt durch Rücktitration eines Überschusses von ÄDTE mit Bleinitrat unter Verwednung von Xylenolorange als Indicator. Dieselbe Titration ohne Maskierungsmittel dient zur Bestimmung der Summe Fe + Cu. Weitere Möglichkeiten der Bestimmung beider Elemente nebeneinander werden diskutiert.

Rèsumè—Les auteurs ont mis au point un simple dosage complexométrique du fer en présence de cuivre. Le cuivre est complexé par de la thiourée. La réduction simultanée du fer est évitée par addition de fluorure d'ammonium. Le dosage du fer est réalisée indirectement, c'est-à-dire par titrage de l'excès d'EDTA par du nitrate de plomb avec le xylénol orange comme indicateur. Le même procédé est employé pour doser la somme Fe + Cu, mais sans avoir complexé préalablement le cuivre.

Les possibilités de dosage de ces deux éléments en présence d'autres sont discutées.

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SHORT COMMUNICATIONS

A method for the determination of dixanthogens

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A METHOD for the determination of dixanthogens has been developed based on the action of chloramine-T on dixanthogen. The action of chloramine-T on xanthates has been studied by Rao and Murthy[1] who have utilised the reaction as a means of determining carbon disulphide after converting it into ethyl xanthate. It was suggested that the reaction can be extended to dixanthogens and so experiments were conducted to study the action of chloramine-T on diethyl, dibutyl and diamyl dixanthogens, with a view to standardising their methods of determination.

Reagents

Chloramine-T: 0.1N solution prepared by dissolving a recrystallised sample of chloramine-T (14·5 g per litre) and standardising iodimetrically in an acid medium as described earlier.[2,3]

Diethyl dixanthogen: Pure potassium ethyl xanthate was oxidised by iodine to obtain an insoluble oily diethyl dixanthogen. The oil was extracted with petroleum ether and the solvent evaporated in vacuum. The resulting diethyl dixanthogen had a melting point[4] of 28°. Analysis for sulphur (Carius) 53·12%; calculated 52·93%.

Dibutyl and diamyl dixanthogens were prepared under similar experimental conditions using the corresponding freshly prepared xanthates.

Dixanthogens are insoluble in water, but soluble in alcohol. Alcohol solutions of dixanthogens of known concentration were therefore used for purposes of oxidation. Alcohol is not oxidised by chloramine-T under the experimental conditions employed.

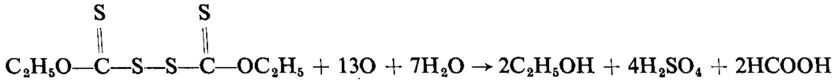
Procedure

A known amount of dixanthogen was mixed with an excess of acidified chloramine-T (10 ml of 0·1N with 5 ml of 2N HCl) in an Erlenmeyer flask and set aside for 1 hr. Then 10 ml of 10% potassium iodide were added and the liberated iodine was titrated against standard thiosulphate solution. From the amount of chloramine-T consumed the number of equivalents of the oxidant required per mole of dixanthogen was calculated. The experimental results were found to be reproducible and are presented in Table I.

TABLE I. OXIDATION OF DIXANTHOGENS BY CHLORAMINE-T

Dixanthogen	Dixanthogen taken, *moles* × 10^5	Chloramine-T consumed, *equivalents* × 10^4	Chloramine-T per mole of dixanthogen, *equivalents*
Diethyl	2·60	6·77	26·03
	1·92	5·00	25·93
Dibutyl	1·86	3·47	18·71
	2·02	3·80	18·84
Diamyl	1·78	3·19	17·86
	2·06	3·66	17·74

The above table shows that 1 mole of diethyl dixanthogen consumes 26 equivalents of chloramine-T. This can be explained by the following mechanism, which is similar to that proposed for the oxidation of xanthate by chloramine-T in acid medium:[1]



$$C_2H_5O-\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-OC_2H_5 + 13O + 7H_2O \rightarrow 2C_2H_5OH + 4H_2SO_4 + 2HCOOH$$

This quantitative reaction can be employed as an elegant method for the determination of diethyl dixanthogen. Reactions between dibutyl and diamyl dixanthogens and chloramine-T were found to be more complicated, consuming only 18–19 equivalents of chloramine-T instead of 26 equivalents. The heavier alkyl radical attached to the carbon atom is perhaps responsible for the incomplete oxidation of carbon disulphide (xanthate or dixanthogen) to formic acid and sulphuric acid. However, with calibration even these can be estimated conveniently.

Acknowledgement—The author wishes to express his grateful thanks to Prof. M. R. A. Rao for his keen interest in the work.

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Summary—One mole of diethyl dixanthogen reacts with 26 moles of chloramine-T, and this reaction can be used for the determination of the dixanthogen. Higher alkyl dixanthogens react in a more complicated fashion, but may still be estimated using an empirical correction.

Zusammenfassung—Ein Mole Diäthyldixangthogenat reagiert mit 26 Molen Chloramin-T, was zur Bestimmung von Dixanthogenat herangezogen werden kann. Höhere Alkylxanthogenate reagieren in komplizierter Weise, können jedoch gleichfalls bestimmt werden, wenn eine empirische Korrektur angebracht wird.

Résumé—Une mole de diéthyldixanthogène réagit sur 26 moles de chloramine T; cette réaction peut être utilisée pour le dosage du dixanthogène. Les alcoyl dixanthogènes supérieurs réagissent de manière plus compliquée, mais ils peuvent encore être dosés en faisant une correction empirique.

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A self-sampling indicator tube for carbon dioxide

(*Received* 8 *May* 1961. *Accepted* 20 *May* 1961)

FOLLOWING the development of an indicator tube for the determination of oxygen in air,[1,2] the production of a similar type of test for carbon dioxide covering the range 10–90% has been investigated. This work was undertaken mainly to provide a simple and rapid means of obtaining the correction for the oxygen tube when it is used in the presence of appreciable amounts of carbon dioxide,[1,2] produced by combustion or respiration. Such a test would also be useful in industrial applications where the oxygen content of an atmosphere has to be reduced to minimise fire or explosion risks (*e.g.* in the grinding of inflammable powders such as sulphur) by dilution with carbon dioxide or flue gases which contain a high proportion of carbon dioxide.

Both the oxygen and carbon dioxide tests employ reagents contained in evacuated glass tubes. To use the tubes, the sealed end is broken and the entering gas changes the colour of the reagent over a distance which depends on the concentration of reacting gas (oxygen or carbon dioxide).

Of the many fairly rapid methods available for determining carbon dioxide, most are of the titrimetric or colorimetric type and utilise the absorption of carbon dioxide by alkalies and the measurement of the original and residual volumes, or the reaction with an acid/alkali indicator.

Initially, attempts were made to use tubes in which silica gel and alumina were impregnated with phenolphthalein, bromothymol blue or alkali blue indicators. Although some of these showed a suitable colour change, the chemical reaction was not sufficiently rapid to produce a sharp front. However, when acid-washed sand was impregnated with rosaniline hydrochloride which had been decolorised with hydrazine hydrate,[3,4] carbon dioxide in concentrations of 5% and above rapidly restored the pink colour of the reagent and gave a sharp front sufficiently stable for its position to be marked. Powdered glass, alumina, and silica gel pretreated by heating to 1200°, were also tried but, in each case, rapid fading of the colour occurred.

The method of preparation of the tubes is as follows:

160 g of acid-washed sand, as near colourless as possible and between 50 and 100-mesh in size, are placed in a bottle fitted with a bung and a glass stopcock. Eight ml of a 1% rosaniline hydrochloride in methanol solution are added, and the contents are shaken until a uniform pink colour develops. The methanol is removed by vacuum drying at room temperature. After a further period of mixing, nitrogen is admitted to the bottle, and 0.12 ml of 99–100% hydrazine hydrate is added. The bottle is again shaken until the pink colour is completely discharged and a slightly damp, almost white mixture remains. At this stage, 0.4 g of magnesium carbonate (sieved through a 200-mesh sieve and dried at 110°) is added, and the bottle is purged with nitrogen and again shaken. The purpose of the magnesium carbonate is to produce a free-flowing mixture capable of being poured into tubes. The mixture is then placed in a hopper and subsequently allowed to pour into glass tubes, which are plugged with a disc of asbestos paper and a phosphor-bronze gauze plug, evacuated and sealed. The tubes are of about 5-mm bore and 25-cm length, 20 cm of which are filled with reagent.

Atmospheric oxygen should be prevented from reaching the mixture as far as possible, as this will oxidise part of the hydrazine, thus increasing the sensitivity of the tubes and making them unsuitable for the range of carbon dioxide contents required.

As with the oxygen tubes, to make a test the sealed end is broken in the atmosphere to be tested, and 5 sec later the position of the front is marked. The ratio (F) of length of pink colour to the total length of reagent is found and the carbon dioxide concentration (P) is obtained from a table calculated from the formula,

$$P = \frac{100aF}{1 - F + aF}.$$

where a, the batch constant

$$= \frac{\text{Volume of carbon dioxide in ml absorbed per cm length}}{\text{Volume of residual gases in ml per cm length}}.$$

This formula is similar to that used for the oxygen tube and is derived in a similar manner.

A figure for the batch constant can be found by breaking a number of tubes of the same batch in an atmosphere of known carbon dioxide content and determining an average figure by calculation. Normally this calibration is done with 50% of carbon dioxide in air.

Experimental figures are similar to figures calculated from the formula over the range 10–90% of carbon dioxide. Below 10%, the front becomes diffuse and at about 5% no colour is visible at all because of rapid fading within the initial 5 sec. At ordinary temperatures and pressures, the test has been found to give results reproducible to within about 1 part in 20 of the carbon dioxide content of the sample under test. This degree of accuracy is ample for making the necessary correction to results obtained from the oxygen tubes.

The quantity of active material used is not important, neither are the dimensions of the retaining tube if the tube has a uniform bore. In principle, the tube will cover the range 0–100% of carbon dioxide. The quantity of reagent impregnated on the base can be altered over a very wide range, to give greater accuracy over different parts of the scale. For example, tubes have been made which are accurate to about 0.1% over the range 98–100% of carbon dioxide.

Little work has been done on the effect of other gases, as the order of concentration of any interfering gas would need to be the same as that of the carbon dioxide before any adverse effect would be possible.

As with the oxygen tubes based on silica gel, these tubes suffer from the disadvantage of requiring batch calibration. Nevertheless, the test can be completed in 1 min, and the tubes appear to suffer no deterioration on keeping for at least 1 year.

The self-sampling indicator tube for carbon dioxide described in this paper is the subject of a provisional patent.[2]

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Summary—A simple indicator tube for the determination of carbon dioxide in an atmosphere is described. The test has been designed to cover the range 10–90% of carbon dioxide in the presence of oxygen and nitrogen or other inert gases. Estimations, accurate to about 1 part in 20, can be completed in 1 min. The prepared tubes are stable for at least 1 year.

Zusammenfassung—Die Herstellung einer einfachen Anzeigerohres zur Bestimmung von Kohlendioxyd in der Luft wird beschrieben. Das Gerät ist geeignet für Mengen von 10–90% Kohlendioxyd in Gegenwart von Sauerstoff, Stickstoff oder anderen inerten Gasen. Bestimmungen mit einer Genauigkeit von 1 Teil in 20 können innerhalb einer Minute ausgeführt werden. Die Beschickten Röhren könne für mindestens ein Jahr gelagert werden.

Résumé—Les auteurs décrivent un simple tube indicateur pour le dosage de l'anhydride carbonique. L'essai a été conçu pour couvrir le domaine 10–90 pour cent d'anhydride carbonique en présence d'oxygène et d'azote ou d'autre gaz inertes . Les dosages, précis à environ 1 pour 20, peuvent être réalisés en une minute. Les tubes préparés sont stables pendant au moins un an.

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Photocolorimetrische Zirkoniumbestimmung in Magnesium-Speziallegierungen mittels Morin

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EINLEITUNG

Bereits in unserer früheren Arbeit[1] (und später auch die ungarischen Arbeiter A. Schneer und Mitarbeiter[2,3]) haben wir auf die Möglichkeit einer einfachen und schnellen photocolorimetrischen Zirkoniumbestimmung unter Ausnützung des gelben Zirkonium-Morinkomplexes hingewiesen. Nach Anwendung der Methode für die Zirkoniumbestimmung in Carbiden (in Isolaten, herstammend von der Isolierung von Strukturbestandteilen aus mit Zirkonium legierten Auftragmetallen) haben wir diese Methode für die Zirkoniumbestimmung in mit diesem Metall legierten Magnesium-Speziallegierungen ausgearbeitet. In Zusammenhang mit der eigentlichen Methode für die Zirkoniumbestimmung überprüften wir zugleich die Genauigkeit der Bestimmung von nicht in dem Grundmetall gelöstem Zirkonium durch Lösen der Probe in verdünnter Schwefelsäure und Chlorwasserstoffsäure.

ZIRKONIUMBESTIMMUNG MITTELS MORIN

Zirkonium liefert bei Gegenwart von Morin in Chlorwasserstoffsäure einen intensiv gelb gefärbten Komplex, welcher bei Anwesenheit von Alkohol sehr gut löslich ist. Die optimale Chlorwasserstoffsäurekonzentration beträgt ca. 0,5–0,6N,[1] die Morinkonzentration 0,02–0,01%, der Alkoholanteil der Lösung 30%. Die Intensität der Ausfärbung ist schwach von der Zeit und der Temperatur abhängig, sodass empfohlen wird die Farbmessung stets nach einer genauen Zeit nach der Ausfärbung durchzuführen (20 oder 60 Minuten) und die Lösungen bei 20° zu halten. Die Abhängigkeiten sind im Einzelnen in der Arbeit[1] enthalten.

Die Reaktion von Zirkonium mit Morin ist weitgehend selektiv, sodass allgemein kein Trennungsverfahren angewendet werden braucht. Mg, Zn, Ce, Fe, Ni, Co, Cr, Mn, die Alkalimetalle stören nicht (vergleiche Tab. I.), Chloride, Perchlorate und Sulfate sind ohne Einfluss. Al stört nur in sehr grossen Mengen, ähnlich wie das Phosphat-Ion. Bei Anwesenheit von Fluoriden ist die Reaktion nicht durchführbar, man kann vielmehr durch Zusatz von Fluorid den Komplex entfärben. Eine bedeutend weniger intensive Gelbfärbung mit Morin gibt auch Ti, die Störung kann jedoch durch Anwendung einer Korrektionskurve eliminiert werden.

TAB. I. VERGLEICH DER MITTELS MORIN UND MITTELS PHENYLARSINSÄURE ERHALTENEN ERGEBNISSE DER ZIRKONIUMBESTIMMUNG

Probe	Zr zugesetzt, *mg*	Morin	Zr gefunden *mg*, mittels Phenylarsinsäure	Differenz beider Methoden
200 mg Mg	0	0	—	—
200 mg Mg 5 mg Ce	0	0	—	—
200 mg Mg 5 mg Zn	0	0	—	—
200 mg Mg	0,15	0,155	—	—
200 mg Mg	0,30	0,292	—	—
200 mg Mg	5,00	—	5,60	—
		in %	in %	in %
1	—	0,064 0,070	0,15	0,08
2	—	0,46 0,45	0,52	0,06
3	—	0,50 0,52	0,60	0,09
4	—	0,72 0,74	0,83	0,10

Lösungen

Morinlösung; 0,2g reinstes Morin werden in 100 ml Alkohol (Methyl—oder Äthylalkohol) gelöst.
HCl: 1:1 und 0,6N.
H_2SO_4: 5% ig.
Ascorbinsäurelösung: 2% in destilliertem Wasser.

Arbeitsgang

Da die Reaktion sehr empfindlich ist, wird eine grössere Einwage in einen Messkolben gebracht und von dieser Vorratslösung ein kleiner Teil zur eigentlichen Bestimmung verwendet. Durch dieses Verfahren wird gleichfalls der Einfluss einer Unhomogenität der Legierung beseitigt und die Lösung kann zu weiteren Bestimmungen gebraucht werden.

Je nach dem Zr-Gehalt werden 1–3g der Legierung in ein Becherglas eingewogen und mit 60 ml HCl 1:1 in Lösung gebracht. Nach Auflösen wird die Lösung in einen 250ml fassenden Messkolben filtriert, das Filter mit dem ungelösten Rückstand im Pt-Tiegel verascht, der Rest mit wenig Ammonipersulfat geschmolzen,[4] mit wenig 5% iger H_2SO_4 ausgelaugt und dem Hauptteil im Messkolben zugegeben. Der Kolben wird nun mit 0,6N HCl bis zur Marke gefüllt.

Von dieser Vorratslösung werden 10 ml in einen 100 ml fassenden Messkolben pipetiert, 5 ml der Ascorbinsäurelösung zugesetzt und mit 0,6N HCl zur Marke gefüllt. Von dieser zweiten Lösung werden wieder 10 ml in ein kleines Becherglas gebracht, 5 ml Alkohol (Methyl—oder Äthylalkohol) zugegeben und mit 1 ml der Morinlösung versetzt. Die Lösung wird gemischt, das Becherglas in einen Thermostaten bei 20° gestellt und nach genau 20 oder 60 Minuten gemessen.

Die Messung wird vorteilhaft mit dem Hilger-Spekker-Absortiometer unter Benützung der Hg-Lampe und den Filtern OB 2 und Wratten 50 (Isolierung der Wellenlänge von 436 mμ) durchgeführt. Wasserwert 1,0, Schichtstärke 10 oder 5 mm. Der Zirkoniumgehalt kann direkt mit Hilfe einer Eichkurve abgelesen werden, wie es unsere Eichkurve auf Abb. 1 für eine Einwage von 2,5g in den 250 ml Messkolben zeigt.

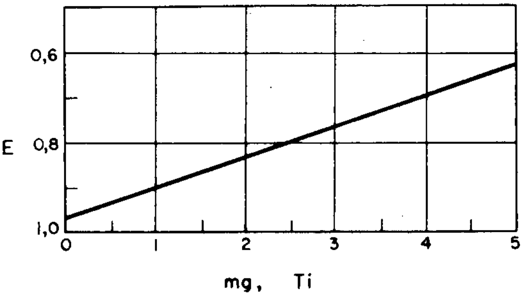

ABB. 1.—Eichkurve für die Zirkoniumbestimmung. 1—für Messungen nach 20 Minuten, 2—nach 60 Minuten für 10 mm Schichtdicke.

Die Eichkurve

Zur Herstellung der Eichkurve wurden 10 mg metallisches, spektralreines Zirkonium (Johnson & Matthey, London) im Platintiegel in 2 ml HNO_3 und einigen Tropfen HF gelöst und dann mit 2 ml H_2SO_4 abgeraucht. Da die Anwesenheit von F-Ionen die Reaktion stört, wurde das Abrauchen nach Anfeuchten mit einigen Tropfen Wasser wiederholt. Nach Auflösen der Sulfate in 5% iger H_2SO_4 wird die Lösung auf 100 ml aufgefüllt und so eine Lösung mit 0,1mg Zr/ml erhalten. Diese Lösung wird in Mengen von 0,5 1,0 . . . 5ml in einen 100 ml Messkolben pipetiert und nach Zusatz von Ascorbinsäurelösung wie beschrieben verfahren.

Die Korrektionskurve für Titan

Für die Konstruktion der Korrektionskurve für Titan wurde das gleiche Verfahren wie für das Zirkonium benützt, nur die Standartlösung wurde konzentrierter hergestellt, so dass 1 ml der Lösung 1 mg Ti enthielt.

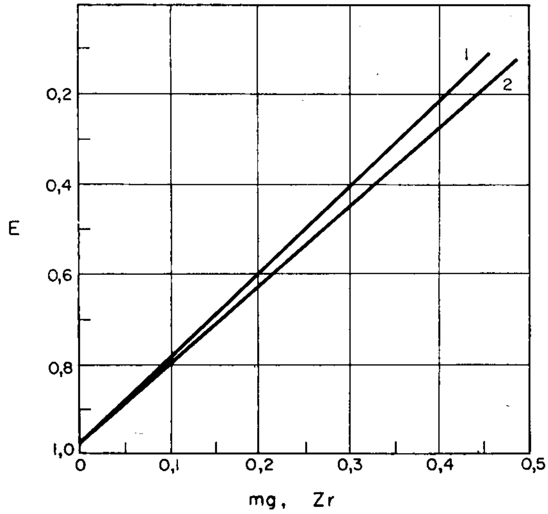

ABB. 2.—Korrektionskurven für die Zr-Bestimmung bei Titananwesenheit. 10 mm Schichtdicke.

Wie aus Abb. 2 zu sehen ist, verläuft die Korrektionskurve für Ti selbst bei 10 mal grösserer Konzentration bedeutend flacher—die Reaktion für Zr ist ca. 25 mal empfindlicher. Im Durchschnitt kann geschlossen werden, dass bei 10 mal grösserem Gehalt an Ti als an Zr die Bestimmung mit hinreichender Genauigkeit ohne vorangehende Abtrennung des Ti durchgeführt werden kann.

Die nach der angeführten Methode erhaltenen Ergebnisse wurden mit direkter gravimetrischer Bestimmung von Zr mittels Phenylarsinsäure kontrolliert[4]; einige Ergebnisse führt Tab. I. an. Wie zu sehen, ist bei der colorimetrischen Bestimmung das Grundmetall Mg selbst in grössten Mengen ohne Einfluss. Die mittels Phenylarsinsäure erhaltenen Werte sind in allen Fällen, selbst bei der Standartlösung höher, als der Tatsache entspricht. Gleichzeitig werden in dieser Tabelle zahlenmässige Ergebnisse an Betriebsproben angeführt.

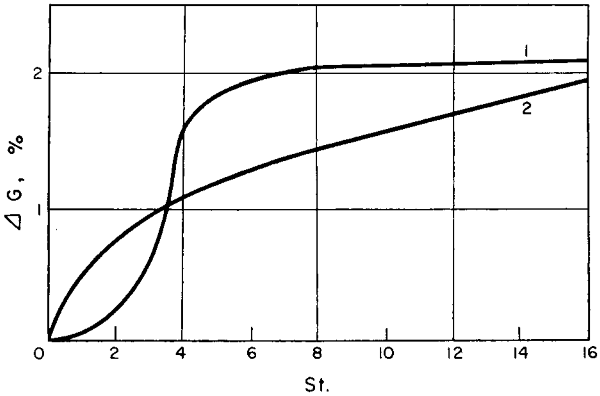

Abb. 3.—Löslichkeit in % von metallischem pulverförmigem Zirkonium (Degussa) bei 20° 1—in 10% HCl, 2—in 10% H_2SO_4.

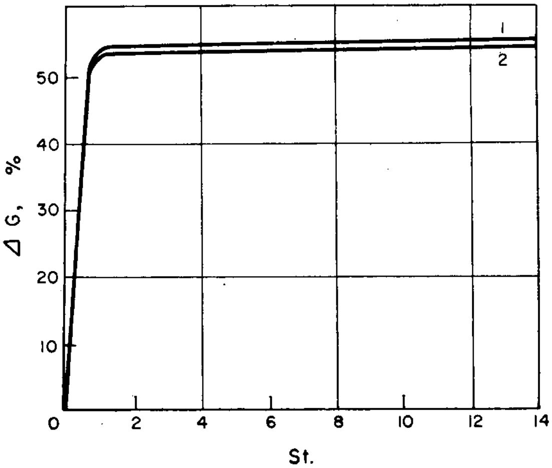

Abb. 4.—Löslichkeit in % von metallischem pulverförmigem Zirkonium (Degussa) bei 90°. 1—in 10 % HCl, 2—in 10% H_2SO_4.

UNTERSUCHUNG DER LÖSLICHKEIT VON METALLISCHEM ZIRKONIUM IN CHLORWASSERSTOFF UND SCHWEFELSÄURE

Die schlechte Löslichkeit von metallischem Zirkonium in Säuren führt zu der Annahme, dass das in der Legierung anwesende metallische Zirkonium beim Lösen der Probe in Chlorwasserstoffsäure als unlöslicher Schlamm zurückbleibt, während das in metallische Phasen eingegangene Zirkonium in Lösung geht.* Informative Zirkoniumbestimmungen nach Auflösen der Probe Nr. 3 in HCl 1:2 und 2:1 ohne nachträgliches Erwärmen und nach Abfiltrieren des ungelösten Rüskstands zeigten jedoch steigende Resultate: 0,27% und 0,42% Zr. Nachträglich durchgeführte Beständigkeitsprüfungen von Zirkonium-Metallpulver (Degussa) in HCl- und H_2SO_4—Lösungen bei 20 und 90°C zeigten, dass bereits zu Beginn der Säureeinwirking und niedriger Temperatur grosse Anteile an

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* So wird z.B. nach dem britischen Standart B.S.2970:1959, Appendix A gearbeitet: Das "wirksame" Zirkonium ("available zirconium") wird durch Lösen der Probe in 30 ml HCl 1:2 auf lg und 5 Minuten Sieden bestimmt; das unter diesen Bedingungen nichtgelöste Zirkonium wird abfiltriert.

Zirkonium in Lösung gehen (Abb. 3 und 4), wobei die Löslichkeit mit der Temperatur stark ansteigt. Die erhaltenen Ergebnisse schliessen also eine Trennung des gelösten und ungelösten Zirkoniums mittels einfacher Säureauflösung der Probe aus.

Zusammenfassung—Zur Schnellbestimmung von Zirkonium in Legierungen wurde eine kolorimetrische Methode herangezogen die auf einer Farbreaktion mit Morin beruht. Die benötigte Zeit *ist etwa eine Stunde, doch reduziert sich diese Zeit im Serienbetrieb. Grosse Mengen von Mg, Zn, Ce, Fe, Ni, Co, Cr, Mn,* Cl^-, ClO_4^- *und* SO_4^{2-} *stören nicht. Für Titan muss eine Korrektionskurve konstruiert werden. Fluorid stört.*

Eine nähere Untersuchung zeigte, dass lösliches und unlösliches Zirkonium in Magnesiumlegierungen nicht einfach durch Lösen in Salz—oder Schwefelsäure getrennt werden können. Fein verteiltes Zirkoniummetall wird durch die beiden Säuren in beträchtlichem Ausmasse gelöst.

Summary—For the rapid determination of zirconium in magnesium alloys a colorimetric method based on colour formation between zirconium salts and morin can be used. The time needed for a simple determination is about 1 hr, but this can be reduced in routine analysis.

The reaction between zirconium and morin is not affected by large quantities of Mg, Zn, Ce, Fe, Ni, Co, Cr, Mn, chloride, perchlorate or sulphate. For Ti a correction curve can be constructed. Fluoride interferes with the colour development.

Investigation of the reactivity of zirconium metal and actual experience indicate that the soluble and the insoluble zirconium in magnesium-alloys cannot be separated by simple dissolution of the base metal in HCl or H_2SO_4. Finely divided zirconium is dissolved to a considerable extent by these acids.

Résumé—Pour le dosage rapide du zirconium dans les alliages de magnésium, on peut utiliser une méthode colorimétrique basée sur la formation d'une coloration entre les sels de zirconium at le morin. Le temps nécessaire pour un simple dosage est environ une heure, mais il peut être réduit dans une analyse de routine.

La réaction entre le zirconium et la morin n'est pas modifiée par de grandes quantites de Mg, Zn, Ce, Fe, Ni, Co, Cr, Mn, chlorure, perchlorate ou sulfate. Pour Ti, une courbe corrective peut être établie Le fluorure perturbe le développement de la couleur.

L'etude de la réactivité du métal zirconium et l'expérience présente indiquent que le zirconium soluble et le zirconium insoluble dans les alliages de magnésium ne peuvent pas être séparés par simple dissolution du métal dans HCl ou H_2SO_4. Le zirconium finement divisé est dissous à un degré considerable par ces acides.

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Spectrophotometric determination of bismuth with Xylenol Orange after dithizone-chloroform extraction

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METHODS for the spectrophotometric determination of bismuth with Xylenol Orange have been described independently by the present authors[1] and by Cheng.[2] In general the two sets of results agree reasonably well.* In order to extend the applicability of the Xylenol Orange method, it was

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* The present authors made a mistake in the calculation of the formation constant for the bismuth-Xylenol Orange complex. The correct value is $3{\cdot}3 \times 10^5$ in 0·1N nitric acid.

thought worthwhile to investigate a selective separation method for bismuth. Metals that interfere with the determination of bismuth rather seriously are copper, indium, titanium, zirconium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten and iron.[1] Because as much as 10 mg of lead and 1 mg of thallium[1] do not interfere with the determination of bismuth,[1] the separation of bismuth from these two elements is not very important. When bismuth is to be determined in the presence of large amounts of lead, cupferron extraction[3] or oxychloride precipitation[4] is probably suitable. It is considered that the separation of bismuth by dithizone-chloroform extraction has a general applicability. However, there is some difference of opinion in the literature concerning the completeness of extraction of bismuth dithizonate.[5] From these considerations, extraction with dithizone has been studied in some detail, and the results are reported in the present paper.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Hitachi Model EPU-2A spectrophotometer, using 1-cm cells. A glass-electrode pH meter (Horiba Model M-3) was used for pH measurements. A shaking machine with a time switch was used for extractions.

Reagents

All the reagents used were of reagent grade.

Potassium cyanide: 35 g in 100 ml of water.

Ammonium citrate: 20 g of $(NH_4)_2HC_6H_5O_7$ in 100 ml of water.

Hydroxylamine sulphate: 30 g in 100 ml of water.

Dithizone: 0·10 g in 1000 ml of redistilled chloroform.

L-Ascorbic acid: 10 g in 100 ml of water.

Sodium fluoride: 0·10 g in 100 ml of water.

Xylenol Orange: 0·10 g in 100 ml of water.

Standard bismuth solution: Dissolve 0·500 g of bismuth metal in nitric acid and evaporate to dryness on a water bath. Dissolve the residue in 1:9 nitric acid and make up to 500 ml with the same solvent. From this stock solution (1·00 mg of bismuth per ml), prepare a working standard of appropriate concentration by dilution.

Procedure

Separation of bismuth. Transfer the sample solution (dilute nitric acid solution containing 10 to 100 μg of bismuth in a volume of 10 to 30 ml) to a separatory funnel. Add 7·5 ml of ammonium citrate solution and 5 ml of potassium cyanide solution. Adjust the pH of the solution to 9·4–10·2 with 1:1 ammonium hydroxide and dilute to about 50 ml with water. Shake the solution for at least 1 min with 10 ml of dithizone solution. When the layers have separated, drain off the chloroform phase into another separatory funnel. Extract with two further 10-ml portions of dithizone solution. Combine the extracts and discard the aqueous phase. Wash the extracts with 5 ml of 1:99 ammonium hydroxide.

Shake the organic phase for at least 1 min with 10 ml of 0·5*N* nitric acid. Repeat the back-extraction with another 10-ml portion of nitric acid. Discard the organic phase and collect the aqueous phase into a 100-ml porcelain dish. Evaporate the solution to dryness on a water bath.

Determination of bismuth. Dissolve the residue in 2·0 ml of 1·2*N* nitric acid and transfer the solution to a 25-ml volumetric flask. Wash the dish with small amounts (totalling not more than 15 ml) of water.

Add 1·0 ml of ascorbic acid solution, 1·0 ml of sodium fluoride solution, and 1·0 ml of Xylenol Orange solution, in the order mentioned. Dilute to the mark with water, mix, and measure the absorbance of the solution in a 1-cm cell at 530 mμ using water as the reference.

Construct a calibration curve by taking 0 to 100 μg of bismuth, adding ascorbic acid, sodium fluoride, and Xylenol Orange, and proceeding as described above.

Run a blank through the entire procedure.

RESULTS AND DISCUSSION

Determination of bismuth

In the method described by Cheng,[2] the absorbance of the bismuth-Xylenol Orange complex in 0·1N sulphuric acid is measured at 545 mμ. It appears that the absorption maximum varies with the ratio of bismuth to Xylenol Orange.[6] Kotrlý and Vřešťál[6] titrated microgram amounts of bismuth in nitric acid photometrically at 530 mμ with EDTA. The molar absorptivity of 24,000 given by Cheng[2] is a little higher than the value of 16,000 obtained by the present authors.[1] The difference is probably caused by the purity of the Xylenol Orange reagents. Although Cheng[2] states that perchloric acid inhibits the formation of the bismuth-Xylenol Orange complex, the present authors[1] have not been able to observe this phenomenon.

Separation of bismuth

For the extraction of bismuth with dithizone-chloroform solution, Haddock[7] used a 0·1 % dithizone solution, while Hubbard[8] used a 0·006 % (w/v) dithizone solution. In the present work, a 0·01 % (w/v) dithizone solution has been used. The amounts of potassium cyanide (1·75 g) and of ammonium citrate (1·5 g) used in the present work are close to those used by Haddock.[7]

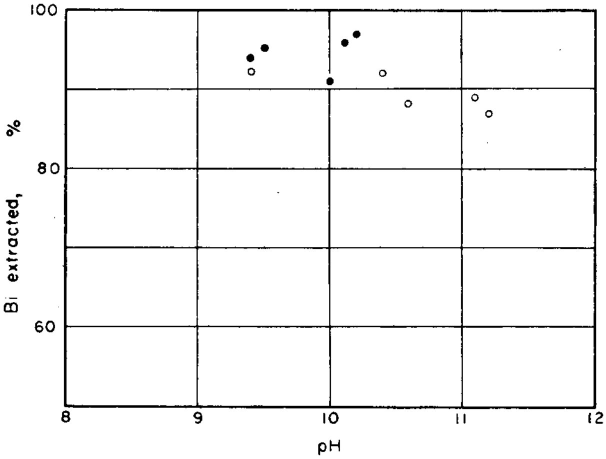

Fig. 1—Extraction of bismuth

○ In the presence of potassium cyanide

● In the presence of ammonium citrate and potassium cyanide

Recoveries of bismuth dithizonate from solutions containing potassium cyanide or ammonium citrate plus potassium cyanide are shown in Fig. 1. Forty or fifty μg of bismuth were taken in each case. The organic extract was evaporated to dryness. Two ml of 30 % hydrogen peroxide and 1 ml of concentrated sulphuric acid were added to the residue, and the solution was evaporated to dryness on a hot plate. The residue was treated with 2·0 ml of 1·2*N* nitric acid and the colour development was then carried out. At pH 9·4 to 10·4, 92 % (average) of bismuth is extracted from a solution containing potassium cyanide. In the presence of ammonium citrate and potassium cyanide, the pH of the solution does not change greatly upon the addition of ammonium hydroxide. At pH 9·4 to 10·2, the average recovery of bismuth is 94 %.

The effect on the overall recovery of bismuth of varying the nitric acid concentration used in the back-extraction is shown in Fig. 2. The experiments were carried out by the proposed procedure, using 50 μg of bismuth each time. By using 0·5 to 1·0*N* nitric acid, more than 95 % of the bismuth is recovered. With higher concentrations of nitric acid (>1*N*), oxidation of dithizone occurs markedly.

Table I summarises the results obtained in applying the proposed method in the presence of other metals. Most of the metals used were in the form of nitrate or sulphate. In the presence of aluminium (aluminium metal was dissolved in sodium hydroxide and the solution was then acidified with nitric acid) and zirconium (zirconium metal was dissolved in sulphuric acid in the presence of ammonium sulphate), the extraction of bismuth with dithizone is slow, and it is necessary to extract for as long as 15 and 5 min, respectively. The proposed method has been applied successfully to aluminium metal containing 40 to 150 ppm of bismuth.

Since indium is also extracted with dithizone in chloroform and more than 0·1 mg of this element interferes with the determination of bismuth,[1] ethyl ether extraction of indium bromide has been

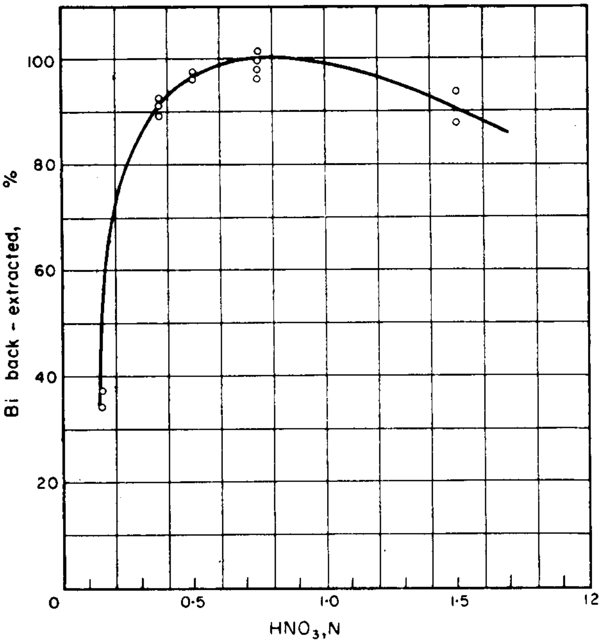

FIG. 2—Back-extraction of bismuth with nitric acid

TABLE I—DETERMINATION OF BISMUTH WITH XYLENOL ORANGE AFTER DITHIZONE-CHLOROFORM EXTRACTION

Addition, *mg*	Bi taken, *μg*	Bi found, *μg*[a]	Average recovery, %
—	20·0	19[b], 19[b], 18[c], 18[c]	93
—	100	101[b], 100[b], 97·6[c], 98·8[c]	99·3
Al 500	50·0	47·0, 46·5	93·5
Cr^{III} 20	50·0	47·0, 46·5	93·5
Cu 500	50·0	50·0, 50·0, 49·0, 48·0	98·5
Fe^{III} 100	50·0	49·6, 49·6	99·2
Mo^{VI} 55	50·0	49·5, 50·5	100
Nb 10	50·0	47·5, 46·5	94·0
Th 50	50·0	47·5, 49·5	97·0
Ti^{IV} 10	50·0	49·5, 47·5	97·0
Ti^{IV} 20	50·0	44·0, 44·0	88·0
U^{VI} 500	50·0	50·0, 50·0, 51·5, 51·5	102
V^{V}25	50·0	50·0, 48·5	98·5
W^{VI} 25	50·0	47·5, 48·0	95·5
Zr 25	50·0	48·0, 48·0	96·0
Zr 50	50·0	46·0, 46·0	92·0

[a] Correction applied for blank: 0·0 μg with no addition, Cu, and Fe; 0·2 μg with Th, V, W, and Zr 0·5 μg; with Mo; 1·2 μg with Cr, Nb, and Ti; and 4·7 μg with U.

[b] Time of shaking for each extraction: 1 min.

[c] Time of shaking for each extraction: 5 min.

studied (Table II). The procedure used was as follows: Twenty ml of sample solution, which is approximately 4·5*N* in hydrobromic acid, are shaken with three 10-ml portions of ethyl ether. The aqueous phase is then transferred to a 100-ml dish and evaporated to dryness. (The organic phase that contains indium is discarded.) The residue is dissolved in 2·0 ml of 1·2*N* nitric acid, and the bismuth is determined according to the proposed method. The results are slightly low.

TABLE II—DETERMINATION OF BISMUTH AFTER REMOVAL OF INDIUM

(50·0 μg of bismuth taken in each determination)

Addition, *mg*	Bi found, μg^a	Average recovery, %
In 10	44·1, 44·5	88·6
In 5·0	45·2, 46·1	91·3

[a] Correction applied for the blank (0·4 μg of Bi with 5 mg of In).

Summary—For the purpose of extending the applicability of the spectrophotometric determination of bismuth with Xylenol Orange, the separation of this element from interfering elements has been studied. Bismuth is extracted as its dithizonate with chloroform from an alkaline solution containing citrate and cyanide, then back-extracted into 0·5*N* nitric acid. After evaporation of the solution, the bismuth is determined spectrophotometrically with Xylenol Orange.

Zusammenfassung—Zwecks Ausdehnung des Anwendungsbereiches der spektralphotometrischen Bestimmung von Wismut mit Xylenolorange wurde die Abtrennung dieses Metalles von störenden Elementen studiert. Wismut wird als Dithizonat in alkalischem Medium in Gegenwart von Zitrat und Cyanid in Chloroform extrahiert und sodann in 0·5 N Salpetersäure rückgeschüttelt. Nach Abdampfen der Lösung wird Wismut mit Xylenolorange bestimmt.

Résumé—Afin d'étendre l'application de la méthode spectrophotométrique de dosage du bismuth par le xylénol orange, les auteurs ont étudié la séparation de cet élément des éléments gênants. Le bismuth est extrait à l'état de dithizonate par du chloroforme à partir d'une solution alcaline contenant du citrate et du cyanure, puis extrait à nouveau dans de l'acide nitrique 0,5 N. Après évaporation de la solution, le bismuth est dosé par spectrophotométrie avec le xylénol orange.

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BOOK REVIEWS

Advances in Analytical Chemistry and Instrumentation, Volume 1. Edited by CHARLES N. REILLEY. Interscience Publishers, Inc., New York, 1960. pp. vii + 445. $12.00.

IN the first volume of a proposed annual series the editor and contributors have achieved their goal in presenting chapters which "deal not only with significant new developments in idea and techniques, but also with critical evaluations and the present status of important, but more classical, methods and approaches". A well qualified group of workers was selected to prepare this volume.

Tetraphenylboron (TPB) as an Analytical Reagent. H. FLASCHKA and A. J. BARNARD, JR. (117 pages). This chapter provides a full treatment of the precipitation of potassium TPB as well as application to other metal ions and organic compounds. These authors also have provided detailed working directions for several of the procedures.

Recent Advances in Gas Chromatography Detectors. ROBERT B. SELIGMAN and FORREST L. GAGER, JR. (32 pages). Emphasis is placed on the development of the high sensitivity ionisation detectors; however, recent developments in flame detectors, and improvements in the density balance and thermal conductivity cells are included.

Trends in the Determination of Fluorine. C. A. HORTON. (47 pages). Discussion is limited primarily to developments since 1953. Especially valuable are the sections on difficulties and shortcomings of the past and present methods and the challenges for future investigations. No attempt was made to cover the determination of fluorine in organic compounds.

New Ideas in Organic Microanalysis Part I. C–H, O, N. Halogens, S, and Other Elements. WOLFGANG SCHÖNIGER. (42 pages). Information on modifications of classical methods is presented and reviewed critically. New methods, many of which were developed and tested in the author's laboratory, are included.

Theory of Electrode Processes. W. H. REINMUTH. (52 pages). The author surveys the rapidly growing volume of literature on the theoretical aspects of electrode reactions, and emphasises those publications of greater value and interest to analytical chemists.

The Analytical Chemistry of Thioacetamide. ERNEST H. SWIFT and FRED. C. ANSON. (53 pages). From the laboratories of the authors have come many of the more basic studies of the use of thioacetamide for the precipitation of metal sulphides. The authors review the literature thoroughly and point out the dangers of the indiscriminate use of thioacetamide as a substitute for hydrogen sulphide without more extensive investigations. Future trends in research in the field are discussed.

Near-Infrared Spectrophotometry. ROBERT F. GODDU. (78 pages). The development of commercially available spectrophotometers has produced a rapid increase in analytical research in the near-infrared region of 1 to 3 microns. The author makes excellent evaluations of recent work and predicts that the near-infrared region will continue to find greatest value in quantitative organic functional group analysis.

This volume of *Advances* will make a valuable addition to the libraries of many analytical chemists and analysts. Some chemists with more specialised interests might prefer to have such volumes divided and published as monographs or collections of more closely related topics. The additional cost of publication, however, probably is justified to provide the broad scope for those who wish to keep abreast of all developments in analytical chemistry. The editor and authors should be commended for the excellence of this volume, especially for the critical evaluations included in the presentations.

WILLIAM F. WAGNER

Gas Chromatography. Edited by HENRY J. NOEBELS, R. F. WALL and NATHANIAL BRENNER. Academic Press Inc., New York and London, 1961. pp. xvi + 463. 114s. 6d.

THIS volume comprises the thirty-four papers read at the Second Symposium on Gas Chromatography held under the auspices of the Analysis Instrumentation Division of the Instrument Society of America in June 1959. It reflects the present state of gas chromatography, which, despite its tender years and the large flux of papers to which it still gives rise, is passing now into the stage of instrumentation and elaboration. The initial period of hectic development of detectors and columns, in face of the fundamental advancement of the technique, seems now to be passing into a period of consolidation and application which are the criteria of a mature technique. For example, in this volume there are papers concerned with process control systems embodying gas chromatography analysers, with general problems of design of gas chromatographic apparatus, with automatic fraction collection and with integration of peak areas. In this connection, it is ironical to note a wistful reference by A. T. James, in an amusing historical account of the birth of the technique, to the subject's "sealing wax and string" origins in A. J. P. Martin's laboratory. Just as is true of another subject which had its origins in a laboratory noted for its skill in handling "sealing wax and string," namely that of Rutherford, gas chromatography has very little to do nowadays with these primitive materials, as a glance through the volume under review will very quickly show. Indeed, part of the great power of the technique lies in the fact that it lends itself so naturally to instrumentation. In some circles, instrumentation is regarded as a euphemism for gadgeteering; it is not, though doubtless there are occasions when it may be so. Perhaps one of the dangers currently besetting gas chromatography is that its instrumentation could degenerate into elaborate contrivances which are not an integral part of the technique. One becomes aware sometimes of this possibility when reading through this collection of papers, but not often. A substantial portion of the book is concerned with detailed reports of separations, which, despite their specificity, are usually of general value because they are concerned with classes of compounds which are continually involved in analytical problems of current interest. The fundamental aspect of the technique, while not figuring so prominently as in earlier proceedings of this kind, is certainly not neglected and there are valuable reports of advances in fraction detection and column operation. Concluding the book is a bibliography of 1515 references to papers concerned with gas chromatography published in the period 1958 to June 1960, requiring 81 pages for its presentation. This bibliography is a continuation of the bibliography started in the volume in which were reported the proceedings of the First Gas Chromatographic Symposium held in 1957. The usefulness of this collection of titles, listed in alphabetical order of the authors, is limited greatly by the absence of a subject index to its contents.

The standard of presentation is up to the high quality associated with the publishers. The price, too, is well up to the level expected for this type of publication, but which few scientists have become accustomed to accept without complaint. Bearing in mind the high cost of the book, there is frequently an excessive expansiveness and leisureliness in the presentation of information which is irritating. Far too many chromatograms are given, and the practice of introducing numerous photographs of apparatus which convey little or nothing about the design and function of the apparatus is particularly to be deplored.

DESMOND BRENNAN

Spectrochemical Analysis. L. H. AHRENS and S. R. TAYLOR. Pergamon Press, London–Paris, 2nd Edition, 1961. 454 pp. £5. 5s.

THE scope of this excellently produced volume is more correctly described by the subtitle, "A treatise on the d.c. arc analysis of geological and related materials." It is the second edition of AHRENS' *Spectrochemical Analysis* (1950), but also incorporates much of AHRENS' *Quantitative Spectrochemical Analysis of Silicates* (1954). This edition has been revised up to December 1959, and, as an indication of the completeness of this revision, the bibliography has been extended from twenty-one pages to forty-six by the inclusion of references to articles published during the last ten years.

The book follows the same pattern as the first edition in being divided into two parts—"General Principles" and "The Elements." Chapters in the first part include an adequate summary of the origin of spectra, and discussions on physical features of the d.c. arc discharge, sample preparation and operating procedures, qualitative and quantitative analysis, enrichment procedures, and photographic photometry. Two excellent chapters on selective volatilisation and the effect of change of matrix on line intensity are included. The second part deals with general methods of analysis and with schemes for the analysis of silicates. Thereafter, methods are described for the determination of elements individually or in groups. The final chapter is concerned with the determination of major constituents. Wavelength tables are given in an appendix of seventy-one pages. Although the reviewer feels that the inclusion of such tables is not justified, it would be an advantage if the meaning of such notations as (aa), (bb), (M and S) and (S and W) were included at the beginning of the tables and not on pages 69 and 70.

The presentation of the book in two parts results in duplication in many instances, examples of which are the concentration procedure of Mitchell and Scott (pp. 130, 191–192), Jaycox's method (pp. 182, 299–300), volatilisation effects (pp. 81–87, 95, 123–124) and self-absorption (pp. 32–36, 99–101, 106–109). The reviewer regrets the author's decision to alter, as compared with the first edition, the method of presentation of the working curve (section 11–4), by using the abscissa for the intensity ratio. This is the more regrettable since numerous figures remain with the concentration on the abscissa (pp. 121, 122, 158, 159, 220, 239, 266). Although errors in a book of this size are inevitable, only two have been noted—the reference to Strock (1948b) on p. 61 should be 1948, and on p. 270, line 7, 11 mm should read 2.75 mm.

Direct photometric methods are mentioned in the introduction only, and a short discussion of such methods might have been included in the text, since they are now being employed both in industry and research for the analysis of non-conducting materials.

The above remarks in no way detract from the value of the book. It is an excellent publication and should be of great interest and use both to geochemists and to spectrochemical analysts dealing with either non-conducting powders or metallic samples.

R. O. Scott

Treatise on Analytical Chemistry. A Comprehensive Account in Three Parts. Part I, Theory and Practice, Volume 2. I. M. Kolthoff and Philip J. Elving, with the assistance of Ernest B. Sandell. Interscience Publishers, New York, 1961. pp. xx + 498. $16.00 (single), $14.00 (subscription).

This second volume of Part I of Kolthoff and Elving's Treatise follows the conceptual and organisational patterns established in Volume 1, with which most analytical chemists are now familiar. Volume 2 contains the concluding two chapters of Section B, on application of chemical principles to analytical chemistry, and nine of the chapters of Section C, on separations.

The first two chapters, by Leo Schubert and Irving May, deal with organic and inorganic applications of reactive groups as reagents. These chapters are primarily concerned with classifying types of reactions and reagents of analytical significance; the brief individual discussions of about thirty chelating agents will be found useful by many.

The editors have secured the services of L. B. Rogers to act as advisor for Section C, Separations, and Rogers has also contributed the opening chapter of this section, an excellent presentation of the common theory of separations. This is followed by a rigorous, rather general discussion of the phase rule (L.O. Case), two practical chapters on decomposition and dissolution of samples—inorganic (H. H. Willard and C. L. Rulfs) and organic (E. C. Dunlop), and chapters on separations by mechanical methods (H. C. Mattrow and E. D. Leipziger), diffusion methods, with emphasis on thermal diffusion (A. L. Jones and G. R. Brown), electromigration and electrophoresis (J. R. Cann), distillation (A. Rose), and vacuum methods (W. S. Horton).

No index has been provided; however, the editors state that Volume 3 will contain an index for Volumes 1, 2 and 3, and that subsequent volumes will be provided with individual indexes.

As was the case with Volume 1, the depth of treatment is sufficient in most cases to permit this volume to stand alone as a survey of, or introduction to, the topics covered. The lists of references at the ends of the chapters are more extensive than in the previous volume, and appear to cover the literature through 1958.

It is unfortunate that a tendency exists to compare Volume 2 with Volume 1, for Volume 2 suffers from such a comparison. Where the first volume showed a remarkable degree of unity, the second is more in the nature of a series of monographs. The first volume was nearly free from typographical and other flaws in production; the second has its full share. Minor, but rather jarring, defects in style have found their way into Volume 2, *i.e.*, "in two general ways may the McLeod gage be used". Such editorial lapses do not, of course, detract from the significance of this volume, but they do make it somewhat less readable, and therefore less desirable, than its predecessor.

David H. Klein

Oszillographische Polarographie mit Wechselstrom. J. Heyrovský und R. Kalvoda, Akademie-Verlag, Berlin, 1960. pp. viii + 198. DM.23.

This book, in the German language, gives a survey of the technique of oscillographic polarography using alternating current. In it is collected most of the important published information on the subject, which is mainly from the numerous papers by Heyrovský and his co-workers. Theory and basic principles are given and the various methods of working, both direct and derivative, are described in detail. The influence of parameters such as temperature, frequency and cell and electrode capacity are considered and the effect of the degree of reversibility of the system being studied upon the resulting oscillogram, and kinetic phenomena in general, are discussed.

The electronic instrumentation associated with the method is described and some circuit diagrams are given, together with details of the commercially-available instruments. These are known as "Polaroscopes". In spite of the comparative simplicity of the instrumentation fuller descriptions would have been valuable in view of the novelty of the method.

The type of working which has proved most fruitful is a derivative system by which $\frac{dE}{dt}$ is plotted against the applied potential, E. This gives rise to an elliptical trace on the cathode-ray tube screen, upon which the changes in the voltage-time curve at constant current, caused by oxidation or reduction of a depolariser, appear as superimposed "cuts-in". The dynamic nature of the trace and the shape of the "cuts-in" make accurate quantitative measurement difficult. This type of polarography is therefore more satisfactory for qualitative studies, although semi-quantitative, or quantitative determinations are sometimes possible and useful. Considerable space is devoted to descriptions of methods for improving the quantitative measurement of the depths of these "cuts-in", including instrumental devices, such as the use of a double-beam cathode-ray tube with a calibrated Y shift on the reference beam and oscillographic and comparative titrations.

Important chapters describe the oscillopolarographic behaviour of many inorganic and organic species and special groups of substances such as noxious gases and vapours. These have great value because the most important application lies in the rapid qualitative, and sometimes semi-quantitative, characterisation of species, the oscillopolarographic behaviour of which is often very different from that observed by classical polarography. This has special value in organic polarography, since many compounds may be characterised, although they do not yield a conventional polarographic step.

Finally the book gives brief details of newer instrumental devices designed to replace the dynamic trace on the screen by a standing wave, by methods such as the use of a synchronised dropping mercury electrode. This should put the technique on a firmer quantitative basis. A bibliography of 172 references is appended.

The development of the oscillopolarographic techniques has been carried out almost entirely by Heyrovský and his co-workers in Prague, but apart from a small volume by Heyrovský and Forejt in 1953, this is the first book on the subject. It must, therefore, be welcomed as an important addition to the literature of polarography. It will assist the more general understanding of this technique, but it should be criticised for making these methods appear more important and universally applicable than they are at present. It is well written and adequately illustrated and a good balance is maintained between the various topics discussed. An English translation would be valuable.

G. F. Reynolds

Organic Analysis, Vol. IV. Edited by John Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer and A. Weissberger. Interscience Publishers, Inc., New York. 429 pp. $13.50.

The titles and authors of the contributions to the fourth volume of this well-known series are: Determination of Organic Peroxides (A. J. Martin), Enzyme Analytical Reactions (John B. Neilands), Gas Chromatography (Stephan Dal Nogare and Leo W. Safranski), Application of Nuclear Magnetic Resonance Spectroscopy to Organic Analysis (Harlan Foster), Crystallographic Methods of Analysis: X-Ray Diffraction and Microscopy (John Krc, Jr.) and Application of Differential Thermal Analysis to High Polymers (Bacon Ke).

A glance at these titles will immediately reveal the character of this work—its keynote is diversity. We have here methods as old as chemistry itself (crystallography) and the very latest (NMR); specific (determination of peroxides) and specialised (enzyme) methods, and those capable of very broad applications (NMR, GPC). Thus users of this book will include those looking for specific procedures as well as those interested in surveying broader fields.

Although all of the sections are adequate and well-written, it seems clear to this reviewer that the one on Gas Chromatography is the outstanding contribution of this volume to the chemical literature. Written by two outstanding experts in the field, this treatment is a fine balance of theory, instrumentation and applications. Of special interest are the attention paid to special applications, and the very useful Table XVI which lists liquid phases and temperature ranges suitable for the separation of a variety of typical classes of compounds. A bibliography of 336 references puts the reader in easy access of the important original papers and monographs in the field.

The only section that seems to come off less than well is that on Crystallographic Methods. The reason is obvious: an attempt is made to cover the subjects of crystal optics, crystal morphology and X-ray diffraction in 30 odd pages—a patently impossible task. A reader with little previous experience in this area will learn little, except some terminology, from these pages. The portion on fusion methods is more useful.

The book is attractively bound and printed, and the few typographical errors noted were obvious ones (such as in the legend for fig. 2. p. 68). Finally, the volume has a rarity value. It is undoubtedly the only analytical chemistry work where one can learn where Mozart composed the music for "*Cosi fan tutte*".

Robert L. Litle

Monographs on the Radiochemistry of Elements. The Sub-Committee on Radiochemistry, National Academy of Sciences. National Research Council, U.S.A.

This is a series of monographs on the radiochemistry of the elements. Each monograph is written by an authority on the radiochemistry of the particular element, and has been written to a standard format. Contents include general reviews of the inorganic, analytical and radio-chemistry of the element, a table of its isotopes, a review of properties of particular interest to radiochemists, counting techniques pertinent to the element under consideration, and a collection of detailed radiochemical procedures.

The major part of the monograph is taken up by the last section, and a critical selection of the known radiochemical techniques for each element has obviously been made. A number of the procedures have originated in Atomic Energy Establishments and it is possible that their appearance in these monographs marks their first open publication. The literature has, in some of the monographs, been covered up to 1960.

This series will be of particular interest to the radiochemist or the analytical chemist. It will also be of value to the biochemist and the physicist who often use radiochemical techniques in the solution of specific problems.

The most recent monographs in the series now available are:—

NAS–NS–3010 **The Radiochemistry of Barium, Calcium and Strontium.** D. N. Sunderman and C. W. Townley. January 1960. $1.25.
3011 **The Radiochemistry of Zirconium and Hafnium.** E. P. Steinberg. January, 1960. $0.50.
3013 **The Radiochemistry of Beryllium.** A. W. Fairhall. May 1960. $0.75.
3014 **The Radiochemistry of Iridium.** D. N. Sunderman and C. W. Townley. May 1960. $0.50.
3015 **The Radiochemistry of Zinc.** H. G. Hicks. June 1960. $0.75.
3016 **The Radiochemistry of Protactinium.** H. W. Kirby. December 1959. $1.00.
3017 **The Radiochemistry of Iron.** J. M. Nielsen. August 1960. $0.50.
3018 **The Radiochemistry of Manganese.** G. W. Leddicotte. October 1960. $0.50.
3020 **The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium.** P. C. Stevenson and W. E. Nervik. Februrary 1961. $3.00.
3021 **The Radiochemistry of Technetium.** E. Anders. November 1960. $0.50.
3023 **The Radiochemistry of Tin.** W. E. Nervik. October 1960. $0.50.
3024 **The Radiochemistry of Magnesium.** A. W. Fairhall. January 1961. $0.50.
3025 **The Radiochemistry of the Rare Gases.** F. F. Momyer, Jr. October 1960. $0.75.

3026 **The Radiochemistry of Mercury.** J. ROESMER and P. KRUGER. December 1960. $0.50.
3027 ***The Radiochemistry of Copper.*** *F. F. DYER and G. W. LEDDICOTTE. April 1961. $0.75.*
3028 ***The Radiochemistry of Rhenium.*** *G. W. LEDDICOTE. April 1961. $0.50.*

In the same series the following publication has now appeared:—

*Publication 825—**Source Material for Radiochemistry** (1st Revision) July 1960. This is an attempt to list current source material of interest to the radiochemist. It includes books on radiochemistry,* nuclear chemistry, nuclear physics, collection of radiochemical procedures, references on ion-exchange and solvent extraction, activation analysis, nuclear geochemistry, counting techniques, nuclear data compilations, and even references on laboratory design and safety. It has undoubtedly something for every radiochemist or analytical chemist and it can be obtained, free of charge, from the Division of Physical Sciences, National Research Council, National Academy of Sciences, 2101, Constitution Avenue, Washington 25, D.C.

R. J. MAGEE

Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlamm-Untersuchung. Herausgegeben von der Fachgruppe Wasserchemie in der Gesellschaft Deutscher Chemiker, 3rd Edition. Verlag Chemie, Weinheim, 1960. Pts. 1 and 2, DM 27.50.

THIS is the second part of the third new and enlarged edition of the German standard methods of examination of waters *etc.* (For a review of Part 1, see Talanta 1960, **5**, 291.) Colorimetric methods are given for the determination of nitrite and nitrate. Ammonia is determined by nesslerisation or titration, after distilling off the ammonia from a solution buffered at pH 7.4. The permanganate value is carried out with $0.01N$ $KMnO_4$ at the boil for 10 minutes. A full description is given of the procedure for estimating the Biochemical Oxygen Demand for periods of up to 20 days and the relationship which might be expected between the results and Permanganate Value is shown in tabular form. A method for the analysis of Organic Nitrogen is given. The longest section in this second part is devoted to the estimation of anionic synthetic detergents by the methylene blue method, or the formation of insoluble salts with *p*-toluidine hydrochloride, and the colorimetric estimation of cationic detergents, based on their formation of coloured compounds with bromophenol blue.

In the part dealing with the bacteriological examination of waters the recommendations of the World Health Organization regarding the frequency of examination in relation to the population supplied are given. This is followed by a description of standard procedures for determining the total count of bacteria, estimation of the number of coliform bacteria and E. coli. Concise instructions are given for the preparation and use of culture media. It is of interest that the membrane method of counting and identifying bacteria is described; the bacteria are filtered through a sterile membrane which is placed in sterile culture media so that the filtered bacteria grow to countable and identifiable colonies.

It is noted that no description has yet appeared for determining organic carbon, or phosphorus in its various forms. This book is recommended to all concerned with the examination of potable and polluted waters.

S. H. JENKINS

Talanta, 1961, Vol 8, pp. 764 to 767. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

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

BELGIUM

Tuesday–Friday 12–15 *June* 1962: **International Symposium on the Organic Chemistry of Natural Products:** organised by *Société Chimique de Belgique* on the occasion of the 75th anniversary of its foundation, under the auspices of I.U.P.A.C. Brussels.

The proceedings will be divided into 5 sections working simultaneously:

1. Structure of new natural Products.
2. Methods used for the determination of chemical structures.
3. Syntheses and chemical reactions (excluding degradation reactions).
4. Biosynthetic theories and their experimental verifications.
5. Mode of action of naturally occurring compounds in biological processes.

Section 2 is subdivided into:

(a) Analytical methods and chemical degradation.
(b) Physical methods.
(c) Stereochemical investigations (configurational and conformational).

Papers may be delivered in any language. Summaries, which should not exceed 200 words and should be written in one of the following languages: French, Dutch, English or German, must reach the Secretariat of the Symposium before 1st February, 1962.

Further information may be obtained from Professor A. Bruylants, Chairman of Société Chimique de Belgique, c/o Fédération des Industries Chimiques de Belgique, 32, rue Joseph II, Bruxelles 4, Belgium.

FRANCE

Wednesday 25 *April–Friday* 4 *May* 1962: **Sixth Salon International de la Chemie** and **Conférence Internationale des Arts Chimiques.** Paris.

The Conférence Internationale des Arts Chimiques will include a series of scientific and technical meetings, including the **Journées Techniques de Paris** which will take place in the Maison de la Chimie. Subjects featured in the Journées Techniques de Paris will be:

Petroleum chemistry	Rubber
Plastics	Nuclear techniques
Paints, pigments and varnishes	Analytical tests
Measurement, control, regulation and automation	Alloy and special steels
Organic syntheses	Perfumery and cosmetics
Aerosols	Prevention of atmospheric pollution

Further information can be obtained from 28, rue Saint-Dominique, Paris VII^{e}.

Sunday–Saturday 26 *May*–1 *June* 1963: **Sixth International Mineral Processing Congress:** *la Société de l'Industrie Minérale.* Cannes.

This Congress will be concerned with all aspects of mineral processing and papers will be selected entirely on the basis of their scientific and technical value. However, particular emphasis will be placed on the following subjects:

1. The concentration of iron minerals, including magnetic roasting but excluding agglomeration.
2. Measurement, control and automation.
3. Hydrometallurgy.

MEXICO

Tuesday–Friday 21 *November*–1 *December* 1961: **Radioisotopes in Animal Biology and Medical Sciences:** *International Atomic Energy Agency.* Mexico City.

UNITED KINGDOM

Wednesday 1 November 1961: Meeting for reading of **Original Papers:** *Society for Analytical Chemistry.* Burlington House, London, W.1. 7.00 p.m.

Thursday 2 *November* 1961: **Symposium on Electron Spin Resonance:** *Chemical Society.* Queen Mary College, London. 2.00 p.m.

Wednesday 8 *November* 1961: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group. The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Wednesday 15 *November* 1961: **The Analysis of Finishes on Yarns and Fabrics:** Mr. E. Mytum: *Society for Analytical Chemistry, Midlands Section.* Lanchester College of Technology, Coventry. 7.00 p.m.

Wednesday 15 *November* 1961: **Chemical Services on British Railways:** Dr. G. H. Wyatt, F.R.I.C.: *Society for Analytical Chemistry, North of England Section* and *Royal Institute of Chemistry, Newcastle and North-East Coast Section.* King's College, Newcastle. 6.30 p.m.

Wednesday 15 *November* 1961: **Recent Developments in Chromatography on Cellulose and Ion-exchange Cellulose:** Mr. N. F. Kember, A.R.I.C.: *Society for Analytical Chemistry, Scottish Section.* Royal Society of Edinburgh, George Street, Edinburgh. 7.15 p.m.

Friday-Saturday 17-18 *November* 1961: **Autumn Conference on Imperfections in Crystals:** *Institute of Physics and Physical Society, X-ray Analysis Group.* Institution of Mechanical Engineers, London.

Tuesday 21 *November* 1961: **Annual General Meeting** followed by **Retiring Chairman's Address:** *Society for Analytical Chemistry, Physical Methods Group.* Burlington House, London, W.1. 6.30 p.m.

Monday–Thursday 9–12 *April* 1962: **Feigl Anniversary Symposium:** *Society for Analytical Chemistry, Midland Section.* University, Edgbaston, Birmingham, 15.

This International Symposium on Analytical Chemistry will be held in honour of Professor F. Feigl to commemorate his 70th birthday. The programme will consist of:

(a) Contributions on original scientific work.
(b) Reviews of recent advances in selected branches of analytical chemistry.
(c) Exhibition of new scientific equipment.

Following the Symposium there will be a half-day Conference on the morning of Friday, 13 April, dealing with **The Teaching of Analytical Chemistry.** To this all delegates are invited.

The social programme will include a civic reception to the delegates and their ladies, a Symposium dinner, informal luncheons and dinners and a special programme arranged for lady visitors.

Plenary lectures will be given by Professor R. Belcher (U.K.), Professor F. Feigl (Brazil) and Professor P. W. West (U.S.A.).

To date the following lecturers have agreed to contribute:

R. Belcher	U.K.	A. C. Menzies	U.K.
E. W. Berg	U.S.A.	G. W. C. Milner	U.K.
J. Berger	Denmark	F. L. Moore	U.S.A.
T. S. Burkhalter	U.S.A.	L. Ottendorfer	Austria
J. K. Carlton	U.S.A.	J. W. Robinson	U.S.A.
F. Clanet	France	A. A. Smales	U.K.
C. Duval	France	S. Veibel	Denmark
G. V. M. Duyckaerts	Belgium	A. Walsh	Australia
F. Feigl	Brazil	H. F. Walton	U.S.A.
H. Freiser	U.S.A.	H. Weisz	Germany
L. Gordon	U.S.A.	F. Welcher	U.S.A.

I. M. Kolthoff	U.S.A.	P. W. West	U.S.A.
H. A. Laitinen	U.S.A.	C. L. Wilson	U.K.
R. J. Magee	U.K.	P. Zuman	Czechoslovakia
H. Malissa	Austria	J. Zyka	Czechoslovakia

Applications forms and further information can be obtained from the Honorary Symposium Secretary: Mr. M. L. Richardson, c/o John & E. Sturge Ltd., Lifford Chemical Works, Lifford Lane, Kings Norton, Birmingham 30, England.

The purpose of *NLL News*, a bulletin to be issued as occasion demands by the **National Lending Library for Science and Technology,** will be to inform potential users of the services which are available. The first issue describes the National Lending Library buildings at Boston Spa, Yorkshire, then deals briefly with what literature is available, how to obtain it, some notes on the loan service, and the London area office.

The following New British Standard is announced by B.S.I. News: *B.S. 3406: The determination of particle size of powders: Part I: 1961: Sub-division of gross sample down to 0·2 ml.* This describes methods of sub-division of gross samples of particulate material in preparation for determination of particle size for the purpose of size analysis by methods described in other parts of the standard. The total range covered is from 1,500 litre to 0·2 ml. Simple methods such as halving and coning and quartering are first described; then mechanical sub-dividers of the turntable and of the slotted cone type which are preferred as being faster and more accurate. For further sub-division below 1 litre, the grid type and the oscillating hopper type dividers are described. (Price 6s.)

B.S.I. News also announces the following Revised British Standard: *B.S. 1647: 1961: pH scale.* This applies to aqueous solutions at temperatures between 0 and 95°. The difference in pH between two solutions is defined in terms of a specified electrometric measurement, and the definition of pH is completed by assigning a value of pH at each temperature to one chosen solution (the primary standard). This primary standard is a 0·05 molar solution of pure potassium hydrogen phthalate. The solution is intended to ensure that, when different workers refer to a stated measured value of pH, they mean the same thing within ±0·005. Within this degree of accuracy there is no practical difference between the British Standard pH scale and the scale adopted by the National Bureau of Standards (U.S.A.). The standard includes recommendations on the use and calibration of the glass electrode, and pH values of aqueous solutions suitable for this purpose. (4s.6d.)

The following Amendment Slips are announced:

B.S. 1016: Methods for the analysis and testing of coal and coke: Part 8: 1959: Chlorine in coal. Amendment No. 1: PD 4185.

Addendum 1: 1960 to B.S. 2690: 1956: Methods of testing water used in industry. Amendment No. 1: PD 4211.

B.S. 2782: Methods of testing plastics: Part 4: 1958: Analytical methods and viscosity in solution. Amendment No. 5.

Methods 402: Analysis of water extract of phenolic mouldings. PD 4214.

B.S. 3278: General recommendations for the sampling of imported iron ores: Part I: 1960: Hammer and shovel method. Amendment No. 1. PD 4178.

UNITED STATES OF AMERICA

Monday 30 *October–Wednesday* 1 *November* 1961: **Annual Meeting of Association of Official Agricultural Chemists.** Shoreham Hotel, Washington, D.C.

Amongst other materials, papers will be presented relating to the analysis of antibiotics, beverages, carbohydrates, colours, cosmetics, drugs, feeds, fertilizers, flavours, foods, fruits, oils, pesticides, radioactivity, vegetables and vitamins.

Further details are available from the Association of Official Agricultural Chemists, Inc., Box 540, Benjamin Franklin Station, Washington 4, D.C.

Wednesday–Friday 1–3 *November* 1961: **Annual Pittsburgh Diffraction Conference:** *Mellon Institute.* Mellon Institute, Pittsburgh.

Thursday–Friday 2–3 *November* 1961: **Tenth Instrumentation Conference.** Louisiana Polytechnical Institute.

Monday–Wednesday 6–8 *November* 1961: **Atomic Industrial Forum Annual Conference.** Conrad Hilton Hotel, Chicago, Ill.

Monday–Thursday 6–9 *November* 1961: **Atom Fair Exhibit.** Conrad Hilton Hotel, Chicago, Ill.

Tuesday–Thursday 7–9 *November* 1961: **American Nuclear Society Annual Meeting.** Conrad Hilton Hotel, Chicago, Ill.

Wednesday–Friday 15–17 *November* 1961: **1961 Eastern Analytical Symposium and Instrument Exhibit.** Statler Hilton Hotel, New York City. (See also *Talanta*, 1961, **8**, 691).

Monday–Friday 27 *November*–1 *December* 1961: **Twenty-Eighth Exposition of Chemical Industries.** The Coliseum, New York City.

An authoritative reference work on food additives is to be prepared jointly over a five year period by the Food Protection Committee, National Academy of Sciences—National Research Council and the Toxicology Study Section, National Institutes of Health with some financial help from the U.S. Department of Health, Education and Welfare. The *National Food Chemicals Codex*, as the volume will be known, will be similar to the *U.S. Pharmacopeia and National Formulary* and will set forth methods of analysis and standards of identity and purity of chemicals used as intentional additives in foods. The project will be directed by Dr. JUSTIN J. POWERS.

Talanta, 1961, Vol. 8, p. 768. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Analysis of gases and vapours by spectroscopic techniques—I: Emission spectroscopy: W. D. McGrath, R. J. Magee, W. F. Pickering and C. L. Wilson. (20 *July* 1961).

Analysis of gases and vapours by spectroscopic techniques—II: The absorption spectra of gases and vapours: W. D. McGrath, R. J. Magee, W. F. Pickering and C. L. Wilson. (20 *July* 1961).

Analysis of gases and vapours by spectroscopic techniques—III: Applications of electronic absorption spectra: W. D. McGrath, R. J. Magee, W. F. Pickering and C. L. Wilson. (20 *July* 1961).

The determination of tantalum, niobium and titanium by homogeneous precipitation: R. Dams and J. Hoste. (22 *August* 1961).

Tetramethylguanidine—A new solvent for titration of weak acids: Theodore R. Williams and Jack Custer. (22 *August* 1961).

Improved electrodes for the continuous measurement of sodium and potassium: H. D. Portnoy, L. M. Thomas and E. S. Gurdjian. (22 *August* 1961).

Die Bestimmung kleiner Fluormengen—II: Roman Valach. (23 *August* 1961).

Spectrophotometric determination of palladium with didodeceyldithio-oxamide: William D. Jacobs, Clara M. Wheeler and William H. Waggoner. (23 *August* 1961).

The determination of interstitial elements in the refractory metals: Manley W. Mallett. (23 *August* 1961).

Precipitation of metal *8*-hydroxyquinolates from homogeneous solution V—magnesium: James T. Corkins, Richard F. Pietrzak and Louis Gordon. (23 *August* 1961).

Applications of infrared spectroscopy—VI: D. M. W. Anderson. (23 *August* 1961).

The complexometric determination of plutonium in reactor fuel processing plant solutions—I. Nitric acid solutions of irradiated uranium: D. G. Boase, J. K. Foreman and J. L. Drummond. (1 *September* 1961).

The regeneration of spent magnesium perchlorate desiccant: G. Frederick Smith. (1 *September* 1961).

The flame photometric determination of lead in lead alloys: C. L. Chakrabarti, R. J. Magee, W. F. Pickering and C. L. Wilson. (4 *September* 1961).

An automatic-recording titration apparatus for use with slow reactions: L. R. Leake and G. F. Reynolds. (4 *September* 1961).

Analytical aspects of the oxidation of organic nitrogen compounds with chromic acid: M. Jurecek, V. Novak and P. Kozak. (4 *September* 1961).

Azofarbstoffe als Reagenzien zur spektrophotometrischen Bestimmung von UranIV, VI und Thorium in Losungsmittelgemischen: G. E. Janauer und J. Korkisch. (8 *September* 1961).

Photometric titrations—VI: The determination of submicrogram quantities of calcium and magnesium: H. Flaschka and P. Sawyer. (10 *August* 1961).

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, but should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. **Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced.** Where possible, research papers should follow the pattern: *Introduction*, *Discussion*, *Conclusion*, *Experimental* (or such of these headings as apply.)

3. Because the bulk of material will be set directly in page proof, every attempt should be made to ensure that before being submitted, manuscripts are essentially in the final form desired by the authors, and that no alterations of moment will be required at the proof stage. Alterations suggested by the referee will be agreed with the authors at the manuscript stage. Authors whose native language is not English are advised that in submitting papers in English they should endeavour to have the paper thoroughly corrected before submitting for publication. If the manuscript requires considerable editing, it may have to be returned to the authors for re-typing, resulting in a serious delay in publication.

4. The essential contents of each paper should be briefly recapitulated in a summary placed at the beginning of a paper, or at the end of a preliminary or short communication. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

5. Illustrations should be separate from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, since they are easily available to the printers:

△ △ ⊡ □ ● ○ ⟁ ⊙ ⊕ ⊖ ⌽ ⊗

6. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, *e.g.*, standard deviation. The same information should not be reproduced in both tables and figures.

7. The preferred positions for all figures and tables should be indicated in the manuscript by the authors.

8. **References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:**

[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.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

9. Except in the case of preliminary communications, proofs will be sent out to authors for correction. For papers these will be in page form. **It is emphasised that at this stage extensive alterations to the text or failure to return the corrected proofs promptly may result in serious delay in publication.**

10. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units. In editing papers for publication the conventions used, on the whole, will be English spelling for all matter in the English language, and the general usages described in *Handbook for Chemical Society Authors* (The Chemical Society, London, Special Publication No. 14, 1960). It would be helpful if authors would consult this for guidance in the preparation of their manuscripts. (Authors who wish to retain American spelling, or to adhere to other generally accepted usages, should indicate this clearly at the time of submission of the manuscript.)

11. Where several authors are involved in a paper, an indication of the author to whom requests for reprints should be addressed may be given by placing the symbol ® after the name of that author.

By following the Script Requirements carefully, authors will assist greatly in ensuring rapid publication.

OCTOBER 1961 VOLUME 8 NUMBER 10

CONTENTS

Short Communications

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