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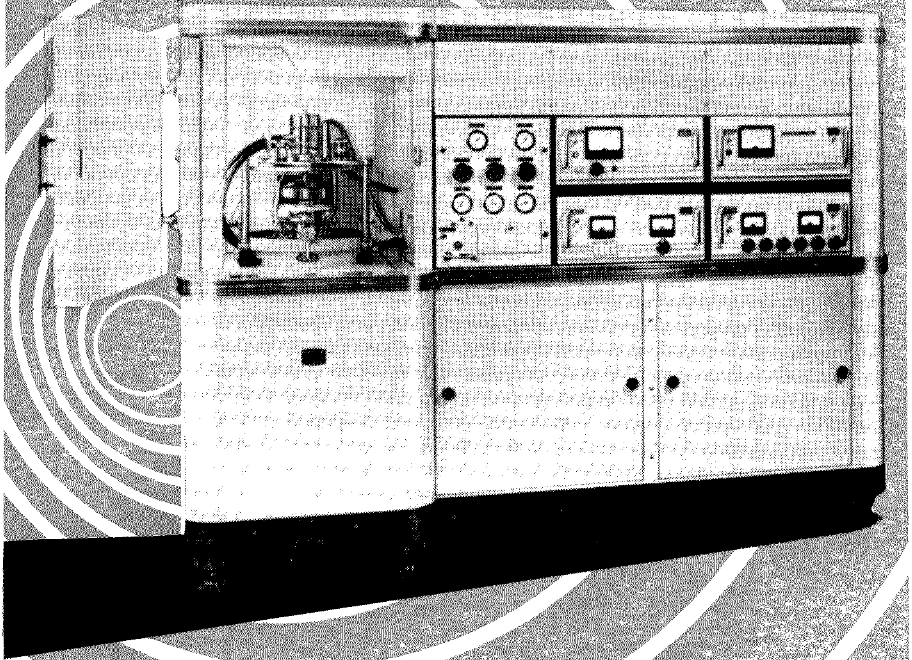

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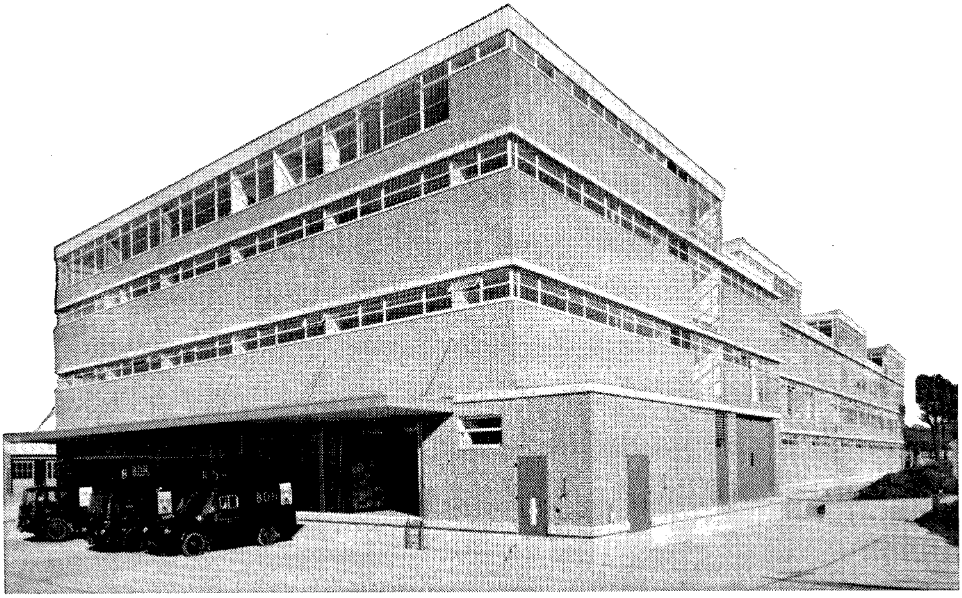

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SUMMARIES FOR CARD INDEXES

Some theoretical and practical problems in the use of organic reagents in chemical analysis—II: Effect of hydrogen bridge and donor π bond on the stability of transitional metal chelates of dioximes: K. Burger and I. Ruff, *Talanta*, 1963, **10**, 329

Summary—Stability constants and magnetic properties of transitional metal chelates of dimethyl- and diphenylglyoximes have been determined, the former with Bjerrum's potentiometric method and the linear plot evaluation method of Rossotti, the latter on the basis of magnetic proton resonance. Using this data the stability influencing effects of the hydrogen bridge and the donor π bond have been demonstrated. Results of the measurements also prove that dioximes, in the investigated complexes, exert a strong ligand field. In the course of determining the stabilities of the investigated complexes, hydrolysis of the manganese^{II}, iron^{II}, cobalt^{II} and zinc^{II} complexes has been demonstrated and the hydrolysis constants have been determined.

Sorption of ferroïn on silica and its analytical use: František Vydra and Věra Marková, *Talanta*, 1963, **10**, 339.

Summary—Sorption of ferroïn on silica is studied and the influence of pH, volume, ionic strength, flow rate, particle size and pore size of silica, and the presence of EDTA and citric acid on the sorption, is found. This has led to the development of procedures for the determination of traces of iron in nickel, chromium, molybdenum and tungsten, and the possibility of other uses of silica for the separation of metals is discussed.

Extraction of the cupferron complex of niobium: James F. Reed, *Talanta*, 1963, **10**, 347.

Summary—The precipitation of the cupferron complex of niobium is well known, but the literature states that the extraction of the complex with an organic solvent is either not quantitative or suitable for separating only milligram amounts of niobium. The present work shows that under suitable conditions in sulphuric acid solution, chloroform extraction of the cupferron complex of niobium can be made quantitative. Less than 0.05% of the niobium remains in the acid layer. Non-extracted elements may be determined by any standard method.

Coprecipitation with uranium^{IV} oxalate: JACOB BLOCK and LOUIS GORDON, *Talanta*, 1963, **10**, 351.

Summary—The coprecipitation of cerium^{III} with uranium^{IV} oxalate is studied using dimethyl oxalate to precipitate uranium^{IV} from homogeneous solution. A limited study is also made using scandium^{III} and uranium^{IV}. These systems obey the logarithmic distribution law more closely than the homogeneous distribution law. The distribution coefficient is found to be functionally related to the experimentally determined first-order precipitation rate constants when a *trace* quantity of cerium^{III} is coprecipitated with *carrier* uranium^{IV} oxalate. The coefficient λ is found to be equal to K_T/K_C where K_T, the fractional rate of precipitation of tracer, is determined in the presence of the carrier. The cerium^{III}-uranium^{IV} oxalate system obeys a distribution law modified to include ion charge rather than the unmodified Doerner-Hoskins logarithmic distribution law.

Elimination of anionic interferences in the flame spectrophotometric determination of calcium: Use of glycerol as a releasing agent: T. C. RAINS, H. E. ZITTEL and MARION FERGUSON, *Talanta*, 1963, **10**, 367.

Summary—A method is devised for circumventing anionic interferences in the flame spectrophotometric determination of calcium in concentrations from 0·1 to 10 μg/ml at a wavelength of 422·7 mμ. The sample is atomised as a solution that contains 10 v/v% glycerol and is 0·1*M* in perchloric acid. The effects of various anions, including nitrate, sulphate and phosphate, on the emission intensity of calcium are studied. Also, glycerol is used to reduce interferences from various cations and anions in the determination of calcium. The method has been applied to the determination of calcium, without prior separation, in phosphate pickling solution, soil extracts, plant tissue, fish tissue, animal bones, and National Bureau of Standards samples. The relative standard deviation of the method is less than 3%.

Isotopic dilution analysis by solvent extraction—V: Determination of traces of iron: J. STARÝ, J. RŮŽIČKA and M. SALAMON, *Talanta*, 1963, **10**, 375.

Summary—Iron is determined with cupferron in amounts of 10^{-7} to 10^{-9} g/ml with an average precision of ±4·3% and in amounts of 10^{-10} g/ml with an average precision of ±8·3%. The sensitivity of the method might be further increased by using carrier-free radioiron. The method is very simple and rapid, consisting of a single extraction of the analysed solution and measurement of the activity of the extract. The procedure is far more sensitive and precise than other methods of trace analysis. Errors arising from traces of iron present in reagents and vessels are avoided by careful purification.

Contributions to the basic problems of complexometry—XI: Determination of titanium, iron and aluminium in the presence of each other: Rudolf Přibil and Vladimír Veselý, *Talanta*, 1963, **10**, 383.

Summary—Aluminium can be masked in an acidic medium with salicylic acid (or *p*-aminosalicylic acid). This enables the complexometric determination of titanium (or iron) to be carried out in the presence of relatively high concentrations of aluminium (100 mg/100 ml) without previous separation. A selective separation of titanium from iron and aluminium with triethanolamine and sodium hydroxide, in combination with salicylic acid, is utilised with advantage for the determination of titanium even in the presence of g-amounts of aluminium. The determination of iron and aluminium in the filtrate after separation of titanium is also described.

Application of constant current potential limit coulometry to chemical analysis: I. J. McColm, V. M. Sinclair and R. S. Roche, *Talanta*, 1963, **10**, 387.

Summary—Constant current potential limit coulometry has been examined as an alternative to controlled potential coulometry. It has been shown that the accuracy and precision obtainable by this new technique compare favourably with those obtained by controlled potential coulometry. Data are presented on its use in the determination of uranium^{VI}, cadmium^{II} and copper^{II} using various base electrolytes. The study of uranium has been extended to cover the presence of various impurities.

Separation and spectrophotometric determination of rare earths: Hiroshi Onishi and Charles V. Banks, *Talanta*, 1963, **10**, 399.

Summary—At the present time arsenazo appears to be widely used for the spectrophotometric determination of rare earths. Unfortunately, the method is not selective. The separation of rare earths and yttrium from interfering elements has been studied, and the following method is proposed. Rare earths are precipitated as fluorides using calcium fluoride as the carrier. Thorium and zirconium are removed by extraction with thenoyltrifluoroacetone (TTA) in xylene at pH 1·3. Small amounts of residual aluminium, iron, *etc.*, are removed by extraction with 8-quinolinol-chloroform at pH 4·5. Rare earths are separated from calcium by TTA extraction at the same pH, then they are back-extracted into 1*M* nitric acid. After evaporation of the solution, the rare earths are determined spectrophotometrically with arsenazo.

Determination of copper in high-purity niobium, tantalum, molybdenum and tungsten metals with bathocuproïne: Elsie M. Penner and W. R. Inman, *Talanta*, 1963, **10**, 407.

Summary—A spectrophotometric method for determining 0·0005–0·125% of copper in high-purity niobium, tantalum, molybdenum and tungsten metals is described. After sample dissolution and reduction of copper to the univalent state with ascorbic acid, the yellow complex formed by copper^{I} and bathocuproïne (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) is extracted into n-amyl alcohol and the absorbance of the resulting extract is determined at 476 mμ. Other impurities present in the four high-purity metals described do not interfere in the proposed method.

The preparation of fortified 70–80% perchloric acid employing anhydrous magnesium perchlorate as desiccant: G. Frederick Smith, *Talanta*, 1963, **10**, 413.

Summary—The preparation of 73·6% perchloric acid, $HClO_4 \cdot 2H_2O$, by a new procedure is described; this is the vacuum distillation of commercially available 70–71% acid to which anhydrous magnesium perchlorate has been added. The process can be extended to the preparation of 75–80% perchloric acid concentrations, for which there exists commercial demand. The processes involved are described in detail.

Coulometric reduction of iridium^{IV} in perchloric acid media: G. A. Rechnitz and J. McClure, *Talanta*, 1963, **10**, 417.

Summary—The anomalous behaviour of iridium^{IV} during electrolysis in perchloric acid media has been investigated by controlled-potential coulometric techniques. The observed variation in apparent *n* values is attributed to a chemical interaction between the initial electrolysis product, iridium^{III}, and perchlorate ion, to regenerate iridium^{IV}.

The reactions of biacetyl, hydroxylamine and metal ions to form chelates: Orville E. Hileman, Jr., Paul R. Ellefsen, R. J. Magee and Louis Gordon, *Talanta*, 1963, **10**, 419.

Summary—Two additional reaction intermediates in the reaction between biacetyl and hydroxylamine (E. D. Salesin, E. W. Abrahamson and Louis Gordon, *Talanta*, 1962, **9**, 699) are reported. The effect of the presence of Ni^{II} or Pd^{II} on the course of the reaction is being studied.

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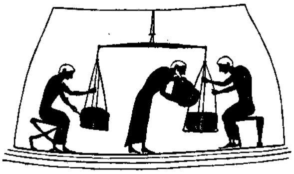

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Because TALANTA is an international journal, contributions are expected to be of a very high standard. They should make a definite contribution to the subject. Papers submitted for publication should be new publications. The submission of a paper is held to imply that it has not previously been published in any major language (English, French, German, Russian), that it is not under consideration for publication elsewhere, and that, if accepted for publication, it will not be published elsewhere without the written consent of the Editor-in-Chief. 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-in-Chief will welcome correspondence on matters of interest to analytical chemists.

Original papers, short communications and reviews will be refereed (see *Talanta*, 1962, **9**, 89.) 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-in-Chief, 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.

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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Talanta, 1963, Vol. 10, pp. 329 to 338. Pergamon Press Ltd. Printed in Northern Ireland

SOME THEORETICAL AND PRACTICAL PROBLEMS IN THE USE OF ORGANIC REAGENTS IN CHEMICAL ANALYSIS—II*

EFFECT OF HYDROGEN BRIDGE AND DONOR Π BOND ON THE STABILITY OF TRANSITIONAL METAL CHELATES OF DIOXIMES

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(*Received* 17 *July* 1962. *Accepted* 10 *November* 1962)

Summary—Stability constants and magnetic properties of transitional metal chelates of dimethyl- and diphenylglyoximes have been determined, the former with Bjerrum's potentiometric method and the linear plot evaluation method of Rossotti, the latter on the basis of magnetic proton resonance. Using this data the stability influencing effects of the hydrogen bridge and the donor π bond have been demonstrated. Results of the measurements also prove that dioximes, in the investigated complexes, exert a strong ligand field. In the course of determining the stabilities of the investigated complexes, hydrolysis of the manganese^{II}, iron^{II}, cobalt^{II} and zinc^{II} complexes has been demonstrated and the hydrolysis constants have been determined.

DIMETHYLGLYOXIME, suggested by Tschugaeff[1] in 1905, was the first selective organic reagent used in metal analysis. The analytical application of dioximes has now been developed to a very great extent,[2] and the different dioximes form an important and frequently used group of reagents.

The reactions serving as a basis for analytical determinations are interesting to study from a theoretical and a practical point of view. In the present work, the object was to study the stability, structure and magnetic properties of complexes of transitional metals with dimethyl- and diphenylglyoxime.

The stability of the dioximes of cobalt^{II}, nickel^{II}, copper^{II} and zinc^{II} have been studied potentiometrically.[3,4,5] Also the iron^{II} complexes have been investigated,[6] but their stability constants have not yet been determined. Stability values of dioxime complexes of manganese^{II} and of iron^{II} and that of zinc^{II} diphenylglyoxime have not been reported.

It is difficult to interpret the data in the literature, because the authors make use of the half $\bar{n}$ evaluation method of Bjerrum,[7] which involves a serious error in the case of nickel^{II}, copper^{II} and zinc^{II} where $k_1 \leq k_2$. Thus the data available do not give a reliable ratio of $k_1:k_2$.

Dyrssen and coworkers[8] determined the stability of the nickel^{II} and copper^{II} dimethylglyoxime complexes in water (saturated with chloroform) by solvent extraction and proved that $\log k_1 \leq \log k_2 - 1{\cdot}2$. This is in accordance with our results, but the data cannot be directly compared because of the different solvents used.

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* Part I: see *Talanta*, 1961, **8**, 769.

The structure of the copper^{II}, nickel^{II} and cobalt^{II} dioxime complexes are well known from X-ray diffraction and infrared absorption investigation.[9] Magnetic data of some complexes in the solid state are reported in literature.[10] Nevertheless, it would be useful to determine their magnetic properties in solutions with the same composition as used for determining the stability constants, because the magnetic susceptibility of some complexes may differ in the solid state from that of the complex in solution.[11]

Our aim was to obtain reliable values so that the physical parameters characteristic of these complexes could be utilised to provide a uniform picture about the structure of the complexes and nature of the bonds.

EXPERIMENTAL

The complex stability constants have been determined by Bjerrum's potentiometric method.[7] The evaluation of the formation curves was made by the linear plot method of Rossotti *et al.*[12]

The measurements were made in a 50% dioxan–water medium, using a pH meter produced by Orion KTS with glass and saturated calomel electrodes. Oxygen and carbon dioxide were removed by bubbling hydrogen gas through the solution during the course of the titration.

For investigating the dimethylglyoxime complexes, $10^{-3}M$ perchloric acid, $2{\cdot}5$–$5{\cdot}0 \times 10^{-4}M$ metal ion and $1{\cdot}0$–$2{\cdot}5 \times 10^{-3}M$ dimethylglyoxime concentrations were used and $0{\cdot}3M$ sodium perchlorate for maintaining constant the activity coefficients. The titration was made with $0{\cdot}2M$ sodium hydroxide solution from a microburette.

For investigating the diphenylglyoxime complexes, concentrations of $10^{-3}M$ perchloric acid, $0{\cdot}62$–$1{\cdot}25 \times 10^{-4}M$ metal ion, $2{\cdot}50$–$6{\cdot}25 \times 10^{-4}M$ diphenylglyoxime and $0{\cdot}3M$ sodium perchlorate were used. The smaller solubility of diphenylglyoxime made the decrease of concentration necessary. The titration was made in this case with $0{\cdot}1M$ sodium hydroxide. The temperature was 25°.

The maximum error of the determinations (including the error of measurements and that of graphical evaluation) was $\pm 0{\cdot}2$ pK. For controlling the reliability of the stability data, we computed by a Ferranti electronic computer the theoretical formation curves of the postulated complexes and compared them with the experimental ones. As seen from Fig. 1, they are in good agreement. (We wish to thank Professor L. G. Sillén and Dr. N. Ingri, Royal Institute for Technology, Stockholm, Sweden, for their valuable help in this computation).

The low solubility of the investigated complexes made the determination of their magnetic susceptibility in solution impossible with the accustomed methods. Therefore we had to use an indirect method, based on magnetic proton resonance measurements, which made it possible to decide whether the complex is para- or diamagnetic (in the presence of paramagnetic compounds the relaxation time in magnetic resonance of the protons of water decreases).

The magnetic measurements were made at a concentration of $5 \times 10^{-2}M$. (We are indebted to Dr. L. Korecz, Department of Atomic Physics, L. Eötvös University, for carrying out these measurements.)

THEORETICAL AND RESULTS

I. The results of the magnetic measurements are summarised in Table I. The most important result is that the 1:2 iron^{II} dimethylglyoxime complex is diamagnetic. Taking into consideration the structure of the electron shell of the iron^{II} ion, this proves that dioximes in the systems investigated are *ligands with a strong ligand field, i.e.* they are able, in the course of complex formation, to pair the unpaired electrons of the iron^{II} ion. The diamagnetism of this complex is *proof that a real complex of iron^{II} is formed and not of iron^{III}* as supposed by Jillot and Williams.[6]

II. In the course of our investigations we have found that in the formation of the complexes of manganese^{II}, iron^{II}, cobalt^{II} and zinc^{II} in a higher pH interval, four protons are released per metal ion. We could not suppose that more than two dimethylglyoxime ligands took part in formation of the complexes. It was more probable that after the formation of 1:2 complexes, the central atom can hydrolyse and form a complex of $Me(Gly)_2(OH)_2^{2-}$ with an octahedral or distorted octahedral structure. (The configuration of the 1:2 complex in the case of cobalt^{II} is square

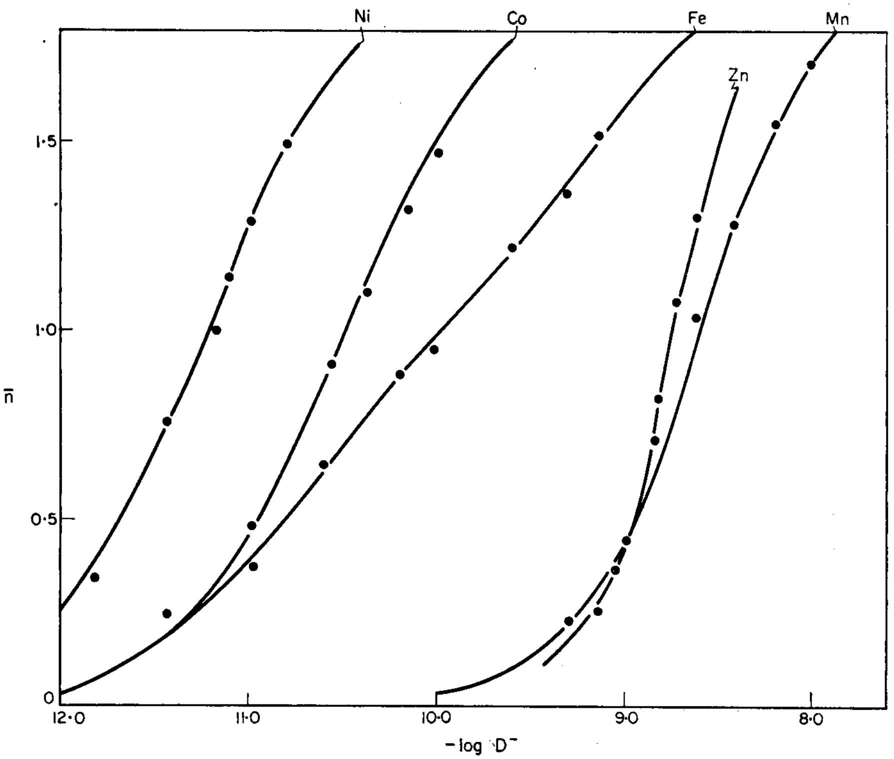

FIG. 1.—Calculated formation curves of metal dimethylglyoxime complexes and experimental points.

TABLE I. MAGNETIC PROPERTIES OF TRANSITIONAL METAL DIOXIME CHELATES

Metal	Ion	MeD$^+$ Complex	MeD$_2$ Complex
Mn^{2+}	paramagnetic	paramagnetic	paramagnetic
Fe^{2+}	paramagnetic	paramagnetic	diamagnetic
Co^{2+}	paramagnetic	paramagnetic	weakly paramagnetic
Ni^{2+}	paramagnetic	paramagnetic	diamagnetic
Cu^{2+}	paramagnetic	paramagnetic	paramagnetic
Zn^{2+}	diamagnetic	diamagnetic	diamagnetic

planar, but in the case of manganese^{II}, iron^{II} and zinc^{II} it is probably octahedral, with water molecules filling the fifth and sixth co-ordination positions) The hydrolysis provides the last two protons.

For deciding this question, we repeated the potentiometric titrations of the Bjerrum method in solutions containing both a 1:2 and 1:3 metal:ligand ratio. The titration curves obtained were the same as in the previous experiments.

The hydrolysis constants could be determined from the $\bar{n}_{OH}$-pH formation curves with Rossotti's linear plot evaluation method (Table II).

From Table II it can also be seen that hydrolysis takes place only in the cases of those complexes where, according to ligand field theory of strong ligand fields, octahedral or distorted octahedral structures are expected. This confirms that the investigated complexes involve strong ligand fields.*

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* Calculations made by Maki[13] on complexes of nickel also support this statement.

TABLE II.—STABILITY CONSTANTS OF TRANSITIONAL METAL CHELATES

Metal	log k_1	log k_2	log K	log k_1/log k_2	Hydrolysis		
					log k_1	log k_2	log K
			Dimethylglyoxime				
Mn^{2+}	8·6	8·6	17·2	1·00	4·8	3·9	8·7
Fe^{2+}	10·8	9·2	20·0	1·17	4·4	4·1	8·5
Co^{2+}	10·8	10·2	21·0	1·05	5·6	4·8	10·4
Ni^{2+}	11·5	11·0	22·5	1·05	—	—	—
Cu^{2+}	11·0	12·5	23·5	0·88	—	—	—
Zn^{2+}	8·1	9·3	17·4	0·70	6·2	5·1	11·3
			Diphenylglyoxime				
Mn^{2+}	7·9	7·4	15·3	1·07	3·9	—	—
Fe^{2+}	11·5	9·7	21·2	1·18	4·6	5·2	9·8
Co^{2+}	11·9	9·3	21·2	1·28	5·8	3·8	9·6
Ni^{2+}	—	—	—	—	—	—	—
Cu^{2+}	11·0	11·9	22·9	0·92	—	—	—
Zn^{2+}	7·4	8·1	15·5	0·92	5·3	3·6	8·9

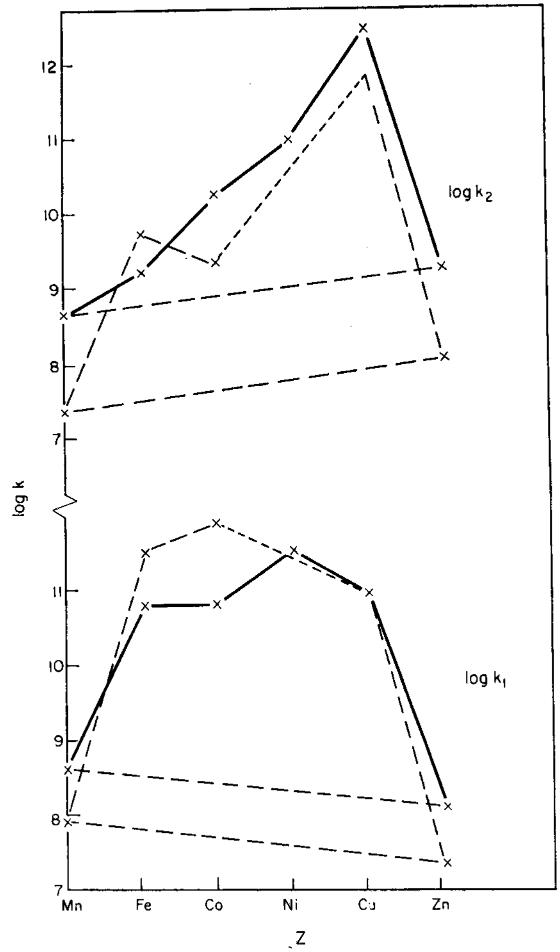
The occurrence of hydrolysis proves also that the two dimethylglyoxime groups are in the same plane, or nearly so even in the case of the manganese^{II}, iron^{II} and zinc^{II} complexes whose structures have not yet been determined. This kind of hydrolysis would not be expected to occur if the complexes were tetrahedral.

III. To obtain a real picture about the structure of the investigated complexes and the nature of bonding in them, the stability constants have been drawn as a function of the atomic number of the metals (Figs. 2-4).

The low stability of the manganese^{II} and zinc^{II} complexes can be explained by the spherical symmetry of their d-electron shell. The ligand field stabilisation exists, however, in the complexes of iron^{II}, cobalt^{II}, nickel^{II} and copper^{II}, with their d^6, d^7, d^8, d^9 electronic configuration. This stabilisation effect is proportional to the distance between their stability values and the line connecting the stabilities of the manganese and zinc complexes in Figs. 2-4. These data are summarised in Table III. It is seen in this table that the values derived from log k_1 are, except in the case of nickel, nearly equal. Those derived from log k_2 values show a monotonous increase. These facts show that other effects besides ligand field stabilisation influence the stability of the complexes.

IV. The stability values as a function of the ionic radius (r) of the metal ions (or e^2/r, where e is the charge of the ion) show an increase with decreasing ionic radius, except for log k_1 values (Figs. 5-7). In the case of the copper and zinc complexes, the values of log k_2 are greater than those of log k_1 (Table I).

These two facts can be explained, taking into consideration the structure of the copper complex determined by X-ray measurements, by the *hydrogen bridges* between the oxime groups. The smaller ionic radius favours the formation of a hydrogen bridge. This is the reason why the log k_2 and log K values show an increase with decreasing ionic radius of the metal. However, the log k_1 values, where this effect does not play any part, are almost equal for iron^{II}, cobalt^{II}, and copper^{II} complexes.



FIGS. 2–3.—Log k values as a function of the atomic number of the metals: ——— dimethylglyoxime; - - - - diphenylglyoxime.

The formation of the hydrogen bridge must also be the reason for the unaccustomed relation (reversed order) of the k_1 and k_2 values in copper, zinc, and partly in the manganese complexes. With the formation of the hydrogen bridge in the 1:2 complex two new rings are formed, accounting for the greater values of k_2. Because the ionic radius of manganese is the greatest in the series of metal ions investigated, we have to conclude that the formation of the hydrogen bridge is possible in all of

TABLE III.—STABILISATION EFFECT OF LIGAND FIELD

Ligandum	Composition		Mn	Fe	Co	Ni	Cu	Zn
Dimethylglyoxime	MeD	L_1	0	2·6	2·7	6·2	3·3	0
	MeD_2	L_2	0	0·4	1·3	1·9	3·2	0
Diphenylglyoxime	MeD	L_1	0	3·7	4·4	—	3·5	0
	MeD_2	L_2	0	2·2	1·7	—	3·9	0

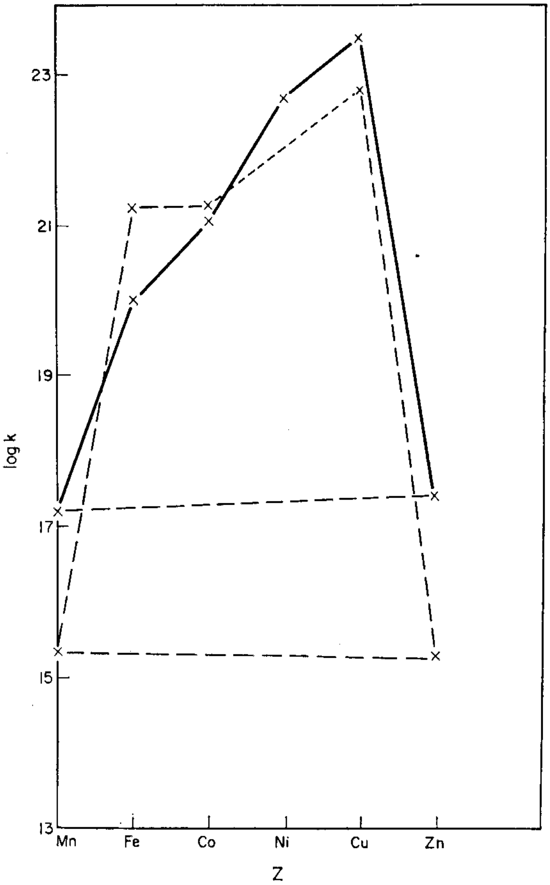


FIG. 4.—Log K values as a function of the atomic number of the metals: ——— dimethylglyoxime; - - - - diphenylglyoxime.

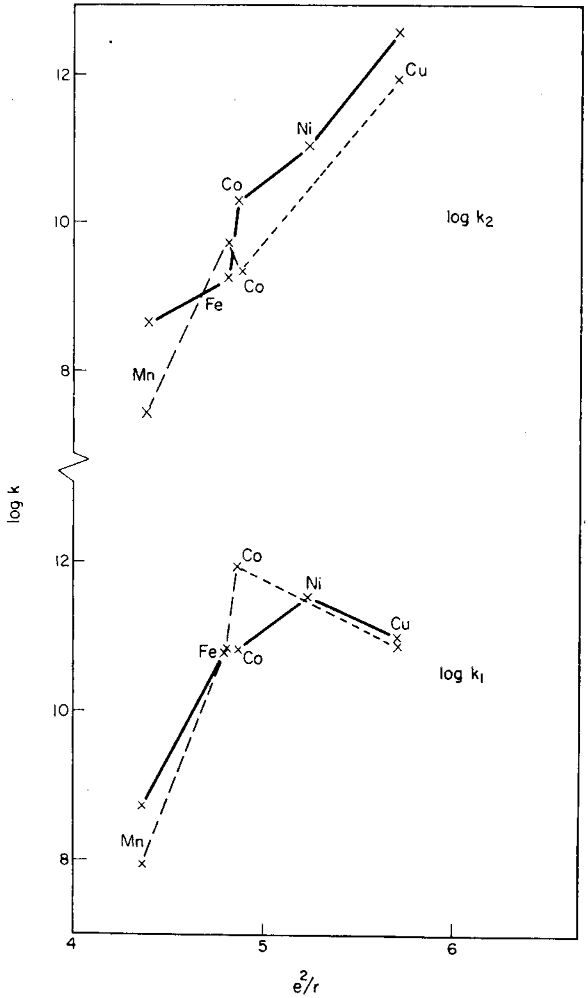
these complexes. Nevertheless, the order of the consecutive stability constants of the complexes of iron^{II}, cobalt^{II} and nickel^{II} is not reversed. The difference between k_1 and k_2 is greatest in the case of the iron complexes.

These facts show that still another stabilising influence must also be taken into consideration.

V. The iron^{II} complex has a k_1 which exceeds that predicted from the Irving-Williams stability row;[14] this effect and the difference between k_1 and k_2 can be explained by a *donor π bond* in this complex.

Other diamagnetic iron^{II} complexes (*e.g.*, 2:2′-bipyridyl, 1:10-phenanthroline) having stabilities which exceed the values predicted by the Irving-Williams row are also known.[15] In these complexes, however, the 1:3 complex has the outstanding stability and $k_2k_3^{1/2} > k_1$.

In iron^{II} dioxime complexes on the other hand, $k_1 > k_2$ and k_1 values are the outstanding ones. The two phenomena are thus not altogether analogous. In the former case the diamagnetic spin-paired complex has the greater stability. In the



FIGS. 5–6.—Dependence of log k values on e^2/r; ———dimethylglyoxime; - - - - diphenylglyoxime.

latter case the increased stability of the paramagnetic 1 : 1 complexes can be explained on the basis of a donor π bond. (We have to remark that in the 2:2′-bipyridyl- and 1:10-phenanthroline-iron^{II} complexes donor π bonds also exist.)

VI. The log k_1-ionisation potential curves (Fig. 8) also show the existence of a donor π bond in the iron^{II} complexes. The great mobility (low ionisation potential) of d electrons of the iron^{II} ion is favourable for the formation of this kind of bond.

VII. From the stability values of the investigated complexes and from the figures it can be seen that the effects on stability of the hydrogen bridge and that of the donor π bond are not additive. On the contrary, supposing a mesomeric shift of the π electrons in direction Me $\rightarrow$ N $\rightarrow$ O, which shortens the N—O bond length, a hindering effect of donor π bond for the formation of the hydrogen bridge can be supposed.

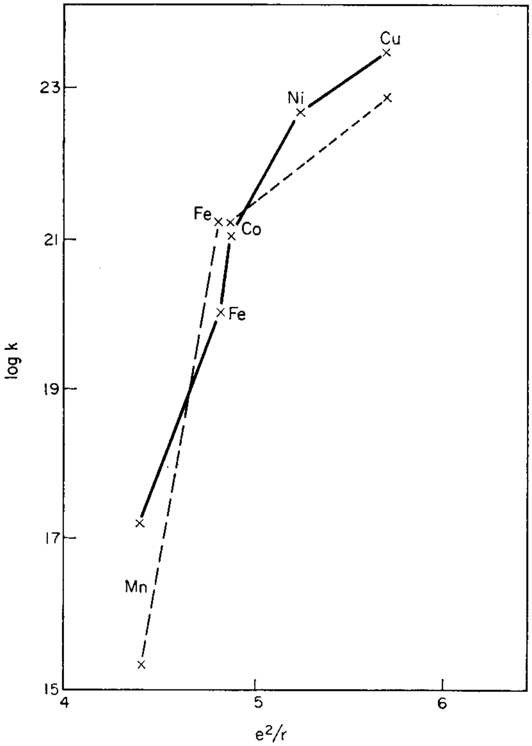


FIG. 7.—Dependence of log K values on e^2/r: ———— dimethylglyoxime; - - - - diphenylglyoxime.

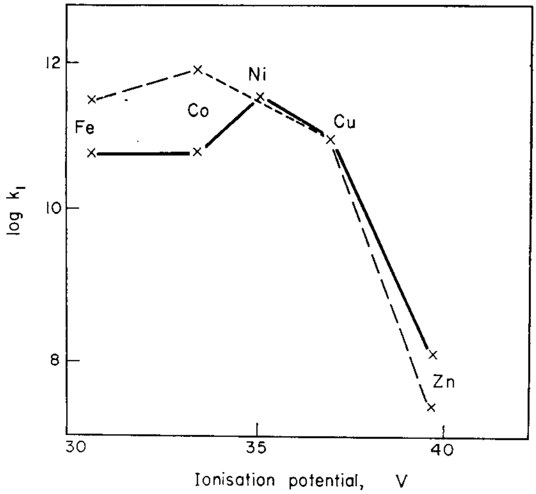


FIG. 8.—Log k_I-ionisation potential curves ($Me^{II} \rightarrow Me^{III}$): ———— dimethylglyoxime; - - - - diphenylglyoxime.

In this way in iron^{II} and to a smaller extent in cobalt^{II} complexes the donor π bond has the more significant effect in influencing the stability, while in the other complexes it is the hydrogen bridge. This is why the former effect can be observed only in the row of the 1 : 1 complexes, where hydrogen bridges cannot be formed, and thus do not mask the effect of the donor π bond.

VIII. The stability values of complexes of diphenylglyoxime show a more expressive effect of the donor π bond (Tables II and III). This fact can be explained on the ground that a phenyl group substitution for the methyl in dioximes increases the π acceptor capability of the ligand.

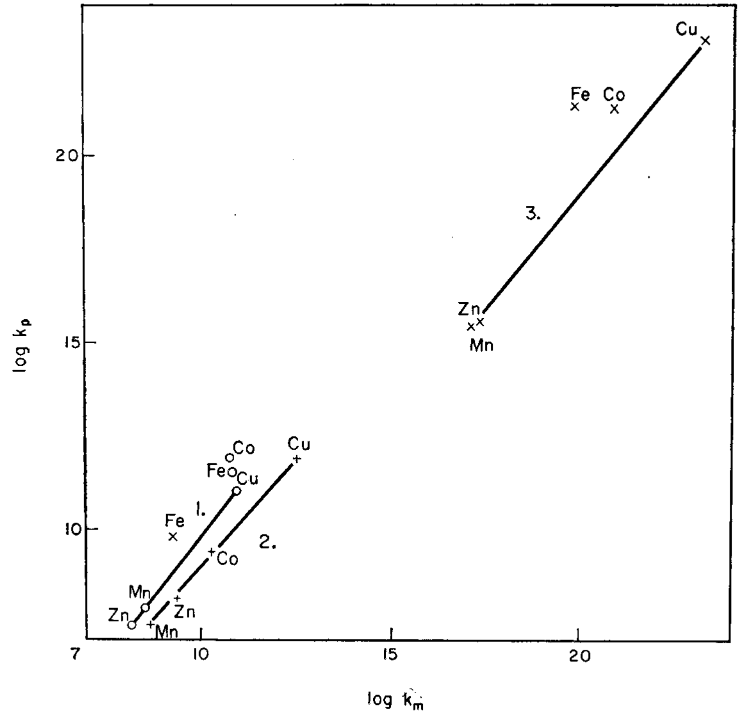


FIG. 9.—Stability constants of dimethylglyoxime complexes as a function of those of diphenylglyoxime.

For comparing the stabilities of complexes of the two ligands investigated, we had to choose a method where the stability change caused by the change in the acidic dissociation constant of the ligand does not appear. Thus we have plotted the stability constants of diphenylglyoxime complexes as a function of those of dimethylglyoximes (Fig. 9). The deviation of the slope of this straight line from unity shows an increase in the stability in diphenylglyoxime complexes because of the greater effect of the donor π bond in these complexes. The slope of the straight line of log k_1 values is 1·3 and that of log k_2 is 1·2. The value of the iron^{II} complexes show a significant positive deviation from the line. The greater mobility of d-electrons of the iron^{II} ion favours the formation of a donor π bond.

Zusammenfassung—Die Stabilitätskonstanten der Dimethyl- und Diphenylglyoximkomplexe der Übergangsmetalle wurden nach der potentiometrischen Methode von Bjerrum und der Methode der linearen Extrapolation nach Rosotti bestimmt. Magnetische Eigenschaften wurden mittels magnetischer Protonenresonanz ermittelt. Auf Grund der Daten wurde der Einfluss der Wasserstoffbrücken und der Donor-π-Bindungen auf die Stabilität der Komplexe aufgezeigt. Es wurde auch gezeigt, dass die Dioxime ein starkes Ligandenfeld aufweisen. Im Laufe der Untersuchungen wurde die Hydrolyse der Komplexe von Mn(II), Fe(II), Co(II) und Zn studiert und die Hydrolysenkonstanten bestimmt.

Résumé—Les constantes de stabilité et les propriétés magnétiques des complexes formés entre les métaux de transition et la diméthyl et la diphénylglyoxime ont été déterminées, les premières par potentiométrie selon la méthode Bjerrum et la méthode de Rossotti, les dernières par résonnance magnétique. A partir des résultats obtenus, l'influence de la liaison hydrogène et des liaisons π sur la stabilité des complexes a été démontrée. Au cours de l'étude de la stabilité des complexes, l'hydrolyse des complexes de manganèse (II), fer (II), cobalt (II) et zinc a été prouvée et les constantes d'hydrolyse ont été mesurées.

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SORPTION OF FERROÏN ON SILICA AND ITS ANALYTICAL USE

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Summary—Sorption of ferroïn on silica is studied and the influence of pH, volume, ionic strength, flow rate, particle size and pore size of silica, and the presence of EDTA and citric acid on the sorption is found. This has led to the development of procedures for the determination of traces of iron in nickel, chromium, molybdenum and tungsten, and the possibility of other uses of silica for the separation of metals is discussed.

IN a preliminary communication[1] dealing with the sorption of cationic complexes on silica some data connected with the sorption of the complex of iron^{II} with 1,10-phenanthroline and the conditions for determination of iron were given. In this determination, ferroïn was desorbed with potassium iodide solution and its concentration determined colorimetrically. Mention was made of the possibility of increasing the selectivity by use of EDTA[2] and citric acid,[3] which mask a number of metals interfering by formation of complexes with 1,10-phenanthroline.

Recently Bozhevol'nov and Karakovskaya[4] used the phenomenon of sorption of ferroïn for the determination of traces of iron. Iron was concentrated on silica (particle size 2-6 μ) at pH 5·5–6·0. By comparison of the heights of coloured columns with a series of standards, it is possible, according to the authors, to determine down to 10^{-7}% of iron in the presence of metals which do not interfere with the formation of ferroïn.

In the present paper both the sorption of ferroïn on silica and the optimum conditions for its desorption are studied in detail. From the results obtained a procedure which gives increased selectivity and sensitivity to the colorimetric method, was devised.

EXPERIMENTAL

Reagents

Reagent grade chemicals were used throughout this work.

Preparation of silica: Silica, generally stored in a desiccator, with average size of pores 50 Å (determined from the maximum sorption of water[5]), was used for the columns. Common silica was pulverised in an agate mortar and sieved through a series of standard sieves. Each fraction according to the size of grain was washed by flotation with twice-distilled water. Iron was removed by shaking with hydrochloric acid (1:1), then again washing the silica with twice-distilled water. Sorption under kinetic conditions was carried out on silica columns of 12 mm internal diameter and 50 cm length. For the sorption of ferroïn, the fraction of silica of particle size 0·2–0·3 mm was used.

Standard iron^{III} chloride solutions: Prepared and standardised gravimetrically as Fe_2O_3.

1M EDTA solution: Prepared by dissolving 372 g of reagent in warm water; the solution was made alkaline with aqueous ammonia (1:1) and diluted with water to 1 litre. The resulting pH of this solution was 8.

0·1M 1,10-phenanthroline solution: Prepared by dissolving 18 g of reagent in hot water; the solution was acidified with 3–5 drops of acetic acid and diluted to 1 litre.

20% *citric acid solution*: Prepared by dissolving 200 g of reagent in the minimum amount of water and after adjusting the pH to *ca.* 3·5, the solution was diluted to 1 litre.

Buffer solutions: Prepared with the aid of a potentiometer by neutralising suitable acids (trichloracetic, monochloracetic, acetic or boric) with aqueous ammonia or sodium hydroxide. All buffer solutions were prepared to give a final concentration which was *ca.* 1*M*.

Other solutions employed were standardised using recommended procedures.

Purification of EDTA, citric acid, buffer and potassium iodide solutions from iron. To 1 litre of 1*M* EDTA solution (pH 7–8) 5 ml of 0·1*M* 1,10-phenanthroline and 5 ml of 10% hydroxylamine hydrochloride were added and the mixture was allowed to stand for 24 hr. The resulting ferroïn was separated by passing the solution through a silica column (diameter 25 mm, height 15 cm). Citric acid, buffer and potassium iodide solutions were purified similarly, keeping in mind that the optimum pH for the formation and sorption of ferroïn in citric acid and potassium iodide solutions is 3·4.

Apparatus

Optical density was measured with a Pulfrich photometer (C. Zeiss, Jena, East Germany), which had an arrangement for objective measuring—Elpho II.

pH values were measured with a glass electrode and pH-meter Multoskop V (Lab.potřeby, Prague, Czechoslovakia).

Influence of pH *on formation and sorption of ferroïn on silica*

Ferroïn is stable in the pH range 1·5–9·5 but it is not formed quantitatively at high pH values because of the ready hydrolysis of iron^{III}. Therefore it is better to determine traces of iron at *ca.* pH 3, taking care, with the subsequent addition of reagents, to avoid hydrolysis.[6] The influence of pH on the formation of ferroïn using the buffer solutions listed above and in the presence of EDTA was studied. In the absence of EDTA the formation of ferroïn is quantitative in the pH range 1·5–5·5 (Fig. 1, curve 1); in the presence of EDTA, quantitative formation occurs in the pH range 1·5–8·0 (Fig. 1, curve 2). At pH > 8 iron^{III} is complexed with EDTA so firmly that the reaction with 1,10-phenanthroline even after a period of 3 hr does not proceed quantitatively.

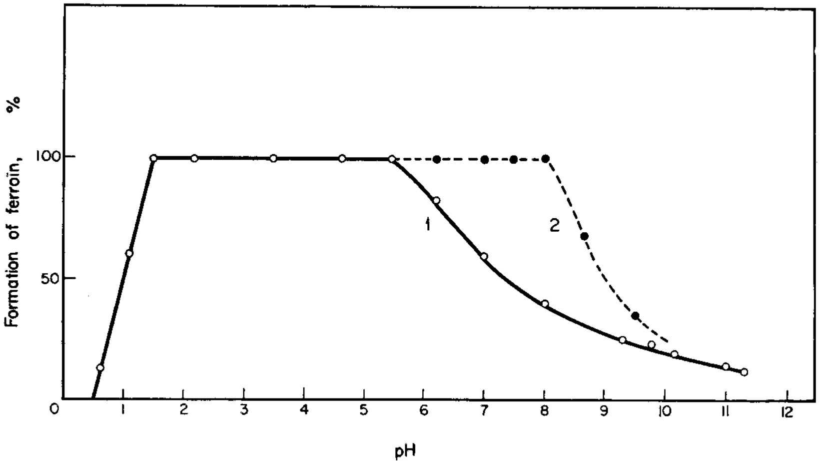

Fig. 1.—Influence of pH and EDTA on the formation of ferroïn:
1. In the absence of EDTA
2. 1 ml of 5 × $10^{-2}M$ EDTA added before buffer solution. Concentration of ferroïn determined colorimetrically.
(2 ml of 1·82 × $10^{-4}M$ iron^{III} chloride; 5 ml of 10% hydroxylamine hydrochloride; 5 ml of buffer; 1 ml of 0·1*M* 1,10-phenanthroline)

The influence of pH was determined as follows: To 2 ml of 1·82 × $10^{-4}M$ iron^{III} chloride solution were added 5 ml of 10% hydroxylamine hydrochloride solution and 1 ml of 0·1*M* 1,10-phenanthroline. The pH of this solution was adjusted to the required value. Five ml of buffer solution of the same pH value were added and the solution was diluted to *ca.* 50 ml with water. After passing *ca.* 25 ml of suitable buffer solution through a silica column (see p. 339), ferroïn was sorbed from the test solution at a flow rate of 3 ml/min. Ferroïn was sorbed to a depth of 5–15 mm and the concentration of unabsorbed ferroïn was determined by measurement of the optical density (at 510 mμ) of the solution passing through the column. Quantitative sorption occurred in the pH range 1·5–9·0.

Influence of flow rate and ionic strength on sorption of ferroïn

Even at the maximum possible flow rate (10 ml/min) sorption is quantitative; the depth of the layer of sorbed ferroïn increases, however, up to 40 mm.

The influence of ionic strength during the sorption of 10 μg of iron/50 ml at pH 3·5 was checked by adding a strong electrolyte, namely, 5–25 ml of a saturated solution of sodium nitrate, to 50 ml of the iron solution. Quantitative sorption was found in all cases but the layer of sorbed ferroïn lengthened with increasing ionic strength.

Influence of particle size of silica on its sorption capacity for ferroïn-static measurements

The capacity of silica for ferroïn at constant pH was measured as follows: To 1-g amounts of silica (ground to various sizes: 0·5–0·3, 0·3–0·2, 0·2–0·12 and 0·12–0·08 mm) in 100-ml polyethylene bottles, 40 ml of 0·1*M* buffer solution (pH 3·1) were added. After shaking for 5 min, the solution was removed and 1 ml of 10% hydroxylamine hydrochloride (pH 3·1), 1 ml of 0·1*M* 1,10-phenanthroline and a known amount of iron$^{\text{III}}$ salt were added and the resulting volume adjusted to about 40 ml.

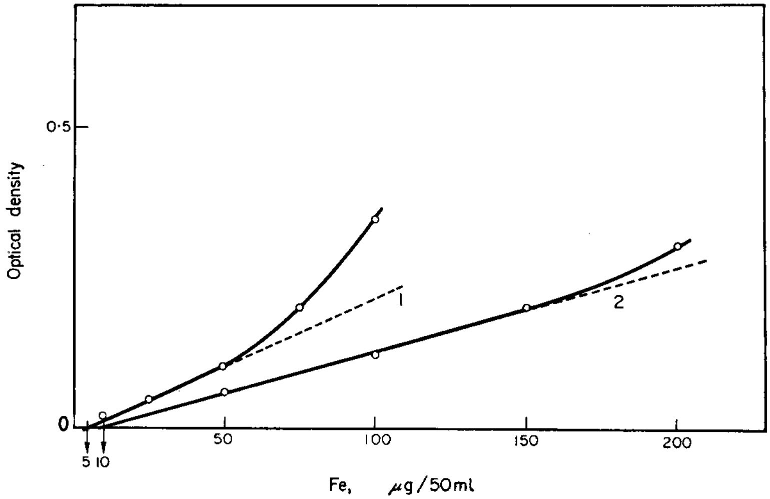

FIG. 2.—Dependence of extinction of ferroïn on initial concentration of iron, after static sorption on silica (1 g): 1. 0·5–0·3 mm. 2. 0·3–0·2 mm.

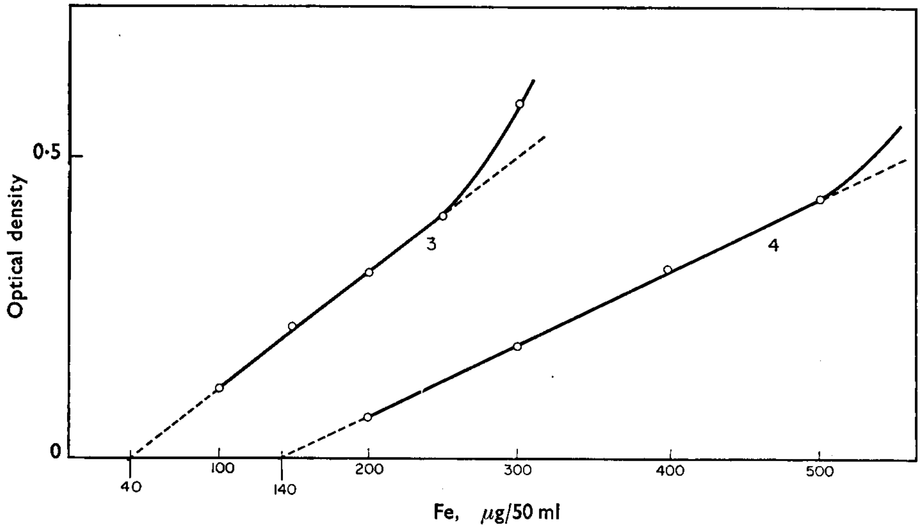

FIG. 2a.—Dependence of extinction of ferroïn on initial concentration of iron, after static sorption on silica (1 g): 1. 0·2–0·12 mm. 2. 0·12–0·08 mm.

After 15 min of vigorous shaking (shaking machine), equilibrium was established in all cases. Silica was separated and the filtrate diluted to 50 ml with water. The optical density of ferroïn remaining in solution was measured at 510 mμ in 5-cm cells.

Results obtained for the range of sizes of silica used are given graphically in Fig. 2 and 2a. Amounts of unsorbed ferroïn (A) are plotted against the original concentrations of iron. The capacity of the column (the amount of sorbed iron in the form of ferroïn/1 g of silica) was determined by extrapolation to zero optical density of ferroïn (point of intersection of the curves with the ordinates in Figs. 2 and 2a). The effect of the particle size of the silica on the sorption of ferroïn is evident from Fig. 3. The curve is seen to be hyperbolical, which is in good agreement with the relationship to be expected for the effect of size of particles on their absorption capacity. The capacity of the silica increases rapidly with decreasing particle size; however, the resistance of the columns increases too because these are filled with very fine fractions of silica. Particle size of silica of 0·3–0·2 mm is quite sufficient for quantitative sorption of ferroïn used for separation and determination of traces of iron. This fraction, even in a column 5 cm long, has a low resistance. Under static conditions it is possible to use any one of the fractions of silica.

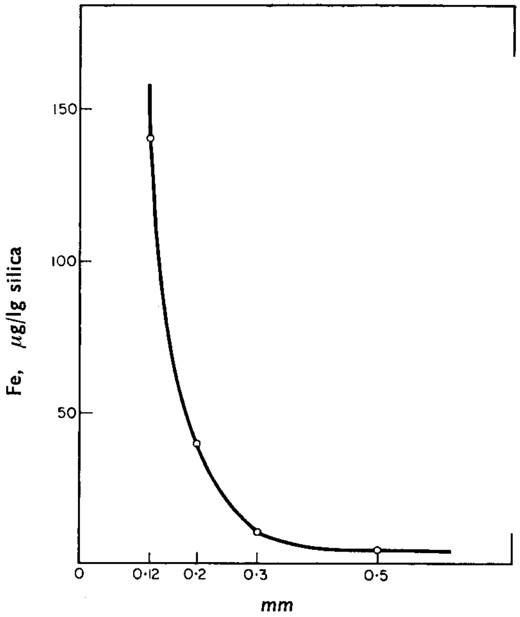

FIG. 3.—Influence of particle size of silica on its sorption capacity for ferroïn (μg of iron/g of silica).

Influence of pore size on sorption of ferroïn

Sorption of ferroïn was studied on several types of silica, specially prepared for chromatography.[5] The silica employed was homogeneous with the pore size 32, 65, 85 and 150 Å, granulated to 0·12–0·20 mm. It was found that all of these fractions were satisfactory, with the exception of that with the pore size 150 Å. On this form of silica sorption of ferroïn is extremely small. Sorption capacity (against ferroïn) of the remaining forms is higher than of the "desiccator" silica, which was used in this work. As special attention was paid to the sorption of μg quantities of ferroïn, for this purpose it was quite sufficient to use even silica of low capacity (it need not be homogeneous). It was, however, necessary to use silica of pore size in the range 30–90 Å.

Desorption of ferroïn with potassium iodide solution

For the desorption of ferroïn sorbed on silica, an alkaline solution of potassium iodide was found to be the best reagent. Desorption takes place because of the formation of the ion-association complex [Fe(phen)$_3^{2+}$, 2I$^-$], which is formed at high concentrations of iodide[2] and has been previously employed for the separation of ferroïn by extraction with chloroform.[2,7] The desorption effect of the potassium iodide solution depends on a number of factors, such as pH, concentration and purity of the solution used. Desorption starts at pH 6, but at pH 9 it is so effective that the elution increases with increasing potassium iodide concentration. As a solvent for potassium iodide (or sodium iodide) it is possible to use with equal effect a mixture of water and methanol or pure methanol instead of water alone. Further details are given later in this paper.

Results obtained showed that 15–20% potassium iodide or sodium iodide solutions made alkaline with aqueous ammonia to *ca.* pH 11 are best for the elution of ferroïn from silica [1 ml of aqueous ammonia (1:1)/per 50 ml of the solution]. Under the conditions described it is possible to desorb μg quantities of sorbed ferroïn using 20 ml of potassium iodide solution. In this way iron could be concentrated and the sensitivity of the final colorimetric determination thus increased.

The pH of alkaline (not buffered) potassium iodide solution decreases during the desorption of ferroïn, nevertheless the pH of the eluate must be adjusted to remain below 9·5. When the complex of ferroïn with iodide ions is formed the sorption maximum of ferroïn shifts a little (from 510 to 505 mμ) and the extinction coefficient increases, and this must be kept in mind during the colorimetric determination. The effect of the sodium iodide concentration on the value of the extinction coefficient of ferroïn is given in Fig. 4. In the interval of pH range where ferroïn is completely stable, namely 1·5–9·5, the colour intensity of ferroïn is practically unchanged even in the presence of alkali iodide.

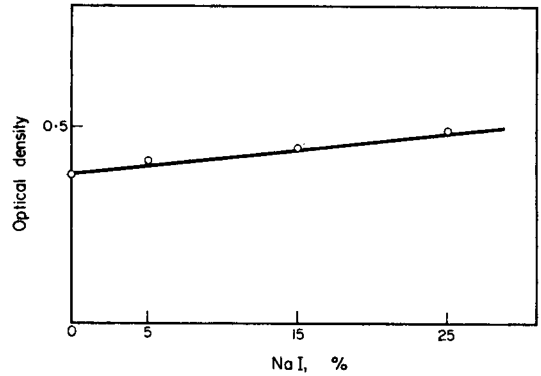

FIG. 4.—Dependence of extinction of ferroïn on sodium iodide concentration (2 ml of $1{\cdot}82 \times 10^{-4}M$ iron^{III} chloride; 5 ml of 10% hydroxylamine hydrochloride; 1 ml of $0{\cdot}1M$ 1,10-phenanthroline; pH 7; 0–25% sodium iodide; volume of 25 ml; 5-cm cell; 505 mμ)

The concentration of traces of iron

Microgram quantities of ferroïn were quantitatively sorbed on silica, even from relatively large volumes of sample solutions. After elution with a small volume of potassium iodide solution, the smallest amounts of iron could be determined without previous concentration.

The results of the determination of iron after its sorption as ferroïn from a volume of 500 ml are given in Table I.

TABLE I.—SORPTION OF FERROÏN FROM A VOLUME OF 500 ml

Iron taken, μg	Iron found, μg	Rel. error, %
5·09	4·88	−4·0
10·19	10·27	+1·0
30·57	30·32	−0·8
50·25	49·85	−2·0

Experiments were carried out in the following manner: 1–5 ml of $1{\cdot}82 \times 10^{-4}M$ iron^{III} chloride solution were diluted with twice-distilled water to a volume of *ca.* 500 ml, and 5 ml of 10% hydroxylamine hydrochloride and 5 ml of $0{\cdot}1M$ 1,10-phenanthroline solutions were added. After adjusting the pH to *ca.* 3, the solution was heated to 50°, then after cooling to room temperature the resulting ferroïn was sorbed on a silica column (diameter 12 mm, height 50 mm, pore size 0·2–0·3 mm) using a flow rate of 3 ml/min. After elution, the column was washed with 25 ml of water and ferroïn was desorbed using 25 ml of an aqueous solution of 15% potassium iodide made alkaline with 1 ml of aqueous ammonia (1:1). The pH of the "ferroïn iodide" solution was finally adjusted to a value below 9·5. The optical density was measured and the results were compared with a calibration curve, obtained under similar conditions.

The procedure has been used for the determination of iron in samples of water containing down to 0·02 mg of iron/litre. It has also been used for the determination of iron in solutions of alkali and alkaline-earth metals, and in solutions of other substances which do not contain ions interfering in the determination of iron as ferroïn. When ferroïn was sorbed from solutions of high ionic strength, the depth of the silica layer was increased to 10 cm.

Masking of interfering elements with EDTA *and citric acid*

The colorimetric determination of iron with 1,10-phenanthroline is affected by a number of metals. Thus, some metals form relatively stable complexes with 1,10-phenanthroline and at higher concentrations they prevent the reaction of iron with the reagent. Complexes are formed which are stable in water, for example, with cobalt, copper, nickel and zinc, and insoluble complexes are formed with cadmium, mercury and silver. Other metal ions can interfere because their salts readily hydrolyse, for example, those of bismuth, titanium, antimony, tin, *etc.* The interference of many of these metals was eliminated by forming stable complexes with EDTA or citric acid. Both of these reagents under suitable pH conditions do not influence the determination of iron even when present in large excess (EDTA: pH 7–8; citric acid: *ca.* pH 3).

Using EDTA relatively high concentrations of zinc, cadmium, nickel, chromium, bismuth, *etc.*, have been masked and with citric acid antimony, tin, molybdenum and tungsten. The ferroïn need not be concentrated in such cases when interfering elements form colourless complexes and when the concentration of iron is higher than $1 \times 10^{-4}\%$. In this way traces of iron in zinc and cadmium metals can be determined using EDTA as a masking agent.[8] For determination of traces of iron in the presence of a large concentration of coloured ions or colour complex-forming reagents, ferroïn must be separated. An alternative method is to extract the complex formed with ClO_4^-[9] or I^-[2] into chloroform. However, it is not possible to concentrate the ferroïn sufficiently. In extreme cases, when the coloured ion is bound as a colourless complex (copper screened with thioglycollic acid), separation need not be done; for instance, the determination of traces of iron in electrolytic copper.[10]

Metal complexes of EDTA and citric acid are not sorbed on silica at the pH values used and therefore do not interfere with the sorption of ferroïn.[1] This technique has been used for the concentration of iron in the form of ferroïn in the presence of high concentrations of some interfering metals and particularly for the separation of ferroïn from coloured solutions. Some analytical applications are given below for the determination of trace quantities of iron in certain metals or in their salts.

Determination of traces of iron in metallic nickel and chromium or in their salts

Large quantities of nickel and chromium are masked with EDTA and do not interfere with the determination of iron. Nickel ions interfere by the formation of a relatively stable complex with phenanthroline. On the other hand, chromium, which hardly reacts at all with phenanthroline, interferes by having a coloured hydrate and because of its ease of hydrolysis. For the screening of both these matals at pH 7–8 the mere addition of molecular equivalents of EDTA is sufficient, but in the case of chromium^{III} it is necessary to boil with EDTA in an acidic medium in order to complex the metal ion quantitatively. For very high chromium concentrations a small fraction of the metal ion remains during this process in the form of the blue hydroxocomplex, $CrOH^{2+}$ or $Cr(OH)_2^+$, which are also sorbed on silica. Fortunately, these species are not desorbed by potassium iodide solution and therefore do not interfere with the determination of iron.

Elution of ferroïn after its sorption in the presence of EDTA must be carried out only with an alkaline mixture of potassium iodide and methanol. So far we have been unable to explain this effect.

Procedure: To 20 ml of the solution containing *ca.* 1g of nickel or chromium^{III} add 20 ml of 1*M* EDTA. For chromium, adjust the pH of the solution to 4·5, boil for 15 min and after cooling the solution adjust the pH to 7·5–8·0; in the case of nickel, simply adjust the pH to 7·5–8·0. After adding 3 ml of 10% hydroxylamine hydrochloride solution (pH 7·5) and 1 ml of 0·1*M* phenanthroline solution, dilute with water to 50 ml and finally pass the solution through a silica column. Elute the sorbed ferroïn with 25 ml of potassium iodide solution [7% in a mixture of methanol and water (1:1) made alkaline with 1 ml of aqueous ammonia (1:1)]. After finally adjusting the pH to *ca.* 9, measure the optical density of the ferroïn solution (505 mμ, 5-cm cells). Calculate the iron content using a calibration curve prepared under similar conditions. Wash the small quantity of the blue hydroxocomplex of chromium^{III} from the silica column with dil. hydrochloric acid solution.

The results given in Table II were obtained by employing the method of standard addition.

Table II.—Determination of traces of iron in the presence of chromium and nickel.

Taken		Iron found, μg	Rel. error, %
Metal, g	Fe, μg		
1·05 Cr	10·19	10·93	+7·3
1·05 Cr	30·57	29·20	−4·5
1·05 Cr	50·95	50·39	−1·1
1·20 Ni	10·19	10·39	+1·9
1·20 Ni	30·57	29·35	−4·1
1·20 Ni	50·95	51·45	+1·0

Determination of traces of iron in metallic molybdenum and tungsten and their salts

In this case large quantities of WO_4^{-2} and MoO_4^{-2} (1 g/50 ml) are screened with citric acid at *ca.* pH 3·5. Interference from these ions may be explained by the formation of slightly soluble complexes with 1,10-phenanthroline. Under the conditions described ferroïn is sorbed quantitatively on silica and the citrates of tungsten and molybdenum pass through the column.

Procedure: To 20 ml of the solution of WO_4^{-2} and MoO_4^{-2} ions, containing *ca.* 1·5 g of W or Mo add 35 ml of 25% sodium citrate solution (pH 3·5) and 5 ml of 10% hydroxylamine hydrochloride solution and adjust the pH to 3·5–4·0. Add 1 ml of 0·1*M* phenanthroline solution and pass the resulting solution through the silica column, previously washed with 25 ml of 2·5% sodium citrate solution (pH 3·5). Extract the sorbed ferroïn with 20 ml of an aqueous solution of 15% potassium iodide made alkaline with 1 ml of aqueous ammonia (1:1). Calculate the iron content using a calibration curve after measuring the separated ferroïn as in the previous procedure.

The method of analysis was verified by analysing synthetic samples using the method of standard addition (see Table III).

Table III.—Determination of traces of iron in the presence of tungsten and molybdenum.

Taken		Iron found, μg	Rel. error, %
Metal, g	Fe, μg		
1·4 W	10·19	10·04	−1·5
1·4 W	30·57	31·33	+2·5
1·4 W	50·95	49·42	−3·0
1·03 Mo	10·19	9·76	−4·2
1·03 Mo	30·57	31·52	+3·1
1·03 Mo	50.95	50·44	−1·0

The relatively high selectivity of the reaction of $iron^{II}$ with 1,10-phenanthroline and the favourable complex-forming properties of EDTA and citric acid, permit the determination of traces of iron in "pure" nickel, chromium, molybdenum and tungsten, and also in the salts of these metals, even in the presence of many other impurities. Using the procedures given above, $6·48 \times 10^{-3}\%$ of iron in $NiCO_3$ (reagent grade, Kahlbaum), $1·9 \times 10^{-2}\%$ of iron in $K_2Cr(SO_4)_2.12\,H_2O$ (pure), $6·6 \times 10^{-4}\%$ of iron in $(NH_4)_6Mo_7O_{24}.4H_2O$ (reagent grade) and $3·2 \times 10^{-3}\%$ of iron in $(NH_4)_2WO_4.2H_2O$ (reagent grade) were determined.

DISCUSSION

The procedures developed for the determination of traces of iron in nickel, chromium, molybdenum and tungsten can also be used for the determination of iron in other metals and their salts and in some non-ferrous alloys. In such cases, namely, when the metal ions do not interfere by forming complexes with 1,10-phenanthroline and there is no hydrolysis at high concentrations, neither EDTA nor citric acid need be used as masking agent, provided the pH > 2. Under these conditions (or in the case when the metal ion forms a colourless complex with EDTA or citric acid), it may be possible to use the sorption of ferroïn for the concentration of traces of iron from large volumes of a sample solution of relatively high ionic strength. Without any special modification of the standard procedure, it is possible to determine traces of iron in nickel, chromium, molybdenum and tungsten and in their salts, in alkali metals, alkaline-earths metals, rare-earth elements, beryllium, lead, aluminium, gallium, titanium, uranium, antimony, tin, thallium and zirconium and under certain conditions[8] even in zinc and cadmium.

As has already been shown, silica is employed for the sorption of cationic complexes under suitable conditions of acidity. The sorption of these complexes from solutions containing ammonia, aliphatic, aromatic and heterocyclic amines is now being studied in detail, especially in relation to the selectivity of the separation process for trace quantities of metals from solutions of high ionic strength. Some previous papers[11–13] dealing with the use of silica in inorganic analysis refer to the sorption of hydroxocomplexes of the type $[Me^{n}(OH)_{m}^{+(n-m)}]$ or the use of silica as a "filter" for colloidal hydroxides. Our results and those of other authors indicate that silica could take the role of a cation exchanger (complexes of anionic nature are not sorbed) with a marked physical sorption effect because of its large surface. This fact makes the exact explanation of the sorption process difficult and further systematic study is necessary as in the case of the sorption of zinc and copper, published recently by Kozawa.[14]

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Zusammenfassung—Die Sorption von Ferroin an Silica wurde studiert. Der Einfluss von pH, Volum, Ionenstärke, Fliessgeschwindigkeit, Granulationsgrad des Silica, Porengrösse und Anwesenheit von ÄDTE und Zitronensäure auf die Sorption wurde untersucht. Auf Grund der Befunde wurde eine Methode zur Bestimmung von Eisenspuren in Ni, Cr, Mo und W ausgearbeitet. Die Möglichkeiten für eine Anwendung von Silica zur Trennung von anderen Metallen wird diskutiert.

Résumé—Les auteurs ont étudié l'influence du pH, du volume, de la force ionique, du débit, de la granulométrie de la dimension des pores de la silice et de la présence d'ÉDTA et d'acide citrique sur l'adsorption de la ferroine sur la silice. En fonction des résultats obtenus une méthode a été mise au point pour le dosage de traces de fer dans Ni, Cr, Mo et W; les possibilités d'autres utilisations de la silice pour la séparation des métaux sont discutées.

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EXTRACTION OF THE CUPFERRON COMPLEX OF NIOBIUM

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Summary—The precipitation of the cupferron complex of niobium is well known, but the literature states that the extraction of the complex with an organic solvent is either not quantitative or suitable for separating only milligram amounts of niobium. The present work shows that under suitable conditions in sulphuric acid solution, chloroform extraction of the cupferron complex of niobium can be made quantitative. Less than 0.05% of the niobium remains in the acid layer. Non-extracted elements may be determined by any standard method.

AT the Westinghouse Research Laboratories experimental niobium alloys have been under study for some time and have required considerable analysis. The main problem in these analyses has been the separation of niobium before its impurities or alloying elements can be determined. Few extraction methods of separating niobium appear in the literature.

One separation of niobium is as its insoluble cupferron complex. Because of bulk and chances of occulsion, precipitation has little to recommend it over other separation methods. Many cupferron complexes can be extracted by chloroform, but Furman, Mason and Pekola,[2] without describing conditions, state that the niobium complex is only slightly soluble.

Steele[4] extracted up to 2 mg of niobium from uranium in 2·4–3·6*M* perchloric acid solution. When the extraction of 200 mg of niobium was attempted, niobium could not be quantitatively extracted with cupferron and chloroform from either perchloric or hydrochloric acid solution.

The present work shows that under suitable conditions in sulphuric acid solution, the extraction of niobium cupferrate with chloroform can be made quantitative. Non-extracted metals remain in the water layer and can be determined by a standard chemical or spectrographic method.

EXPERIMENTAL

Reagents

Mixed acid solution: Dissolve 1 g each of oxalic and tartaric acids in 80 ml of water, then add 20 ml of concentrated sulphuric acid.

Cupferron: 6 g in 100 ml of water.

Chloroform: Reagent grade.

Procedure

Solution of sample. Weigh 0·2 g of chips or powder into a platinum crucible. Heat over a Fisher burner until the metal is completely oxidised. Add 5 g of potassium bisulphate and fuse over an Argand burner until clear. Cool and dissolve the melt in 50 ml of mixed acid solution.

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Some highly alloyed samples may not oxidise readily when ignited. In this case add about 5 ml of hydrofluoric acid and a few drops of nitric acid. Add 2 ml of 9*M* sulphuric acid, evaporate to strong fumes of this acid, then add potassium bisulphate and fuse as described above.

Niobium metal, if fairly pure and finely powdered, will dissolve in fused ammonium bisulphate. This is an advantage when large quantities of potassium salts are not desirable.

Chloroform extraction. Transfer the solution to a 500-ml separatory funnel. Add 25 ml of cupferron solution and 25 ml of chloroform, and shake for 2 min. Discard the chloroform layer. Again add 25 ml each of cupferron and chloroform and shake. This should remove all niobium from a 0·2-g sample. Shake once with 10 ml of chloroform alone.

Drain the water layer into a beaker and evaporate until the organic matter begins to char. Add nitric acid, a few drops at a time, until the liquid is clear. (Do not use perchloric acid because potassium salts are present.)

Metals not extracted may now be determined by any standard method. Thus, aluminium was precipitated with ammonia solution and ignited to Al_2O_3. Calcium was precipitated as the oxalate and titrated with permanganate. Cobalt was determined electrolytically. Uranium was precipitated with ammonia solution and ignited to U_3O_8.

RESULTS AND DISCUSSION

Accuracy and precision

Pure niobium and another element were weighed and carried through the procedure. The results for known amounts of aluminium are reported in Table I. The data for aluminium, calcium, cobalt and uranium were analysed statistically by methods described by Youden[5] and fitted to the equation $y = a + bx$, where y is the amount found, x the amount taken, and a and b are the intercept and slope, respectively. In each case the intercept or blank was found not to differ significantly from zero, so the equation was simplified to $y = bx$. Values for the slope, b, and the standard deviation are shown in Table II. A value of unity for the slope indicates quantitative recovery. Within experimental error these recoveries are seen to be quantitative.

TABLE I.—ALUMINIUM IN NIOBIUM (0·2-g SAMPLES)

Al added, *mg*	Al found, *mg*	Error, *mg*
2·0	1·9	−0·1
5·1	5·2	+0·1
10·2	10·2	0
10·2	10·2	0
10·2	10·1	−0·1
20·6	20·5	−0·1
31·6	31·8	+0·2
99·8	99·4	−0·4

TABLE II.—NON-EXTRACTED METALS, STATISTICAL DATA

Element	Slope, b	95% Confidence interval	Std. dev., *mg*
Al	0·996	0·992–1·000	0·14
CaO	1·000	0·994–1·005	0·30
Co	1·002	0·999–1·004	0·13
U_3O_8	1·000	0·996–1·004	0·19

Other non-extracted elements

Results for several other metals not extracted by chloroform and cupferron appear in Table III. In each case a standard method was used for the final determination.

However, the metals could not be titrated with EDTA because the salt concentration was too high. The high sulphate concentration caused some trouble with the calcium, but it stayed in the water layer and was finally precipitated as oxalate. Oxalic acid was not used in the acid mix to dissolve the bisulphate melts containing calcium and uranium. Five ml of 30% hydrogen peroxide per 100 ml was substituted instead.

TABLE III.—OTHER NON-EXTRACTED METALS

Metal	Added, *mg*	Found, *mg*	Error, *mg*
Ni	20·0	19·8	−0·2
Ni	30·9	30·8	−0·1
Cr	8·7	8·6	−0·1
Cr	17·3	17·3	0
Mn	5·6	5·6	0
Mn	11·1	11·4	+0·3
Zn	54·2	54·8	+0·6
Zn	104·0	103·9	−0·1
Mg	6·4	6·5	+0·1
Mg	12·7	12·8	+0·1
In_2O_3	14·2	14·2	0
In_2O_3	28·4	28·3	−0·1
In_2O_3	71·0	70·8	−0·2

Completeness of niobium extraction

Most of the precipitates were checked spectrographically for niobium. After two extractions about 0·1 mg of niobium was found in the ignited precipitate. More extractions failed to remove the remaining niobium. Although 0·1 mg is insignificant in gravimetric and titrimetric work, it may be significant in trace analysis. The niobium from the chloroform layer was ignited and found to contain less than 0·01% of unextracted elements. Therefore the cupferron extraction under the conditions described here can be used to separate niobium from the elements of Tables II and III. These elements may then be determined chemically or spectrographically.

Partially extracted elements

Some results for partially extracted elements appear in Table IV. Tantalum is especially of interest because it occurs in most niobium minerals and many niobium alloys. Because about 90% of decigram amounts of tantalum is extracted, it is very probable that impurity amounts of tantalum will extract along with the niobium. When alloying amounts of tantalum are present, the procedure must be modified. For

TABLE IV.—METALS PARTIALLY EXTRACTED

Metal	Added, *mg*	Found in water layer, *mg*
Ta_2O_5	99·6	12·3
Ta_2O_5	200·2	17·5
Y_2O_3	55·2	49·9
Y_2O_3	101·5	89·6
Nd_2O_3	102·9	87·5
Nd_2O_3	205·7	174·5
Ga	14·4	0·4
Ga	28·8	0·3

instance, the remaining tantalum may be removed by hydrolysis after the wet ashing of organic matter. The extraction of tantalum with methyl isobutyl ketone as described by Milner and Edwards[3] may also be used. Furman and coworkers[2] and Baudisch and Furst[1] stated that neodymium cupferrate is insoluble in chloroform. This work shows that neodymium and yttrium are partially extracted.

Elements extracted along with niobium

Furman and coworkers[2] stated that iron^{III}, tin^{IV}, titanium and vanadium are quantitatively extracted by cupferron and chloroform. Zirconium is also completely extracted. A few tests showed that iron^{II} is oxidised and almost completely extracted.*

Of particular interest was vanadium. Tests showed that only about 0·1 mg out of 0·1 g is left in the water layer. Thus a separation of either vanadium^{IV} or vanadium^{V} from chromium^{III} is possible. In these laboratories chromium and vanadium are both determined by oxidation with persulphate and titration with iron^{II} sulphate.

Extractions from hydrochloric and perchloric acids

Because lead, barium and strontium form insoluble sulphates, it was hoped that another acid could be substituted for the sulphuric. Unfortunately niobium is not completely extracted from either perchloric or hydrochloric acid. Nitric acid reacts with cupferron.

Acknowledgment—The statistical work was performed by Mrs. Caroline Shaffer of these laboratories. Part of the work was supported by a contract with the United States Air Force.

Zusammenfassung—Die Fällung des Cupferronkomplexes von Niob ist wohlbekannt, aber laut Literaturangaben verläuft die Extraktion des Komplexes mit organischen Lösungsmitteln entweder nicht quantitativ, oder es lassen sich höchstens Milligramm-Mengen Niob abtrennen. Es wird gezeigt, daß sich der Niob–Cupferron-Komplex unter geeigneten Bedingungen aus schwefelsaurer Lösung mit Chloroform quantitativ extrahieren laßt. Weniger als 0,05% des Niob verbleiben in der sauren Phase. Nicht extrahierte Elemente können nach üblichen Methoden bestimmt werden.

Résumé—La précipitation du complexe du cupferron et du nobium est bien connue, mais la littérature indique que l'extraction du complexe par un solvant organique n'est pas quantitative et ne convient pas pour séparer des quantités de nobium de l'ordre du mg. Cet article montre que dans des conditions convenables en milieu sulfurique l'extraction par le chlorofomre du complexe cupferron–nobium peut devenir quantitative. Ilne reste dans la couche acide que des quantités de nobium inférieures à 0,05%. Les éléments non extraits peuvent être dosés par une méthode standard.

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* No work was carried out on the cupferron extraction of molybdenum or tungsten, but both are probably extracted, at least partially.

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COPRECIPITATION WITH URANIUM^{IV} OXALATE

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Summary—The coprecipitation of cerium^{III} with uranium^{IV} oxalate is studied using dimethyl oxalate to precipitate uranium^{IV} from homogeneous solution. A limited study is also made using scandium^{III} and uranium^{IV}. These systems obey the logarithmic distribution law more closely than the homogeneous distribution law. The distribution coefficient is found to be functionally related to the experimentally determined first-order precipitation rate constants when a *trace* quantity of cerium^{III} is coprecipitated with *carrier* uranium^{IV} oxalate. The coefficient λ is found to be equal to K_T/K_C where K_T, the fractional rate of precipitation of tracer, is determined in the presence of the carrier. The cerium^{III}-uranium^{IV} oxalate system obeys a distribution law modified to include ion charge rather than the unmodified Doerner-Hoskins logarithmic distribution law.

DOERNER and Hoskins[1] and Henderson and Kracek[2] have derived expressions describing the crystal-solution distribution of a trace component. Both expressions were based on equilibrium assumptions, and both predict a distribution coefficient whose value should be constant under many experimental conditions.

Many investigators[3,4,5] have obtained coprecipitation data which obeyed the Doerner-Hoskins distribution expression, *i.e.*, yielded a constant value for the distribution coefficient λ. However, if the experimental conditions were altered, the data obeyed the Doerner-Hoskins expression, but with an entirely different value of λ.[5] These variations in the value of the distribution coefficient are not predicted by the Doerner-Hoskins expression, and consequently one of the aims of the present investigation was to gain some insight as to the reason for these discrepancies.

In the present work, the technique of precipitation from homogeneous solution was employed in the study of the coprecipitation of scandium^{III} and cerium^{III} individually with uranium^{IV} oxalate hexahydrate. Dimethyl oxalate, which hydrolyses slowly in acid solution to yield oxalic acid, was the reagent chosen for the precipitation of uranium^{IV} oxalate.

EXPERIMENTAL

Reagents

All chemicals were reagent grade.

Stock uranium solution: Prepared by dissolving 36·71 g of uranium^{VI} acetate in 2 litres of water containing 60 ml of concentrated hydrochrloric acid and standardised gravimetrically by aqueous ammonia precipitation as the diuranate followed by subsequent ignition to the oxide.[6]

Stock cerium solution: Prepared by reacting 2·7057 g of cerium^{IV} ammonium nitrate,

$$(NH_4)_2Ce(NO_3)_6,$$

with excess hydrochloric acid. The product (cerium^{III} chloride) was diluted to volume in a 1000-ml volumetric flask.

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Dimethyl oxalate: Purified by recrystallisation from methyl alcohol; potentiometric titration with alcoholic sodium hydroxide indicated that the recrystallised product contained less than 0·66% free oxalic acid.

Scandium-46 (85 *day half-life*): Obtained from Oak Ridge National Laboratory as scandium^{III} chloride in hydrochloric acid solution. A stock solution was prepared so that 1 μl of solution contained $1{\cdot}4 \times 10^{-4}$ microcurie of scandium-46.

Cerium-144 (290 *day half-life*): Obtained from Oak Ridge National Laboratory as cerium^{III} chloride in hydrochloric acid solution. A stock solution was prepared so that 1 μl of solution contained $7{\cdot}2 \times 10^{-2}$ microcurie of cerium-144.

Apparatus

Radio-tracers were added to the precipitation vessels by means of a Nuclear Ohio, Inc., Cleveland, Ohio, automatic pipettor.

Radio-tracer measurements were made with a high-voltage stabilised gamma-ray spectrometer.

A Beckman, model DU, spectrophotometer equipped with a photomultiplier tube was used for all colorimetric work.

Procedure

All preparatory work was conducted in a glove-box under a nitrogen atmosphere in order to prevent air oxidation of uranium^{IV} to uranium^{VI}.

An aliquot of the stock uranium^{VI} solution was electrolytically reduced to uranium^{IV} at a mercury cathode. The reduced solution was brought to the desired pH with dilute hydrochloric acid, then filtered through a fine porosity glass frit. A weighed amount of dimethyl oxalate was added and aliquots of the resultant solution were pipetted into the reaction vessels described by Gordon and Rowley.[7] Each of these vessels would contain a specific amount of radio-tracer (either scandium-46 or cerium-144) added prior to the addition of uranium. The vessels were then flushed with nitrogen for 30 sec, stoppered, and mechanically agitated in a constant temperature bath at 25° ± 0·5°.

Individual reaction vessels were removed at various time intervals and precipitate and filtrate separated by centrifugation. Both precipitate and filtrate were treated with concentrated nitric acid and analysed for uranium and the trace component. Uranium was determined colorimetrically according to the method of Francois[8] and scandium-46 or cerium-144 by scintillation techniques.

RESULTS AND DISCUSSION

Coprecipitation of scandium

The results of the study of the coprecipitation of scandium^{III} with uranium^{IV} oxalate are summarised in Table I. The distribution coefficient λ was calculated from the Doerner-Hoskins distribution expression

$$\lambda = \frac{\log (T_i/T_f)}{\log (A_i/A_f)} \tag{1}$$

and D was calculated from the Henderson-Kracek distribution expression

$$D = \frac{(T/A)_{\text{crystal}}}{(T/A)_{\text{solution}}} \tag{2}$$

where T represents the concentration of trace species, A represents the concentration of carrier species, and i and f refer to initial and final solution concentrations respectively. (The significance of λ' and D′ which appear in Table I and in the tables following it will be discussed later.) It is apparent from Table I that neither λ nor D is constant, *i.e.*, both coefficients vary inversely with the fraction of carrier precipitated. However, the variation is less pronounced in the values of λ.

Coprecipitation of cerium

The results of the study of the coprecipitation of cerium^{III} with uranium^{IV} oxalate are summarised in Table II. The values of λ show some scatter but are essentially constant whereas the values of D exhibit a definite trend.

TABLE I.—COPRECIPITATION OF SCANDIUM WITH URANIUM^{IV} OXALATE.

Initial [U] = $2{\cdot}52 \times 10^{-3}M$
Initial [Sc] = $1{\cdot}9 \times 10^{-7}M$
Initial [$(CH_3)_2C_2O_4$] = $8{\cdot}5 \times 10^{-2}M$
Initial pH = 1·0

Time, *min*	U pptd., %	Sc pptd., %	$\lambda \times 10^2$	D $\times 10^2$	λ', $\left(\frac{litres}{mole}\right)^{\frac{1}{2}}$	D', $\left(\frac{litres}{mole}\right)^{\frac{1}{2}}$
375	27·7	2·09	6·4	5·6	0·30	0·26
383	43·3	3·08	5·6	4·2	0·26	0·21
389	45·0	4·59	7·8	5·9	0·39	0·30
395	47·8	4·81	7·5	5·5	0·37	0·29
412	51·0	3·27	4·7	3·3	0·22	0·17
431	54·1	3·62	4·8	3·2	0·23	0·16
451	57·0	3·24	4·0	2·5	0·20	0·137
526	59·6	2·85	3·2	2·0	0·156	0·109
470	60·1	3·24	3·6	2·2	0·184	0·123
487	63·3	3·59	3·6	2·2	0·184	0·123
555	64·4	2·98	3·0	1·7	0·150	0·097
585	67·7	2·90	2·6	1·4	0·132	0·083
616	70·5	2·96	2·4	1·3	0·127	0·076
645	73·6	3·06	2·4	1·1	0·127	0·069
636	73·8	3·36	2·6	1·2	0·132	0·076
683	78·8	3·53	2·3	1·0	0·127	0·063
728	90·5	5·27	2·3	0·58	0·138	0·046
800	94·7	5·90	2·1	0·35	0·132	0·032
876	96·9	6·29	1·9	0·22	0·127	0·023
1099	97·5	6·68	1·9	0·18	0·127	0·020
950	97·7	6·33	1·7	0·16	0·121	0·018
1026	97·9	6·51	1·8	0·15	0·121	0·018

TABLE II.—COPRECIPITATION OF CERIUM WITH URANIUM^{IV} OXALATE.

Initial [U] = $2{\cdot}52 \times 10^{-3}M$
Initial [Ce] = $1{\cdot}7 \times 10^{-10}M$
Initial [$(CH_3)_2C_2O_4$] = $8{\cdot}5 \times 10^{-2}M$
Initial pH = 1·0

Time, *min*	U pptd., %	Ce pptd., %	λ^a	D	λ'^b, $\left(\frac{litres}{mole}\right)$	D'^{c}, $\left(\frac{litres}{mole}\right)^{\frac{1}{2}}$
358	28·3	7·28	0·23	0·20	1·04	0·95
347	39·1	6·18	0·13	0·10	0·62	0·51
379	52·1	12·8	0·18	0·13	0·90	0·71
453	53·1	11·3	0·16	0·11	0·77	0·60
401	55·7	13·7	0·18	0·13	0·89	0·68
527	76·6	17·7	0·13	0·066	0·70	0·42
617	83·8	21·9	0·13	0·054	0·74	0·37
750	86·4	23·0	0·13	0·047	0·73	0·34
1585	94·3	52·6	0·26	0·067	1·62	0·60
1462	94·6	48·5	0·23	0·053	1·43	0·49
834	94·7	35·2	0·15	0·030	0·92	0·27
1463	96·6	51·6	0·22	0·038	1·41	0·38

[a] mean = 0·18 ± 0·04.
[b] mean = 0·98 ± 0·26.
[c] mean = 0·53 ± 0·16.

Kinetic aspects of coprecipitation

(1) *Effect of seeding:* Hermann[5] has shown that the value of the distribution coefficient λ is a function of "the fractional rate of precipitation of carrier", *i.e.*, the fraction of carrier precipitated per unit time. From his work and that of others,[3,4] it can be concluded that

$$\lambda \propto k, \text{ for derichment systems } (\lambda < 1)$$

$$\text{and } \lambda \propto 1/k, \text{ for enrichment systems } (\lambda > 1)$$

where k is the fractional rate of precipitation of carrier. In order to obtain the value of k for a particular experiment, Hermann, and subsequently Cohen and Gordon,[4] plotted the logarithm of carrier concentration in solution versus time, *i.e.*, a first-order kinetic plot, and obtained a straight line. The slope of the line is k, the fraction of carrier precipitated per unit time. A plot for the precipitation of uranium, utilising the data of Table II, is shown in Fig. 1. The value of k, the slope, is —2·9 × 10^{-1} hr^{-1}.

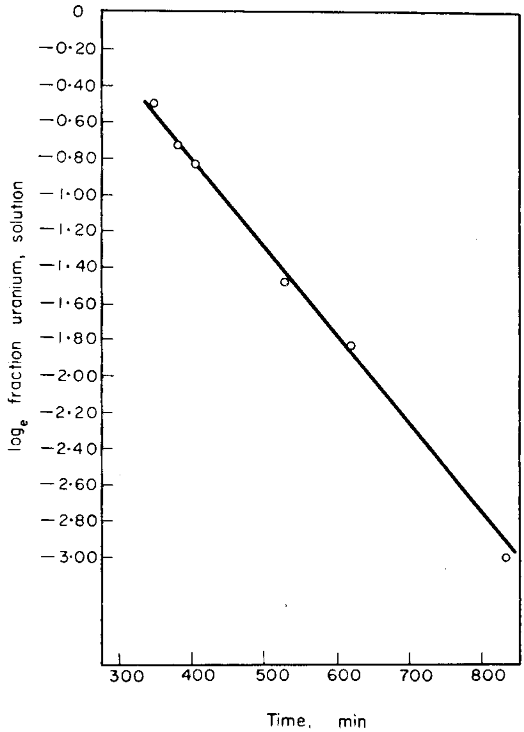

FIG. 1.—Precipitation of uranium^{IV} as oxalate.

Because k is constant, λ should also be constant, providing $\lambda \propto$ k. This is the case for cerium (*cf.* Table II) but not for scandium (*cf.* Table I). The difference in the behaviour of the two systems can be partially explained by assuming that a large degree of supersaturation exists before precipitation occurs. (This was shown in other cases, *e.g.*, the precipitation of silver chloride from homogeneous solution by Klein *et al.*[9]) If the initial formation of precipitate takes place in a highly supersaturated medium, then it is quite likely that the *initial* fractional rate of precipitation is *greater* than the fractional rate of precipitation during the remainder of the precipitation process. Consequently, a larger degree of coprecipitation will take place upon the initial formation of precipitate in derichment systems. The resultant increase in initial coprecipitation would be more readily observed in systems whose distribution coefficients are small, *i.e.*, considerably less than 0·1, as is the case for scandium, than for systems such as cerium where λ is closer to unity.

TABLE III.—COPRECIPITATION OF SCANDIUM IN THE PRESENCE OF ADDED CARRIER. Initial concentrations as in Table I

Time, *min*	Nature of pre-formed carrier[a]	U pptd., %	Sc pptd., %	$\lambda \times 10^2$[b]	D × 10^2[c]
378	B	36·3	1·38	3·1	2·4
388	B	37·7	1·36	2·9	2·2
369	C	46·0	2·14	3·5	2·5
446	B	47·5	1·52	2·3	1·7
400	B	47·8	1·45	2·4	1·6
384	C	49·0	1·35	2·1	1·3
408	A	52·6	1·39	1·9	1·2
426	C	56·8	1·76	2·1	1·3
554	B	60·9	2·01	2·1	1·3
508	A	67·3	1·46	1·3	0·68
650	B	67·6	2·36	2·1	1·1
600	A	77·5	1·87	1·3	0·52
590	C	79·6	3·03	1·9	0·77
654	A	82·2	1·70	1·0	0·36
712	A	85·6	3·00	1·6	0·50
686	C	88·9	3·52	1·6	0·44
830	B	91·9	1·96	0·89	0·24
815	A	92·2	2·35	0·93	0·19
1463	C	94·1	5·74	2·1	0·36
1385	B	98·1	3·32	0·84	0·065

[a] A—crystal aggregates formed with no stirring, B—completely formed crystals, C—newly formed crystals with incomplete faces.

[b] mean = 1·9 ± 0·6.

[c] mean = 1·0 ± 0·6.

If the above assumption is valid, then seeding the solution with carrier crystals should reduce or eliminate the initially large supersaturation. The fractional rate of precipitation should now be nearly constant throughout the *entire* precipitation process and hence a less variable distribution coefficient should be obtained.

Experiments were carried out with seeded solutions utilising the identical procedure previously described except that approximately 0·07 mg of uranium^{IV} oxalate crystals were added in addition to the other reagents. Several different types of crystal were used, *e.g.*, small crystals with incomplete faces, completely formed crystals, and crystal aggregates.

The results using trace scandium are summarised in Table III. (The initial uranium concentration used in the calculations for λ was considered to be independent of the amount of uranium added as seed crystals.) It is evident that the values of λ show a great deal less variation than the values obtained in the unseeded experiments. The initial high coprecipitation is eliminated to a great extent lending support to the assumption made previously. As a further check on the assumption, an experiment was conducted wherein the seed crystals were generated *in situ*. The experimental conditions were identical except that the scandium was added to the solution *after* the start of precipitation. Thus, an initially large supersaturation would be relieved by the initial formation of precipitate in the absence of tracer. The results are summarised in Table IV. (In the calculations for λ, the initial uranium concentration was considered to be the concentration of uranium in the solution at the time of addition of scandium.) The average value of λ was found to be in good agreement with the value obtained in the direct seeding experiments.

(2) *Quantitative relationships:* Feibush *et al.*[3] derived an expression, identical to the Doerner-Hoskins expression, where the distribution coefficient λ is equal to the ratio of the rate constants for the precipitation of tracer and carrier, respectively. The expression was derived on a kinetic model with no equilibrium assumption being made. However, no work has been reported to date on the experimental verification of the Feibush derivation.

TABLE IV.—COPRECIPITATION OF SCANDIUM WITH "ADDED" CARRIER GENERATED *IN SITU*.

Initial conditions as in Table I

U pptd.[a], %	Sc pptd., %	$\lambda \times 10^2$ [b]	D × 10^2 [c]
41·0	1·33	2·4	0·82
54·2	1·15	1·5	0·53
64·4	1·96	1·9	0·59
72·6	1·27	1·0	0·26
91·2	3·90	1·6	0·24

[a] after the addition of tracer.
[b] mean = 1·7 ± 0·4.
[c] mean = 0·49 ± 0·2.

In order to check the validity of this derivation, two requirements must be fulfilled: (i) the data must fit the logarithmic distribution expression, and (ii) λ must equal the ratio of the precipitation rate constants of the two species. The first condition was achieved in the coprecipitation experiments with cerium.

To ascertain if the second condition was obeyed, the precipitation rate constant for the carrier species, k_C, was obtained from a plot of the logarithm of the uranium solution concentration versus time (*cf.* Fig. 1). In order to obtain k_T, the precipitation rate constant for the trace species, it was first decided to precipitate micro quantities of cerium^{IV} oxalate alone under experimental conditions identical to those used for uranium and obtain a value of k_T for different initial concentrations of cerium. A plot was then made of k_T versus the initial cerium concentration (*cf.* Fig. 2) from which an extrapolated value of k_T for the very small concentrations present during the coprecipitation studies would be obtained. However, the values were quite erratic at low concentrations and only an approximate value of k_T could be obtained, *i.e.* *ca.* $-3{\cdot}4 \times 10^{-1}$ hr^{-1}, which divided by the value of k_C, $-2{\cdot}9 \times 10^{-1}$ hr^{-1}, yielded a value of $\lambda = 1{\cdot}2$, not in agreement with the value of $\lambda = 0{\cdot}18$ obtained experimentally.

Obviously, this method, *i.e.* obtaining k_T by utilising different initial concentrations and extrapolating to the desired value of the initial concentration of the cerium, was not satisfactory. Before proceeding to determine k_T by another method, it seemed desirable to elucidate the observed relationship between the initial cerium concentration and the experimental rate constant.

The kinetic expression for the precipitation alone, of the cerium salt (or uranium), is probably of the following form:

$$-\frac{d[C]}{dt} = k_1[C]^x[C_2O_4{}^{2-}]^y\, S^z \tag{3}$$

where C is the carrier, k_1 is the true precipitation rate constant, S^z represents the dependence of precipitation on the surface area of the precipitate, and x, y and z can have any values. From the experiments by Hermann[5] and others[3,4] (*cf.* also Fig. 1) who have used precipitation from homogeneous solution, the expression reduces to

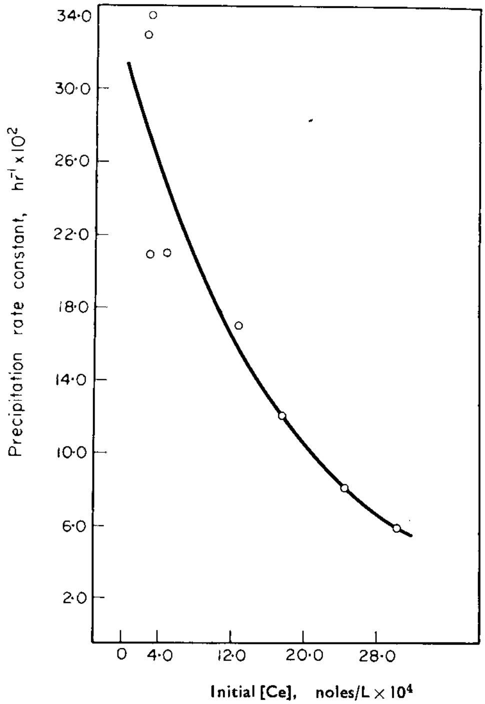

FIG. 2.—Precipitation rate constant as a function of initial cerium concentration.

$$-\frac{d[C]}{dt} = k[C] \tag{3a}$$

where $k = k_1k_2$ and $k_2 = [C_2O_4{}^{-2}]^y\, S^z$ for a given set of experimental conditions. However, when $[C]_i$, the initial concentration of carrier, is changed, it apparently has a profound effect on the value of k_2. For example, if $[C]_i$ is decreased, there is an observed increase in the induction time which proceeds actual precipitation, *i.e.*, a greater concentration of oxalate is required before precipitation begins; thus k_1k_2, the experimentally measured rate constant, must be increasing in value (*cf.* Fig. 2).

An approximate mathematical check of the above assumptions can be made as follows because:

$$\mathrm{k'_{measured}} = \mathrm{k_1k_2'} \tag{5}$$

$$\mathrm{k''_{measured}} = \mathrm{k_1k_2''} \tag{5a}$$

$$\left[\frac{\mathrm{k'}}{\mathrm{k''}}\right]_{\mathrm{measured}} = \frac{\mathrm{k_2'}}{\mathrm{k_2''}} = \frac{[\mathrm{C_2O_4}^{2-}]'}{[\mathrm{C_2O_4}^{2-}]''} \tag{6}$$

If we assume that the solubility product expression

$$[\mathrm{Ce}^{3+}]^2\,[\mathrm{C_2O_4}^{2-}]^3 = \mathrm{K_{sp}}$$

is approximately true *during* precipitation, then

$$[\mathrm{C_2O_4}^{2-}]' \cong \left(\frac{\mathrm{K_{sp}}}{[(\mathrm{Ce}^{3+})']^2}\right)^{\frac{1}{3}} \tag{7a}$$

$$[\mathrm{C_2O_4}^{2-}]'' \cong \left(\frac{\mathrm{K_{sp}}}{[(\mathrm{Ce}^{3+})'']^2}\right)^{\frac{1}{3}} \tag{7b}$$

so that

$$\frac{[\mathrm{C_2O_4}^{2-}]'}{[\mathrm{C_2O_4}^{2-}]''} \cong \left[\frac{(\mathrm{Ce}^{3+})''}{(\mathrm{Ce}^{3+})'}\right]^{\frac{2}{3}} \cong \left[\frac{\mathrm{k'}}{\mathrm{k''}}\right]_{\mathrm{measured}} \tag{8}$$

Thus, if the initial oxalate concentration needed for precipitation is approximately determined by the solubility product, then the measured rate constant ratio is functionally related to the initial cerium concentrations as follows

$$\left(\frac{\mathrm{k'}}{\mathrm{k''}}\right)_{\mathrm{measured}} \cong \left[\frac{(\mathrm{Ce}^{3+})''_{\mathrm{initial}}}{(\mathrm{Ce}^{3+})'_{\mathrm{initial}}}\right]^{\frac{2}{3}} \tag{9}$$

Several initial cerium concentrations were chosen from Fig. 2 and the corresponding values of k′/k″ were predicted using the above expression. These values are compared to the ratios found experimentally as shown in Table V; good agreement was obtained.

TABLE V.—A COMPARISON OF THE EXPERIMENTAL AND PREDICTED RATE CONSTANTS IN THE PRECIPITATION OF CERIUM$^{\mathrm{IV}}$ OXALATE.

$\frac{(\mathrm{Ce}^{3+})''_{\mathrm{initial}}}{(\mathrm{Ce}^{3+})'_{\mathrm{initial}}}$	Experimental[a] k′/k″	Predicted[b] k′/k″
12·0/20·0	0·7	0·7
8·0/28·0	0·3	0·4
12·0/28·0	0·4	0·6
8·0/12·0	0·8	0·8
4·0/28·0	0·3	0·3
4·0/12·0	0·7	0·5
20·0/28·0	0·6	0·8
8·0/20·0	0·5	0·5
4·0/20·0	0·4	0·3
4·0/8·0	0·8	0·6

[a] from Fig. 2.

[b] from equation (9).

The next procedure was to obtain the rate constant for the precipitation of tracer in the presence of carrier inasmuch as the extrapolated rate constant for the precipitation of cerium alone could not be correlated with the experimental values of λ and k_c. A plot was made of the logarithm of the cerium concentration (in the presence of uranium) versus time, and a straight line was obtained (*cf.* Fig. 3). The data for the plot were taken from Table II. The slope of the line, $-4\cdot5 \times 10^{-2}\,hr^{-1}$, divided by the rate constant for the precipitation of uranium, $-2\cdot9 \times 10^{-1}\,hr^{-1}$, is 0·15. This is in good agreement with the experimentally determined value of $\lambda = 0\cdot18$.

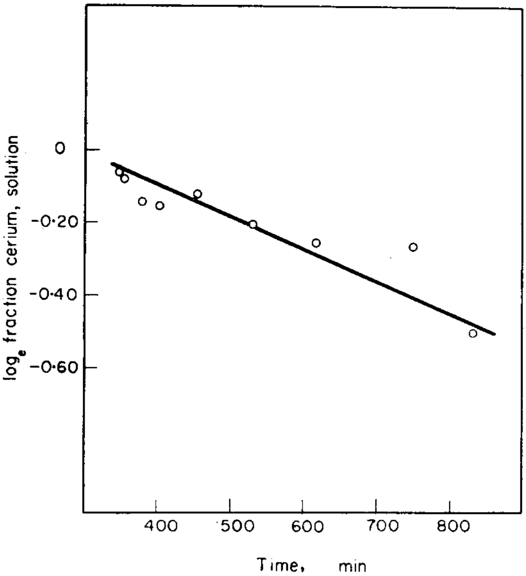

FIG. 3.—Precipitation of tracer cerium^{III} simultaneously with carrier uranium^{IV} oxalate.

Data obtained from Hermann's work were treated in a similar manner and good agreement was found between his experimental value of $\lambda = 1\cdot46$ and the value $\lambda = 1\cdot6$ calculated from the precipitation rate constants.

In the derivation of the Feibush equation there is an implication that the carrier and tracer precipitate by independent mechanisms. However, in the present investigation, inasmuch as the rate constants for the carrier and tracer were not obtained independently there may be a possibility of a mutual effect, *e.g.*, the carrier may impose its own precipitation mechanism on that of the tracer. Because different rate constants were obtained for cerium precipitated in the presence and in the absence of the carrier, there may be some interaction between the two precipitation mechanisms. In any event, the data seem to verify the general form of the Feibush equation, *i.e.*, $\lambda = k_T/k_c$, with the Doerner-Hoskins expression becoming

$$\log \frac{T_i}{T_f} = \frac{k_T}{k_C} \log \frac{C_i}{C_f} \tag{10}$$

only for first order kinetics, which seem quite often to be attained in precipitation from homogeneous solution.

Effect of ionic charge differences

Gordon[10] has modified the Doerner-Hoskins distribution expression for systems in which tracer and carrier have different ionic charges. For a system whose carrier (cation) charge is four and whose tracer (cation) charge is three, the equation assumes the following form

$$\log \frac{T_i}{T_f} = \lambda' \frac{4}{2 \cdot 303} \left(\frac{1}{V^{\frac{1}{4}}}\right) (A_i^{\frac{1}{4}} - A_f^{\frac{1}{4}}) \tag{11}$$

where V is the volume of solution.

Modified distribution coefficients, λ' and D′, were calculated for the experiments as shown in Tables I and II. The values are generally as consistent as are the unmodified coefficients.

Equation (11) indicated that the fraction of tracer precipitated is a function of the initial carrier concentration, whereas no such dependence is predicted from the unmodified Doerner-Hoskins relationship. Therefore, an experimental check on the validity of equation (11) would require two experiments with different initial carrier concentrations but with all other conditions being the same. However, as previously noted, a change in the initial carrier concentration results in a change in the observed fractional rate of precipitation and therefore a change in distribution coefficient. Consequently, in order to check equation (11) it is necessary to vary the initial carrier concentration *at the same time maintaining a constant distribution coefficient.*

Two different approaches were attempted. The first involved a series of coprecipitation experiments at various pH values. The conditions (except for pH) were identical to those summarised in Table II. The fractional rate of precipitation was obtained for each run and a plot made of the fractional rate of precipitation versus initial pH (*cf.* curve A of Fig. 4). Next, a series of experiments was performed at various initial uranium concentrations with the conditions again the same as those in Table II except for the initial uranium and dimethyl oxalate concentrations. (The latter were varied to maintain the mole ratio of dimethyl oxalate to uranium at the same value as in the previous pH experiments.) The fractional rates of precipitation were determined for each run and plotted as a function of initial uranium concentration, *cf.* curve B of Fig. 4. It can be seen from Fig. 4 that initial pH and uranium concentrations can be chosen so that two different experiments would have an identical fractional rate of precipitation but differing initial carrier concentrations, *i.e.*, the conditions necessary to validate equation (11).

Two experiments were performed with fractional rates of precipitation equal to $-2 \cdot 6 \times 10^{-1}$ hr^{-1}. The conditions and results are summarised in Tables VI and VII. Fig. 5, curve B, is a plot of the data from Table VII. If equation (11) holds, then the data from Table VI should fall on the predicted curve C of Fig. 5. As can be seen from Fig. 5, curve A, no such agreement was found.

The second approach was an attempt at keeping the fractional rate of precipitation constant as well as the initial supersaturation which may have been one of the uncontrollable factors in the first approach. An experiment was performed under the conditions of Table II except that cerium was added *after* the start of precipitation. In this manner the fractional rate of precipitation remained equal to that of the initial experiments (*cf.* Table II) owing to the fact that all of the possible rate-controlling variables, *e.g.*, pH, initial uranium and initial dimethyl oxalate concentrations, were

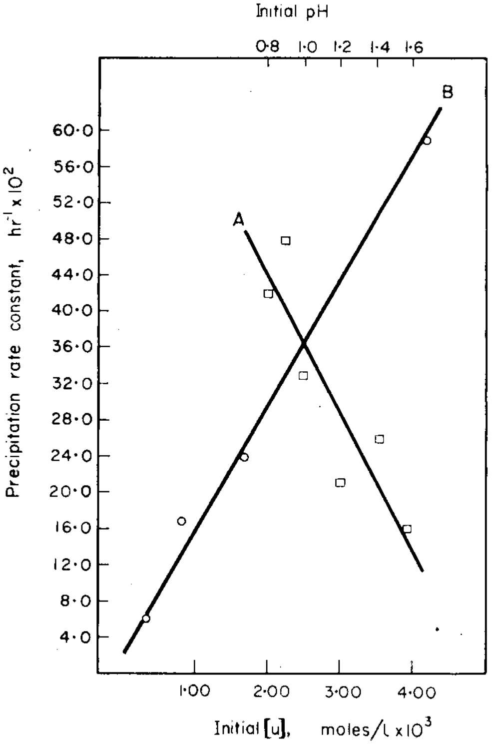

FIG. 4.—Precipitation rate constant as a function of:
A. initial pH,
B. initial uranium concentation.

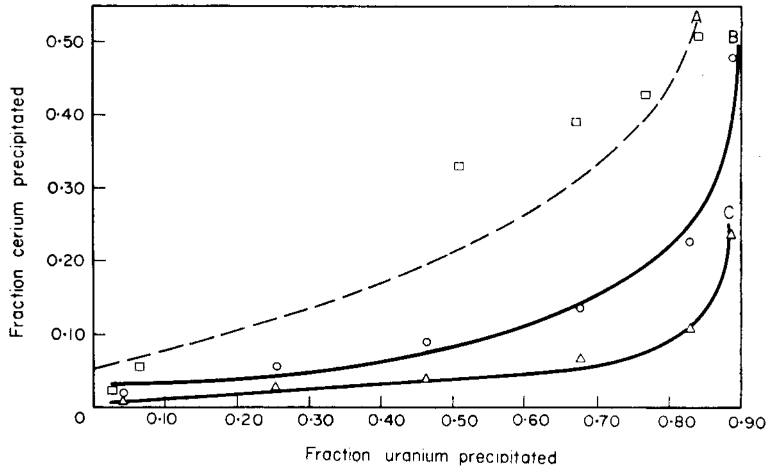

FIG. 5.—Coprecipitation of cerium with uranium^{IV} oxalate:
A. pH = 1·00[a],
B. initial pH = 1·27[b],
C. theoretical curve assuming the modified distribution law applies—conditions of curve A.

[a] Initial concentrations of uranium, dimethyl oxalate and cerium are two-thirds of the values given in Table II.

[b] Initial concentrations of uranium, dimethyl oxalate and cerium are as given in Table II.

TABLE VI.—COPRECIPITATION OF CERIUM WITH URANIUM^{IV} OXALATE[a,b].

Time, *min*	U pptd., %	Ce pptd., %	λ[c]	D[d]	λ'[e], $\left(\frac{litres}{mole}\right)^{\frac{1}{2}}$	D'[f], $\left(\frac{litres}{mole}\right)^{\frac{1}{2}}$
399	2·91	2·14	0·74	0·73	5·4	4·3
446	6·44	5·57	0·85	0·86	4·8	5·1
552	50·6	33·1	0·57	0·48	3·6	3·4
632	67·0	39·3	0·45	0·32	3·0	2·5
727	76·7	43·0	0·39	0·23	2·7	1·9
812	83·8	51·2	0·40	0·19	2·9	1·9

[a] Initial concentrations of uranium, dimethyl oxalate and cerium are two-thirds of the values given in Table II.
[b] initial pH = 1·00.
[c] mean = 0·57 ± 0·14.
[d] mean = 0·47 ± 0·22.
[e] mean = 3·7 ± 0·9.
[f] mean = 3·2 ± 1·1.

TABLE VII.—COPRECIPITATION OF CERIUM WITH URANIUM^{IV} OXALATE[a]

Time, *min*	U pptd., %	Ce pptd., %	λ[b]	D[c]	λ'[d], $\left(\frac{litres}{mole}\right)^{\frac{1}{2}}$	D'[e], $\left(\frac{litres}{mole}\right)^{\frac{1}{2}}$
323	3·93	1·35	0·35	0·33	0·87	1·5
376	26·1	5·92	0·20	0·18	0·96	0·83
433	46·2	9·44	0·16	0·12	0·77	0·62
572	67·5	13·9	0·13	0·078	0·68	0·45
677	82·9	22·9	0·15	0·061	0·83	0·42
796	88·5	47·8	0·30	0·12	1·7	0·89

[a] initial pH = 1·27.
[b] mean = 0·22 ± 0·08.
[c] mean = 0·15 ± 0·07.
[d] mean = 0·97 ± 0·24.
[e] mean = 0·78 ± 0·29.

TABLE VIII.—COPRECIPITATION OF CERIUM WITH URANIUM^{IV} OXALATE–CERIUM ADDED AFTER THE START OF PRECIPITATION.

Time, *min*	U pptd.[a], %	Ce pptd., %	λ[b]	$D \times 10^{3}$[c]	λ'[d], $\left(\frac{litres}{mole}\right)^{\frac{1}{2}}$	D'[e], $\left(\frac{litres}{mole}\right)^{\frac{1}{2}}$
785	49·1	7·27	0·111	5·6	0·89	0·049
818	56·4	9·56	0·121	6·0	0·97	0·056
849	63·2	11·6	0·123	6·5	1·07	0·060
876	67·3	13·8	0·133	6·9	1·12	0·067
948	84·4	18·6	0·110	4·2	1·05	0·051

[a] after addition of cerium; other initial concentrations as in Table II.
[b] mean = 0·120 ± 0·007.
[c] mean = 5·8 ± 0·8.
[d] mean = 1·02 ± 0·07.
[e] mean = 0·057 ± 0·006.

identical; further, the effect of initial supersaturation was eliminated by the delayed addition of tracer. The initial concentration of uranium now became the concentration of uranium present at the time of the addition of tracer. Thus, a study could be made of the coprecipitation of cerium at an invariant fractional rate of precipitation, but at different initial uranium concentrations, *i.e.*, a comparison with the data of Table II.

The results obtained with delayed addition of cerium are presented in Table VIII; here the tracer was added after about 88 % of the uranium had precipitated. When the tracer was added, the time was recorded and the vessels were reflushed with nitrogen and replaced in the constant temperature bath. In order to determine the initial uranium concentration (with respect to the addition of cerium), a plot was made of the "logarithm of the uranium concentration" versus time, and extrapolated to the time of addition of tracer (*cf.* Fig. 6).

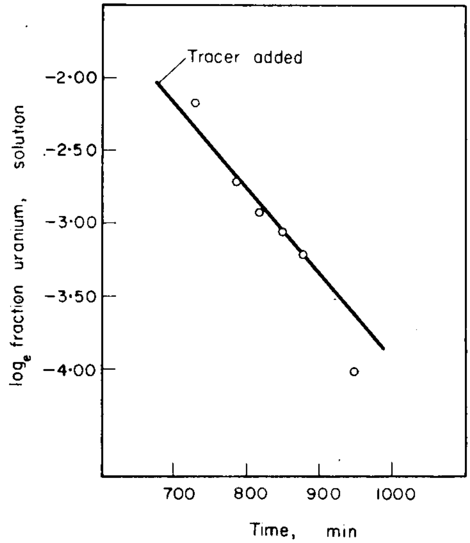

FIG. 6.—Determination of initial uranium concentration. (The first plotted point does not appear in Table VIII; because the sample was removed soon after the addition of tracer, the quantity of uranium precipitated was only 8 % so that the point was only used on the curve to assist in determining the initial uranium concentration but not used to ascertain the mean values given in Table VIII.)

If the modified distribution law is valid, then the values of λ' for each series of experiments (*cf.* Tables II and VIII) should be equal and there should be a shift in the fraction of cerium precipitated as a function of the fraction of uranium precipitated. As can be seen, the values of λ' are essentially equal, *i.e.*, 1·02 ± 0·07 and 0·98 ± 0·26 (litres-mole^{-1})$^{\frac{1}{2}}$, respectively, whereas the values of λ, 0·12 ± 0·01 and 0·18 ± 0·04, are appreciably different.

Fig. 7 shows the slight shift in the fraction of cerium precipitated; further, the experimental curve B agrees very closely with the predicted curve C. It appears, therefore, that the modified distribution equation is valid for the cerium^{III}-uranium^{IV} oxalate system under the experimental conditions used.

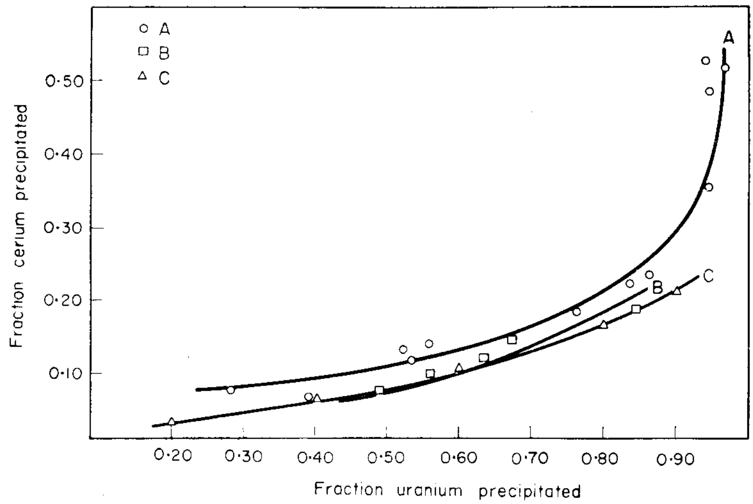

FIG. 7.—Fraction of cerium precipitated versus fraction of uranium precipitated—delayed addition of cerium:

A. tracer added before precipitation,
B. tracer added after precipitation,
C. theoretical curve assuming the modified distribution law applies—conditions of curve B.

Acknowledgement—The authors gratefully acknowledge the support of the United States Atomic Energy Commission under Contract AT(11-1)-582.

Zusammenfassung—Die Mitfällung von Cer(III) bei der Fällung von Uran(IV)—oxalat mittels Dimethyloxalat aus homogener Lösung wird studiert. Das System folgt dem logarithmischen Verteilungsgestz besser als dem homogenen Verteilungsgesetz. Es wurde gefunden, dass der Verteilungskoeffizient in funktioneller Beziehung zur experimentell ermittelten Geschwindigkeitskonstante der Fällungsreaktion (erster Ordnung) steht, wenn Spuren von Cer(III) mit Uran(IV) oxalat als Träger mitgefällt werden. Es wurde gefunden dass $\lambda = K_T/K_C$ wobei λ der Verteilungskoeffizient und K_T die fraktionelle Geschwindikeit der Spurenfällung ist. Letztere wurde in Gegenwart des Trägers bestimmt. Das studierte System gehorcht einem modifizierten Verteilungsgesetz (Einschluss der Ionenladung) besser, als dem unmodifizierten logarithmischem Doerner-Koskins Verteilungsgesetz.

Résumé—La coprécipitation du cérium(III) par l'oxalate d'uranium (IV) a été étudiée en utilisant le diméthyl oxalate pour précipiter l'uranium(IV) en solution homogène. Une brève étude a également été effectuée en utilisant le scandium(III) et l'uranium(IV). Ces systèmes obéissent mieux à la loi de distribution logarithmique qu'à la loi de distribution homogène. Le coefficient de partage est fonction de la constante de vitesse de la réaction de précipitation lorsque une *trace* de cèrium(III) est coprécipitée avec l'oxalate d'uranium(IV) utilisé comme *entraîneur*. Le coefficient λ est égal à K_T/H_C dans lequel K_T, vitesse de précipitation du traceur, est déterminée en présence de l'entraîneur. Le système oxalate de cérium(III)-oxalate d'uranium(IV) obéit à une loi de distribution modifiée pour tenir compte de la charge de l'ion plutôt quiala loi de distribution logarithmique de Doerner-Hoskins.

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ELIMINATION OF ANIONIC INTERFERENCES IN THE FLAME SPECTROPHOTOMETRIC DETERMINATION OF CALCIUM

USE OF GLYCEROL AS A RELEASING AGENT

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Summary—A method is devised for circumventing anionic interferences in the flame spectrophotometric determination of calcium in concentrations from 0·1 to 10 μg/ml at a wavelength of 422·7 mμ. The sample is atomised as a solution that contains 10 v/v% glycerol and is 0·1*M* in perchloric acid. The effects of various anions, including nitrate, sulphate and phosphate, on the emission intensity of calcium are studied. Also, glycerol is used to reduce interferences from various cations and anions in the determination of calcium. The method has been applied to the determination of calcium, without prior separation, in phosphate pickling solution, soil extracts, plant tissue, fish tissue, animal bones, and National Bureau of Standards samples. The relative standard deviation of the method is less than 3%.

INTRODUCTION

THE fact that various anions adversely affect the flame emission intensity of calcium has been reported.[1,2,3,4] In none of these studies have the effects of calcium concentration, the type of photosensitive detection, the excitation source, or anions been investigated thoroughly. Most flame-spectrophotometric work with calcium has been done at concentrations between 40 and 400 μg/ml. Because instruments of high resolution and high sensitivity are now available, it is now practical to work between 2 and 10 μg/ml. In this range there is little self-absorption or ionisation.

The inhibition of the emission intensity of calcium by sulphate or phosphate is thought by some to be caused by the formation of compounds having high temperatures of vaporisation. Several techniques have been proposed to counteract the inhibition effect without chemically separating calcium from the anions prior to analysis. Pro and Mathers[5] observed that dextrose in the presence of phosphate in concentrations from 20 to 1000 μg/ml restores the emission intensity of calcium present in a concentration of 10 μg/ml to within 87% of its nominal value in the absence of the inhibiting anion. West and Cooke[6] have successfully used (ethylenedinitrilo)-tetraacetic acid to restore the emission intensity of calcium in the presence of 0·01*M* sulphuric or phosphoric acid.

Recently, Heeney, Ward and Willson[7] described a method whereby the inhibition of phosphate (20 μg/ml) in a solution that contains calcium in concentration up to

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* Operated by Union Carbide Corporation for the Atomic Energy Commission.

100 μg/ml can be eliminated by aspirating the sample in a solution that contains 2 v/v % glycerol.

The interference of anions on calcium can also be minimised by the addition of a cation that forms a more stable complex with the anion than with the calcium.[8] Strontium, magnesium, beryllium and the rare-earth elements have been suggested as releasing agents for calcium. However, the addition of cationic releasing agents may introduce difficulties in the form of spectral or background radiation that will affect the emission intensity of the calcium.

The objective of the present investigation was to determine what effects on the intensity of the 422·7-mμ emission line of calcium were caused by anions that are found in or introduced during dissolution of nuclear reactor materials, soils, and plant and animal tissues. In this study oxyhydrogen and oxyacetylene flames were used as sources of excitation. Various releasing agents were tested as to their ability to restore calcium emission intensity to its nominal value in the absence of the inhibiting anion.

EXPERIMENTAL

Apparatus

A Beckman Model DU spectrophotometer, equipped with flame sources, an oxyhydrogen or oxyacetylene burner, and the auxiliary control panel for gas regulation, was used. For the detection and recording of spectra, the Beckman instrument was modified by replacing the usual phototube housing with the accessory power supply and recording equipment described by Kelley, Fisher and Jones.[9]

In order to stabilise the multiplier phototube and thus to minimise any drift of its output, the shutter between the phototube and the flame was opened at least 15 min before aspirating the samples. The instrumental settings selected to provide the desired sensitivity and reproducibility were:

Sensitivity control, % adjust	High
Multiplier phototube, RCA 1P28	60 V/dynode
Slit width	0·03 mm
Spectral slit width	0·07 mμ

To eliminate any error from improper focusing of the parabolic mirror in the flame housing, the mirror was removed from the optical system. This slight modification in the optical system increased the precision, especially with the oxyacetylene flame.

Rotameters (Brooks Rotameter Co., Landsdale, Pa.) were installed in the oxygen and fuel lines to monitor the flow of gas and to maintain reproducible flame conditions.

A mixed-bed ion-exchange column was prepared by mixing an equal weight of Dowex 50-X8 (50-to-100 mesh) and Dowex 1-X10 (50-to-100 mesh). After the resin mixture was washed first with 6*M* hydrochloric acid and then with water, sufficient resin was transferred to a 1 × 15-cm glass column to provide a resin bed 10 cm in depth.

Reagents

Standard calcium solution, 2·00 mg/ml: Dissolve 2·497 g of calcium carbonate in 55 ml of 1*M* hydrochloric acid and dilute the solution to 500 ml with 0·1*M* hydrochloric acid. Dilute aliquots of this solution with 0·001*M* hydrochloric acid to prepare more dilute standard solutions.

Glycerol solution, 50 v/v %, calcium-free: Transfer 500 ml of analytical-reagent grade glycerol to a 1-litre flask and dilute it to 1 litre with water. Pass 500 ml of the 50% glycerol solution through a previously prepared cation-exchange resin bed. Discard the resin or regenerate it by washing it with water and 6*M* hydrochloric acid. This procedure decreases the calcium concentration of analytical-reagent grade glycerol from approximately 1 μg/ml to less than 0·001 μg/ml.

Solutions of anions: All test solutions of anions were prepared from reagent-grade acids except the solutions of phosphate, which were prepared from phosphoric acid and from ammonium monohydrogen phosphate.

Releasing agents: All releasing agents tested were the highest purity reagent-grade chemicals that are available.

Procedures

Preparation of calibration curve. Prepare a series of standard solutions that contain 2–10 μg of calcium/ml. Treat the standard solutions of calcium with sufficient 50 v/v % aqueous solution of glycerol to give a final concentration of 10 v/v% glycerol and with sufficient concentrated perchloric acid to make the final solution 0·1*M* in the acid. Measure the emission intensity of the atomic calcium line and of the flame background at wavelengths of 422·7 and 421 mμ, respectively. Obtain the net emission intensity of each standard by subtracting the emission intensity of the flame background from the total emission intensity of the calcium line.

Analysis of plant or animal tissue. To a 250-ml beaker, transfer a 1-g test portion of the previously dried sample of plant or animal tissue. Add 10 ml of 15*M* nitric acid; predigest the test portion. Add 12*M* perchloric acid for the final digestion. Cool the mixture and filter off the silica. Dilute the filtrate to a known volume. To a 10-ml volumetric flask, transfer from the solution an aliquot that is estimated to contain 20–100 μg of calcium. Add 1 ml of 1*M* perchloric acid and 2 ml of a 50 v/v% glycerol. Dilute the portions to 10 ml with water. Determine the calcium content of the final solution by means of the calibration curve.

RESULTS AND DISCUSSION

Effects of anions

A series of solutions was prepared that contained calcium (10 μg/ml) and one of several different anions in various concentrations. Each anion was added as one of its acids; the phosphate was also added as the ammonium monohydrogen phosphate salt. The emission intensity of calcium for each solution was determined at 422·7 mμ in both oxyhydrogen and oxyacetylene flames. The calcium was determined from a calibration curve that was constructed by means of calcium standards prepared in 0·001*M* hydrochloric acid. The results are shown in Figs. 1 and 2.

In general, calcium emission was depressed more for the oxyhydrogen flame than for the oxyacetylene flame. The depression caused by sulphate and phosphate was expected, but few authors have noted the effect of nitrate, a medium in which standard

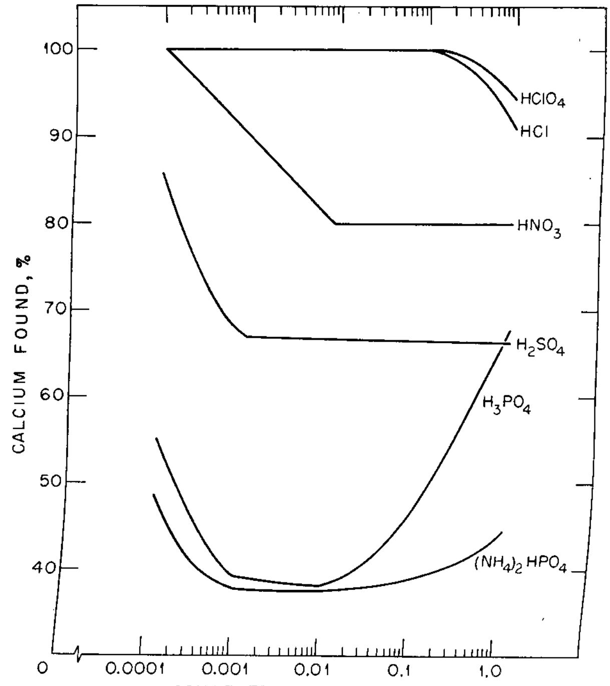

FIG. 1.—Effects of anions on calcium found in absence of glycerol (oxyhydrogen flame; [Ca^{2+}]: 10 μg/ml; wavelength: 422·7 mμ).

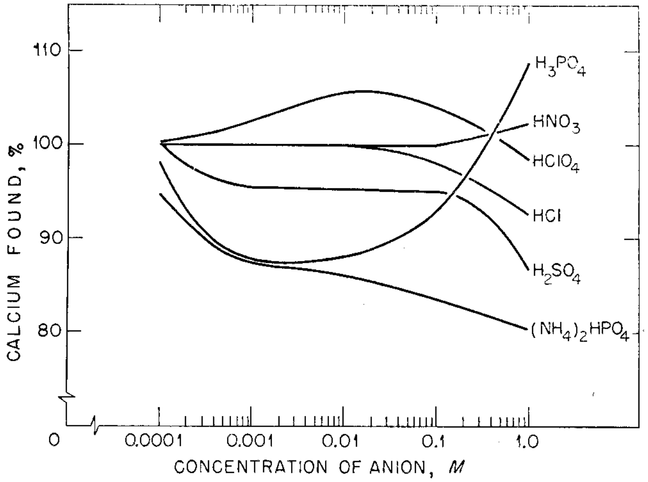

FIG. 2.—Effects of anions on calcium found in absence of glycerol (oxyacetylene flame; [Ca^{2+}]: 10 μg/ml; wavelength: 422·7 mμ).

solutions of calcium are often prepared. The effect of phosphate depends largely on the type of fuel and, if the pH is not adjusted, on the form in which the phosphate is added (*i.e.*, as salt or free acid). In an oxyhydrogen flame, the inhibition of the calcium emission intensity decreases rapidly when the phosphoric acid concentration exceeds 0·1*M*; however, the calcium found is never 100% of that present. By contrast, in an oxyacetylene flame a 1*M* solution of phosphoric acid gave an enhancement of 9% of the calcium emission intensity.

The background corrections for samples that are 1*M* in phosphate are very large because of the continuous emission of phosphorus and must be properly applied. In fact, these bands are so intense that Brite[10] has used them in the determination of phosphorus.

Effects of polyhydric alcohols and saccharides

The effects of various polyhydric alcohols and saccharides as releasing agents for calcium (10 μg/ml) were evaluated in the presence of phosphate (1000 μg/ml) with oxyacetylene and oxyhydrogen flames. The results for the oxyacetylene flame are summarised in Table I. The effect of the same polyhydric alcohols and saccharides as releasing agents in the oxyhydrogen flame at 1 v/v or w/v % was essentially the same as that observed with the oxyacetylene flame. From the data, it was concluded that glycerol was a more effective releasing agent than dextrose, which was suggested by Pro and Mathers.[5] Because the use of glycerol has advantages (*e.g.*, increased solubility and ease of transfer as compared with a solid), additional tests were made to verify this conclusion. A 10 v/v % solution of glycerol was found to be the best releasing agent for various anions and for condensed-phase interferences introduced by a number of elements. Also, the emission intensity of calcium increased 40% to a maximum at 10 to 20 v/v % glycerol, then slowly decreased. This decrease in emission intensity may be caused by the increased viscosity of the reagent.

The only disadvantage encountered in using glycerol is its high viscosity. Because the viscosity of 96 v/v % reagent-grade glycerol is 435 centipoises, it cannot be transferred accurately. This difficulty is circumvented by transferring 25 ml of 96% glycerol

TABLE I.—EFFECT OF VARIOUS RELEASING AGENTS ON CALCIUM FOUND IN THE PRESENCE OF PHOSPHATE (OXYACETYLENE FLAME) ($[Ca^{2+}]$: 10 μg/ml; $[PO_4^{3-}]$:[a] 1000 μg/ml).

Identity of Releasing agent	Concentration of releasing agent, *w/v* or *v/v*, %			
	1	5	10	20
	Calcium found, %			
Ethylene glycol	84	95	95	100
Glycerol	79	100	100	100
Mannitol	89	93		
Dextrose	87	91		
Lactose	91	92		

[a] Phosphate added as ammonium monohydrogen phosphate.

to a 50-ml graduated cylinder and diluting to volume with water. A 50 v/v % solution of glycerol has a viscosity of 5 centipoises and can be transferred accurately and rapidly.

The effects of some of the common anions on the amount of calcium found in a 10 v/v % solution of glycerol are shown in Figs. 3 and 4. In the presence of 0·0001 to 0·1*M* nitric, sulphuric or hydrochloric acids in both the oxyacetylene and oxyhydrogen flames, all of the calcium taken (10 μg/ml) was found.

Because all of the calcium taken was found in the presence of 1*M* phosphoric acid but not in the presence of 1*M* ammonium monohydrogen phosphate (Fig. 3), the effect of pH was studied. When the phosphate was added as the acid, the pH of the solution to be aspirated was less than 2, whereas the solution that contained the ammonium monohydrogen phosphate had a pH of 8. By adjustment of the monohydrogen phosphate salt solution to a pH of 0·5 with nitric acid, all of the calcium taken was found in the presence of 0·1*M* phosphate (Fig. 3). Hydrochloric and perchloric acids were investigated as a means of adjusting the pH but were not as effective as nitric acid for the oxyacetylene flame. With an oxyhydrogen flame, the addition of a mineral acid

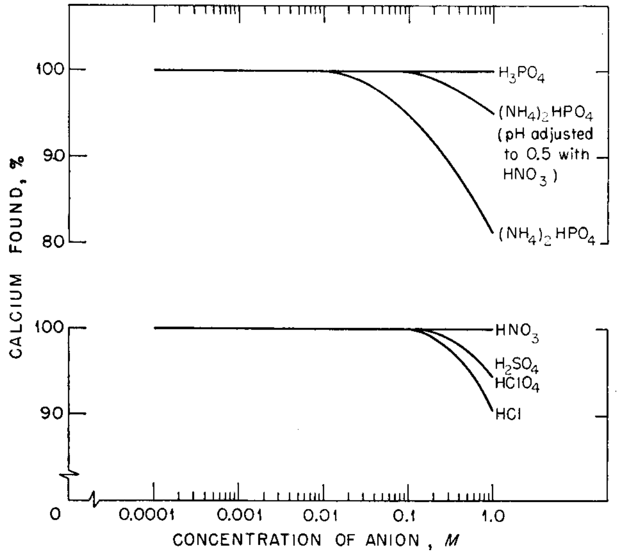

FIG. 3.—Effects of anions on calcium found in presence of glycerol (oxyacetylene flame; $[Ca^{2+}]$: 10 μg/ml; [glycerol]: 10 v/v %; wavelength: 422·7 mμ).

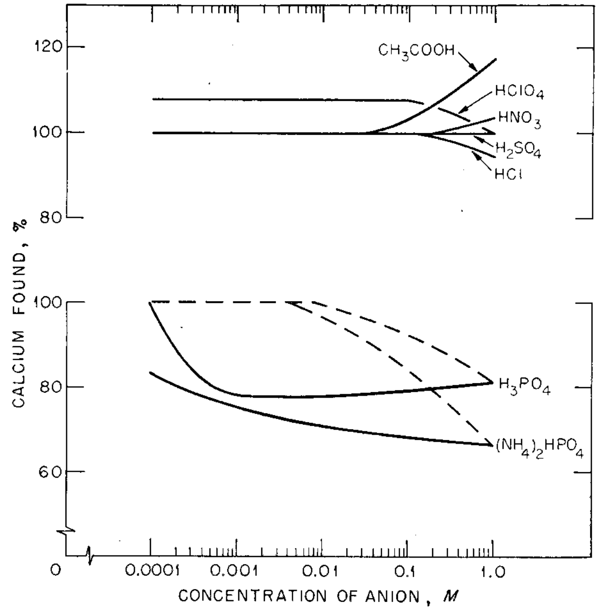

FIG. 4.—Effects of anions on calcium found in presence of glycerol (oxyhydrogen flame; $[Ca^{2+}]$: 10 μg/ml; [glycerol]: 10 v/v%; wavelength: 422·7 mμ):
– – – Aspirated solution contained 0·1*M* $HClO_4$

increased the amount of calcium found in the presence of phosphate as the acid or salt (Fig. 4). Nitric, hydrochloric and perchloric acids in various concentrations were tested. With the oxyhydrogen flame, the most nearly correct amount of calcium was found when the solution to be aspirated contained 0·1*M* perchloric acid. With the use of either the oxyhydrogen or oxyacetylene flames, the addition of a mineral acid is not necessary for solutions that contain sulphate or nitrate.

Effect of glycerol on emission intensity of other elements

The use of glycerol as a releasing agent has been extended to the other alkaline-earth and alkali metals. The effects of the common anions on strontium and barium have been reported previously.[11,12] Glycerol was studied as a releasing agent for strontium (1 μg/ml); in the presence of 0·0001 to 1·0*M* sulphuric or phosphoric acid, the strontium found was greater than 95% of that taken. Similar results were obtained for magnesium and lithium in the presence of sulphate.

Condensed-phase interference is observed with a number of elements, such as, aluminium, chromium, iron and titanium. This type of interference on the emission intensity of calcium is also minimised when the solution to be atomised contains 10 v/v% glycerol and is 0·1*M* in perchloric acid; this effect is shown in Table II.

Applications

The method has been used satisfactorily to determine calcium in phosphate pickling solution, soil extracts, plant tissue, fish tissue, animal bones, and three National Bureau of Standards standard samples. Some of the results are shown in Table III.

TABLE II.—CALCIUM FOUND IN SOLUTIONS THAT CONTAINED VARIOUS AMOUNTS OF CATIONS WITH AND WITHOUT GLYCEROL PRESENT

Cation	Concentration of cation, *μg/ml*	Calcium found, %			
		Calcium present, 1 *μg/ml*		Calcium present, 10 *μg/ml*	
		Without glycerol	With glycerol[a]	Without glycerol	With glycerol[a]
Al^{3+}	1	68	99	92	100
	5	42	81	77	95
	10	42	68	68	87
	20	29	43	56	71
Cr^{6+}	10	76	100	82	100
	100	56	100	57	98
	1000	27	91	30	94
Fe^{3+}	10	81	100	88	100
	100	55	100	54	100
	1000	40	94	34	93
Ti^{4+}	1	49	100	94	100
	5	12	92	63	98
	10	7	85	39	93
	20	5	75	16	80

[a] Solution contained 10 v/v% glycerol and was 0·1*M* in perchloric acid.

TABLE III.—RESULTS OF FLAME SPECTROPHOTOMETRIC DETERMINATION OF CALCIUM IN VARIOUS SUBSTANCES WITH GLYCEROL AS RELEASING AGENT.

Sample	Calcium content			
	Experimental value			
	Calcium found, *wt.* %	Average, *wt.* %	Relative standard *deviation*, %	NBS value, *wt.* %
Limestone[a]	28·5 30·3 29·8			
(NBS-1a)	28·5 29·8 29·1			
	28·9 30·3 29·2	29·4	2	29·53
Phosphate rock[a]	32·2 31·5			
(NBS-56a)	32·3 31·4			
	33·0 32·3	32·1	1	32·55
Dolomite[a]	21·4 22·1 21·3			
(NBS-88)	21·4 21·8 21·3			
	21·4 21·8			
	21·4 21·7	21·6	1	21·79
	mg/g of dry ash			
Plant tissue				
Mulberry twigs	46·3 46·2	46·3		
White oak twigs	21·4 21·0	21·2		
Birch twigs	9·6 9·7	9·7	0·9[b]	
Fish tissue				
1	20·4 20·4	20·4		
2	11·6 11·3	11·5		
3	10·7 10·7	10·7	1[b]	

[a] The determinations on each NBS sample were carried out at different times over a 4-week period.

[b] Determined from the difference between duplicates.

The data given therein indicate the accuracy and precision that can be expected from the method. Because the separation of calcium from the interfering anions is not necessary, the method is both rapid and simple.

Zusammenfassung—Eine Methode wurde entwickelt um anionische Störungen bei der flammphotometrischen Bestimmung von Calcium im Konzentrationsbereich 0·1–10 μg/ml bei 422·7 mμ auszuschalten. Die Probe wird als Lösung zerstäubt, die 10% v/v Glycerin enthält und 0·1 n in Perchlorsäure ist. Der Einfluss verschiedener Anionen, wie Nitrat, Sulfat und Phosphat wurde studiert. Glycerin wurde auch zur Minderung der Störung verschiedener Kationen verwendet. Die Methode wurde auf die Bestimmung des Calciums (ohne vorherige Trennungen) in phosphathältigen Pöckellösungen, Bodenauszügen, Pflanzengewebe, Fischgewebe, Tierknochen und Standardproben des National Bureau of Standards angewendet. Die relative Standardabweichung war unter 3%.

Résumé—Les auteurs ont mis au point une méthode pour éliminer les interférences anioniques dans le dosage par spectrophotométrie de flamme de calcium en concentration de 0,1 à 10 μg/ml à une longueur d'ondes de 422,7 mμ. L'échantillon est atomisé sous forme d'une solution qui contient 10% en volume de glycérol et est 0,1 M en acide perchlorique. Les effets de différents anions, comme le nitrate, le sulfate et le phosphate, sur l'intensité de l'émission du calcium, ont été étudiés. Ainsi, le glycérol a été utilisé pour réduire les interférences de différents cations et anions dans le dosage du calcium. La méthode a été appliquée au dosage du calcium, sans séparation préalable, dans une solution d'attaque de phosphate, des extraits de sol, des tissus de plantes, des tissus de poissons, des os d'animaux et des échantillons du "National Bureau of Standards". L'écart standard relatif de la méthode est inférieur à 3%.

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ISOTOPIC DILUTION ANALYSIS BY SOLVENT EXTRACTION—V*

DETERMINATION OF TRACES OF IRON

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Summary—Iron is determined with cupferron in amounts of 10^{-7} to 10^{-9} g/ml with an average precision of ±4·3% and in amounts of 10^{-10} g/ml with an average precision of ±8·3%. The sensitivity of the method might be further increased by using carrier-free radioiron. The method is very simple and rapid, consisting of a single extraction of the analysed solution and measurement of the activity of the extract. The procedure is far more sensitive and precise than other methods of trace analysis. Errors arising from traces of iron present in reagents and vessels are avoided by careful purification.

INTRODUCTION

It has been shown[1,2,3,4] that isotopic dilution analysis by solvent extraction can be used for the determination of traces of metals if the following conditions can be fulfilled:

1. A radiotracer of suitable half-life and high specific activity is available.
2. It is possible to isolate very small *equal amounts* of test element from solutions containing it in different amounts.

The second condition is fulfilled by adding equal amounts of complexing agent to the standard and test solutions, where the standard solution contains only the radioisotope used and the test solution is a mixture of test sample and a known amount of standard solution. The amount of complexing agent added must, of course, be smaller than corresponds to the stoichiometric ratio of the metal present. Subsequently, the complex formed (in the present paper iron^{III} cupferrate) is isolated by means of solvent extraction.

In Table I a survey of known extraction constants (K) of metal cupferrates is given. From a theoretical consideration[1] it follows that for the determination of 3 μg, 0·3 μg and 0·03 μg of iron^{III} in 10 ml by 1 ml of $10^{-4}M$, $10^{-5}M$ and $10^{-6}M$ cupferron solution in chloroform, respectively, it is necessary to use a pH higher than 3, 4 and 5. These values have been calculated from the assumption that more than 99% of the cupferron reacts to form the iron^{III} complex.

From an investigation of the extraction of metal cupferrates it may be expected that in the determination of iron, quadrivalent metal ions (Ti, Zr, Hf, Th, Pu and U—see Table I) will especially interfere. Bivalent metal ions having, in general, very low values of K will not interfere even when present in great excess (with the exception of Cu—see Table I).

To avoid interference from metals forming insoluble sulphides, thiourea, hexamethylenetetramine or rubeanic acid is often used. From our preliminary experiments it follows that the first two reagents have no influence on the extraction of iron^{III} cupferrate and thus may be used as masking agents for many metals.

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* Part IV: see reference 4.

TABLE I.—SURVEY OF EXTRACTION CONSTANTS (K) OF METAL CUPFERRATES

Metal	log K	Organic solvent	Reference
Fe^{III}	8·7	chloroform	5
Hf^{IV}	>8	chloroform	6
U^{IV}	8·2	diethyl ether	7
Pu^{IV}	7·0	chloroform	8
Ce^{IV}	4·6	n-butyl acetate	9
Th^{IV}	4·4	chloroform	6
Cu^{II}	2·7	chloroform	7
Al^{III}	2·5	chloroform	5
Pb^{II}	−1	chloroform	10
Sm^{III}	−3	methyl isobutyl ketone	6
U^{VI}	−4	chloroform	6
Co^{II}	−4	chloroform	10
Ni^{II}	−4	chloroform	10
Zn^{II}	−4	chloroform	10
Y^{III}	−5	chloroform	10
Mn^{II}	−7	chloroform	10
La^{III}	−12	chloroform	16
Ti^{IV}, Zr^{IV}	*		

* Not precisely known, but of same order as other quadrivalent metals or higher

EXPERIMENTAL

Apparatus

Scintillation counter with well-type NaI[Tl] crystal.

pH-meter: Radiometer TTT-1, Copenhagen, Denmark.

A mechanical shaker.

Glass test-tubes: 25-ml with ground-glass stoppers.

Reagents

Distilled water: Twice distilled, and further purified by passage through an ion-exchange column; used for dissolving all reagents and for other operations. The exchanger used (Dowex 50 AR in the Na-form) was previously purified by treatment with EDTA solution.

Chloroform: A.R., twice distilled.

Cupferron (ammonium salt of N-nitrosophenylhydroxylamine) solution in chloroform: Prepared by extraction of a $10^{-3}M$ solution of A.R. cupferron in 0·1*M* hydrochloric acid with chloroform. This extract was diluted to the required concentration. The concentration of cupferron in this solution and its stability were controlled radiometrically by means of extraction of radioiron (see Fig. 1).

Buffer-masking solution: This is 0·5*M* ammonium acetate—0·1*M* hexamethylenetetramine—0·1*M* thiourea, and is prepared as described later.

Acetic acid: A.R., purified twice by isothermal distillation.

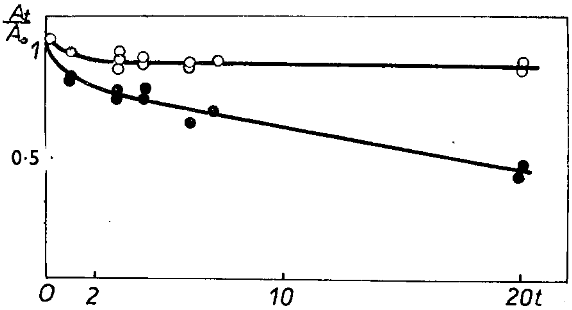

FIG. 1.—Stability of cupferron solution in chloroform:
○—solution stored in dark,
●—solution stored in light.
(A_0 = activity of $^{59}Fe^{III}$-cupferrate extracted at t = 0, A_t = activity of $^{59}Fe^{III}$-cupferrate extracted at time t, and t = time expressed in hr.)

Hydrochloric acid: Prepared by dissolving twice-distilled gaseous hydrogen chloride in water. Gaseous hydrogen chloride was prepared from a mixture of A.R. hydrochloric acid and A.R. sulphuric acid.

Iron^{III} chloride: 148·96 mg of A.R. ferrum reductum were dissolved in hydrochloric acid, boiled with a few ml of A.R. hydrogen peroxide and made up to 1 litre. The solution thus prepared was diluted to the required concentration with 0·01*M* hydrochloric acid.

Radioiron: A solution of iron^{III} chloride tagged by ^{59}Fe (radioisotope of specific activity 500 mc/g of iron produced by Radiochemical Centre, Amersham, England). Radioiron solution was prepared by diluting to the appropriate concentration with 0·01*M* hydrochloric acid and its concentration controlled by reverse isotope dilution.

Purification of vessels and reagents

Before each series of experiments the test tubes were carefully purified with ion-exchange water, then by extraction with dithizone-carbon tetrachloride solution, followed by cupferron-chloroform extraction. The last traces of dithizone and cupferron were removed by chloroform. Final purification was accomplished by washing with ion-exchange water.

The buffer-masking solution was prepared as follows: a solution of 2*M* ammonium acetate—0·4*M* hexamethylenetetramine—0·4*M* thiourea was purified by dithizone-chloroform extraction followed by cupferron-chloroform extraction. The pH was adjusted to the desired value (4·9) with isothermally distilled acetic acid. The last traces of cupferron and dithizone were removed by chloroform. The solution thus prepared was diluted four fold with ion-exchange water and stored in polyethylene bottles.

Stability of cupferron solution

The stability of the cupferron-chloroform solution was determined radiometrically from the activity of radioiron extracted with this solution. The conditions of extraction were the same as in the analytical procedures described below. From the results summarised in Fig. 1 it follows that the solution stored in the dark is more stable than that stored in the light (18°, glass bottles).

Procedure

To 10 ml of the solution containing non-active iron to be determined (in amounts from 10^{-7} to 10^{-10} g of iron/ml) and a large excess of other metals (see Table II), a known amount (y) of radioiron is added. After the addition of 1 ml of buffer-masking solution the mixture is extracted with 1 ml of $10^{-4}M$, $10^{-5}M$ or $10^{-6}M$ cupferron solution in chloroform. The amount of cupferron must be chosen to be smaller than stoichiometrically corresponds to the amount of iron present. After shaking for 10 min on a mechanical shaker the organic phase is separated. The standard solution containing only radioiron is treated in exactly the same way. Although the amount of radioiron present in the standard solution need not be known precisely, it must be greater than stoichiometrically corresponds to the amount of cupferron used for extraction. The activity of exactly the same volumes (*ca.* 0·6 ml) of extracts from the standard (A_1) and test (A_2) solutions is measured in a well-type scintillation counter. It is advantageous to treat a series of samples simultaneously, *e.g.* 10 samples but only 5 standards. The mean value of A_1 is then used for calculation of the amount of iron (x) in each of the samples:

$$x = y \cdot \left(\frac{A_1}{A_2} - 1\right) \tag{1}$$

Some results obtained in this way are summarised in the Table II.

DISCUSSION

Fig. 2 shows the effect of pH on the extraction of iron. The amount of cupferron employed is only 50% of the value which stoichiometrically corresponds to the amount of iron present. The course of the curves is in good agreement with theory.

The proposed method is amongst the most sensitive available[11] for determination of traces of iron. Compared with methods of similar sensitivity, *e.g.*, ion exchange,[12] spark source mass spectrometry, it possesses the additional virtues of rapidity, simplicity and cheapness.

CONCLUSION

In the present paper a selective determination of traces of iron in amounts from 10^{-7} to 10^{-10} g/ml is described. The method is based on the principle of isotopic

TABLE II

EXTRACTION OF IRON BY CUPFERRON

($1{\cdot}5 \times 10^{-7} - 5{\cdot}9 \times 10^{-10}$ g of iron/ml)[a]

Iron taken, μg (X)	Active iron added, μg (y)	Activity of extracts[b]		Iron found, μg (x)	Deviation from mean, μg (Δ)	Other metals present, μg	Deviations[c]
		A_1	A_2				
1·4896	1·2634	16,352	7,213	1·6007	+0·1163	—	$\sigma = 1{\cdot}4844$
			7,786	1·3899	−0·0945	—	$\delta = \pm 0{\cdot}048 = \pm 3{\cdot}24\%$
			7,382	1·5344	+0·0500	Pb 5000	
			8,087	1·2862	−0·1982	Cd 5000	$\sigma - X = -0{\cdot}0052 = -0{\cdot}352\%$
			7,205	1·6027	+0·1183	Ag 5000	
			7,763	1·3978	−0·0866	Tl, Co, Mn 1000	
			7,268	1·5790	+0·0946	Tl, Co, Mn 5000	
0·2979	0·2527	26,276	12,144	0·2941	−0·0077	—	$\sigma = 0{\cdot}3018$
			12,036	0·2989	−0·0029	—	$\delta = \pm 0{\cdot}0045 = \pm 1{\cdot}5\%$
			11,561	0·3216	+0·0198	Cd, Ag 200	
			11,820	0·3108	+0·0090	Cu 250	$\sigma - X = +0{\cdot}0039 = +1{\cdot}29\%$
			12,247	0·2894	−0·0124	Hg 250	
			11,269	0·3365	+0·0347	Bi 250	
		27,361	12,903	0·2831	−0·0187	—	
			12,293	0·3097	+0·0079	—	
			12,760	0·2891	−0·0127	Hg 300	
			12,633	0·2946	−0·0072	Cu 300	
			12,864	0·2848	−0·0170	Cr 300	
			11,675	0·3395	+0·0377	Tl, Co, Mn 500	
			12,893	0·2836	−0·0182	Tl, Co, Mn 300	
			12,742	0·2899	−0·0119	Ni 150	

0·02928	0·0662	2,973	2,073	0·0288	−0·0009	—	$\sigma = 0{\cdot}0297$
			2,159	0·0250	−0·0047	—	$\delta = \pm 0{\cdot}00255 = 8{\cdot}58\%$
			1,727	0·0478	+0·0181	Pb 30	
			1,975	0·0335	+0·0038	Hg 40	$\sigma - X = +0{\cdot}00042 = +1{\cdot}42\%$
			2,248	0·0214	−0·0083	Zn 10	
			1,875	0·0388	+0·0091	Bi 30	
			2,335	0·0181	−0·0116	Cd 30	
			2,209	0·0229	−0·0068	Cu 30	
			2,337	0·0181	−0·0116	Tl, Co, Mn 20	
		2,041	1,406	0·0299	+0·0002	—	
			1,400	0·0303	+0·0006	—	
			1,243	0·0425	+0·0128	Al 30	
0·00586	0·00662	2,244	1,214	0·00562	+0·00018		$\sigma = 0{\cdot}00544$
			1,268	0·00510	−0·00034		$\delta = \pm 0{\cdot}00045 = \pm 8{\cdot}3\%$
			1,402	0·00397	−0·00157		
	0·01324		1,514	0·00638	+0·00094		$\sigma - X = -0{\cdot}00042$
			1,488	0·00672	+0·00128		
			1,680	0·00441	−0·00103		

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[a] Volume of solutions analysed in all experiments listed in table was 10 ml.

[b] Activities (A_1, A_2) are expressed in cpm and are the mean values of 3 measurements.

[c] $\sigma = \frac{\sum_{x=1}^{x=n} x}{n}$; $\delta = \pm \sqrt{\frac{\sum \Delta^2}{n(n-1)}}$.

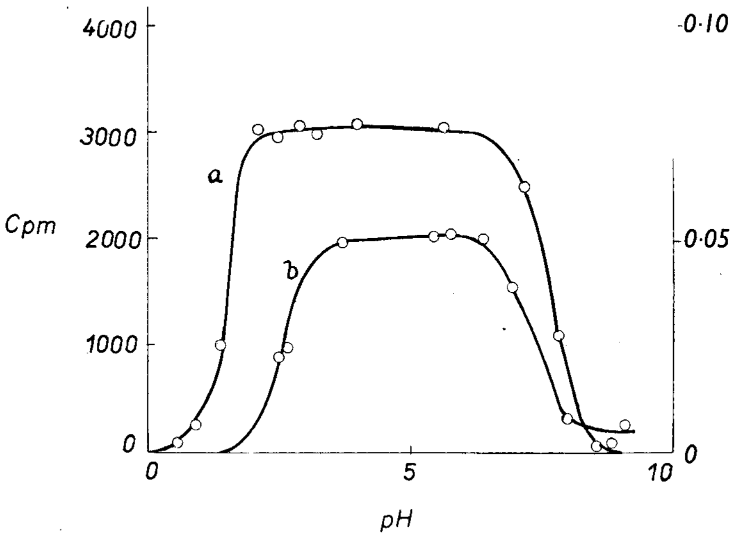

Fig. 2.—Influence of pH on the amount of iron extracted:
(a) $10^{-3}M$ cupferron in chloroform; spectrophotometric measurements.
(b) $10^{-4}M$ cupferron in chloroform; radiometric measurements.

dilution analysis by solvent extraction with cupferron. The possibility of using another reagent than dithizone for the purposes of isotope dilution analysis by solvent extraction has thus also been verified.

Zusammenfassung—Eisen wurde mittels Kupferron in Mengen von 10^{-7}–10^{-9} g/ml mit $\pm 4{\cdot}3\%$ und bei 10^{-10} g/ml mit $\pm 8{\cdot}3\%$ mittlerer Genauigkeit bestimmt. Die Empfindlichkeit der Methode kann möglicherweise noch weiter gesteigert werden, wenn trägerfreies Radioeisen eingesetzt wird. Die Methode ist einfach und rasch und besteht in einer einzigen Extraktion und anschliessender Messung der Aktivität des Extraktes. Die Methode ist empfindlicher und präziser als andere Spurenmethoden. Die durch Eisen in Reagentien und Gefässen möglicherweise verursachten Fehler wurden durch sorgfältige Reinigung vermieden.

Résumé—On a pu doser au moyen du cupferron des quantités de fer, de l'ordre de 10^{-7} à 10^{-9} g/ml avec une précision moyenne de $\pm 4{,}3\%$ et de l'ordre de 10^{-10} g/ml avec une précision de $\pm 8{,}3\%$. La sensibilité de la méthode pourrait être améliorée en utilisant un support exempt de fer radioactif. Cette méthode est simple et rapide; elle consiste en effet, en une simple extraction de la solution à analyser et une mesure de l'activité du produit extrait. Le procédé est beaucoup plus sensible et beaucoup plus précis que les autres méthodes utilisées dans l'analyse de trace. Les erreurs résultant de traces de fer présentes dans les réactifs et les récipients sont évitées par une purification très soignée.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XI*

DETERMINATION OF TITANIUM, IRON AND ALUMINIUM IN THE PRESENCE OF EACH OTHER

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Summary—Aluminium can be masked in an acidic medium with salicylic acid (or *p*-aminosalicylic acid). This enables the complexometric determination of titanium (or iron) to be carried out in the presence of relatively high concentrations of aluminium (100 mg/100 ml) without previous separation. A selective separation of titanium from iron and aluminium with triethanolamine and sodium hydroxide, in combination with salicylic acid, is utilised with advantage for the determination of titanium even in the presence of g-amounts of aluminium. The determination of iron and aluminium in the filtrate after separation of titanium is also described.

A GREAT number of papers dealing with the complexometric determination of iron, aluminium or titanium are known from the literature. Few of them,[2–7] however, describe the determination of binary mixtures of these elements and the determination of the ternary mixture has not yet been reliably solved. Theoretically, the simplest solution would be to use specific masking reagents at least for two of the above-mentioned elements. According to our present knowledge this problem can be solved only partially.

We have now found that a comparatively large amount of aluminium can be masked with salicylic acid (or *p*-aminosalicylic acid) without influencing the formation of the titanium-EDTA-peroxocomplex. This enables a reliable determination of titanium to be made, based on back titration of an added excess of EDTA with bismuth nitrate solution.[6] Because this titration is carried out at pH 1–2 the determination is not disturbed by a number of elements. Tervalent iron, however, is quantitatively cotitrated. With a method based on this principle it is therefore possible to determine titanium in the presence of aluminium, and also the sum of titanium and iron. The determination of all three elements, however, has not yet been solved with the above-mentioned method.

In a previous paper[1] we described a selective method for the determination of titanium in the presence of iron, aluminium and some other elements. This procedure is based on precipitation of titanium with sodium hydroxide in the presence of triethanolamine(TEA). The precipitated titanium hydroxide is filtered off, dissolved in nitric acid and determined complexometrically with high accuracy. In the filtrate iron and aluminium remain as TEA complexes (aluminium partly as aluminate).

This filtrate is very suitable for the complexometric determination of iron and aluminium. The procedures subsequently described are very simple and they make

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* Part X: see *Talanta*, 1962, 9, 1053.

possible a very quick determination of all three elements in a very large range of their concentration ratios, not only in their isolated hydroxides but also in a great number of materials, *e.g.*, titanium alloys, ores, slags, clays, *etc.*

EXPERIMENTAL

Reagents

$0 \cdot 05M$ EDTA, $0 \cdot 05M$ $Bi(NO_3)_3$, $0 \cdot 05M$ $Pb(NO_3)_2$, $0 \cdot 05M$ $Fe(NH_4)_2(SO_4)_3$, $0 \cdot 05M$ $KAl(SO_4)_2$, $0 \cdot 05M$ $Ti(SO_4)_2$, prepared from analytical-grade chemicals. The solution of titanium sulphate was prepared from titanium hydride by dissolution in hydrochloric acid. After oxidation with hydrogen peroxide and evaporation with sulphuric acid to fuming, the reaction mixture was diluted to the given concentration. Other reagents included 20% and 1% triethanolamine, $2M$ sodium hydroxide, $1M$, (1:3) and (1:1) nitric acid, aqueous ammonia (1:10), 10% sodium salicylate (or sodium *p*-aminosalicylate), 10% ammonium fluoride, 10% hydrogen peroxide, 0·2% Xylenol Orange, phenolphthalein solution, solid urotropine. All reagents were also p.a. purity.

1. *Determination of titanium in the presence of aluminium*

Titanium can be very reliably determined in the presence of hydrogen peroxide by back titration of an added excess of EDTA with bismuth nitrate solution at pH 1–2 with Xylenol Orange as indicator. The yellow coloration of the titanium-EDTA-peroxocomplex formed does not influence the colour change at the end-point if the solutions are sufficiently diluted (40 mg of titanium /300–500 ml). Higher concentrations of aluminium affect this determination because of the formation of an aluminium-EDTA complex. At the end-point aluminium is displaced from its complex by bismuth but this displacement proceeds slowly and non-quantitatively, which makes the rapid determination of titanium impossible.

The first experiments with the addition of salicylic acid (or *p*-aminosalicylic acid) to the acid solution were not successful. Only when the solution was made alkaline by addition of triethanolamine and sodium hydroxide was the very stable aluminium-salicylic acid complex formed, which did not then dissociate on acidification to pH 1. It does not dissociate enough to react with EDTA. Addition of triethanolamine is necessary to prevent temporary precipitation of aluminium hydroxide.

Procedure. Dilute the acid solution containing titanium and aluminium to 100 ml, add 10 ml of 10% sodium salicylate solution and 20 ml of 20% triethanolamine solution. Add 2 drops of phenolphthalein followed by $2M$ sodium hydroxide solution to an intense violet (not red) coloration. Now acidify the solution with nitric acid (1:3) to pH 1–2 (pH indicator paper). After stirring, add 10 ml of 10%-hydrogen peroxide solution, cool thoroughly to below 20°, add a measured volume of $0 \cdot 05M$ EDTA (more than enough to complex the titanium), dilute if necessary, add a few drops of Xylenol Orange and titrate with $0 \cdot 05M$ bismuth nitrate solution to the intense red coloration of the end-point. Some results of these determinations are given in Table I.

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

The determination of iron (in the absence of titanium) can be carried out as in 1, except for the following slight modifications: after the addition of triethanolamine, make the solution strongly alkaline with $2M$ sodium hydroxide solution till decoloration (formation of the iron-TEA complex); hydrogen peroxide is not added to the solution. Some results are given in Table I.

3. *Determination of the sum of iron and titanium*

The procedure is as described in 1, except that no phenolphthalein is added (see 2). Some results are presented in Table I.

4. *Determination of titanium in the presence of iron and aluminium*

This procedure has been described previously.[1] It is based on the precipitation of titanium with sodium hydroxide in the presence of triethanolamine. After washing and dissolution of the titanium hydroxide in nitric acid, titanium is determined complexometrically by back titration with bismuth nitrate solution using Xylenol Orange as indicator. We can now add that in further experiments we succeeded in the separation of mg-amounts of titanium in the presence of 10–20 g of potash alum. At a level of 3 mg, the subsequent complexometric titration of titanium was without interference even if no salicylic acid was added. Higher amounts of titanium, about 3–40 mg, in the presence of this very large concentration of aluminium, can be quite reliably determined according to ref. 1 after isolation of titanium hydroxide and its dissolution.

TABLE I.—DETERMINATION OF IRON AND TITANIUM IN THE PRESENCE OF ALUMINIUM

0·05*M* solution taken, *ml*			0·05*M* EDTA added, *ml*	Back titn. with 0·05*M* $Bi(NO_3)_3$, *ml*	0·05*M* solution found, *ml*		Difference, *ml*
Fe	Al	Ti			Fe	Ti	
0·96	1·00	—	4·95	3·95	1·00	—	0·04
0·96	10·00	—	1·98	1·00	0·98	—	0·02
0·96	20·00	—	4·95	3·94	1·01	—	0·05
9·63	1·00	—	11·88	2·22	9·66	—	0·03
9·26	20·00	—	21·78	2·45	19·33	—	0·07
4·82	5·00	—	11·88	6·93	4·95	—	0·13
0·96	30·00	—	1·98	1·00	0·98	—	0·02
0·96	50·00[a]	—	9·90	8·95	0·95	—	0·01
—	1·00	1·00	4·95	3·91	—	1·04	0·03
—	1·00	5·08	6·93	1·88	—	5·05	0·03
—	10·00	5·08	6·93	2·01	—	4·92	0·16
—	10·00	20·30	21·78	1·56	—	20·22	0·08
					Fe + Ti		
19·26	20·00	1·02	24·75	4·59	20·16		0·12
0·96	30·00	1·02	4·95	2·92	2·03		0·05
9·63	10·00	10·15	24·95	5·03	19·72		0·06
0·96	30·00	25·38[b]	29·69	3·71–4·00	—		

[a] Titrate very slowly to the end-point; wait some sec after addition of the last few drops of EDTA.

[b] The colour change is sluggish; too much titanium is present.

5. *Determination of iron and aluminium*

After separation of the precipitate of titanium hydroxide, the filtrate can be used for the determination of iron and aluminium in one of two ways:

(a) *Procedure with ammonium fluoride.* Add to a suitable aliquot of the filtrate, nitric acid (1:1) to pH 4 and an excess of 0·05*M* EDTA, then boil the solution for 1 min. After cooling, adjust the pH to 5–5·5 with solid urotropine, add a few drops of Xylenol Orange and titrate with 0·05*M* lead nitrate solution to an intense red coloration at the end-point. Add 10 ml of 10% ammonium fluoride solution and boil for 3–4 min. The solution becomes slightly alkaline from hydrolysis of the urotropine. Therefore, after cooling, add some drops of 1*M* nitric acid (the solution turns slightly pink to yellow), then again titrate with 0·05*M* lead nitrate solution to an intense red. The second consumption of lead nitrate solution corresponds directly to the amount of aluminium. The content of iron is obtained by difference. Some results of these determinations, together with those for titanium according to 4, are given in Table II. This method is suitable for 2–50 mg of both iron and aluminium.

TABLE II.—ANALYSIS OF MIXTURES OF IRON, ALUMINIUM AND TITANIUM (SYNTHETIC SOLUTIONS)

Taken, *mg*			Found, *mg*			Difference, *mg*		
Fe	Al	Ti	Fe	Al	Ti	Fe	Al	Ti
—	13·66	11·48	—	13·66	11·41	—	0·00	−0·07
—	1·37	22·96	—	1·38	22·89	—	+0·01	−0·07
—	40·98	4·59	—[b]	40·87	4·54	—	−0·11	−0·05
—	68·30	2·29	—[c]	68·46	2·28	—	+0·16	−0·01
2·84	1·37	2·29	3·01	1·35[a]	2·25	+0·17	−0·02	−0.04
28·43	1·37	11·48	28·48[c]	1·35[a]	11·40	+0·05	−0·04	−0·08
85·29	27·32	27·54	85·03[c]	27·51	27·25	−0·26	+0·19	−0·29
142·15	27·32	11·48	142·92[b]	26·65[d]	11·56	+0·77	+0·33	+0·08

[a] After addition of NH_4F (KF), the solution was boiled 5 min instead of 3 min.

[b] For determination of Al plus Fe, a 250-ml aliquot from 500 ml of filtrate was used.

[c] For determination of Al plus Fe, a 100-ml aliquot from 500 ml of filtrate was used.

[d] 50 ml of 20% TEA and 40 ml of 2*M* KOH were used.

The solution can contain moderate amounts of sulphates. Chlorides in the presence of nitric acid interfere, however, because traces of chlorine or nitrosyl chloride are formed by boiling. Free chlorine even in traces, oxidises EDTA.

(b) *Procedure with salicylic acid.* If the filtrate contains too much aluminium in comparison with the amount of iron, it is advantageous to determine only the sum of iron and aluminium after (a) in an aliquot of the filtrate. To another aliquot of the filtrate add 10% sodium salicylate solution and continue as described in 1. Chlorides and nitrates, if present together, interfere [see under (a)].

Zusammenfassung—Es wurde gefunden, dass Aluminium in schwach saurem Medium durch Salizylsäure oder p-Aminsalizylsäure maskiert werden kann. Dies ermöglicht die komplexometrische Bestimmung von Titan (und Eisen) in Gegenwart relativ hoher Aluminiumkonzentrationen (100 mg/100 ml). Die Methode der selektiven Trennung von Titan von Eisen und Aluminium mit Triäthanolamin und Natronlauge wurde in Kombination mit Salizylsäure verwendet um Titan selbst in Gegenwart von Grammengen Aluminium abzutrennen und zu bestimmen. Eisen und Aluminium werden im Filtrat Bestimmt.

Résumé—L'aluminium peut être masqué en milieu acide au moyen de l'acide salicylique ou p-aminosalicylique. Ceci permet le dosage, par formation de complexes, du titane (ou du fer) même en présence de concentrations relativement élevées d'aluminium (100 mg/100 ml) sans nécessiter de séparation préalable. La séparation sélective du titane au moyen de la triéthanolamine et de la soude en combinaison avec l'acide salicylique, dans les solutions contenant aussi du fer et de l'aluminium, permet de doser le titane même en présence de quantités d'aluminium de l'ordre du gramme. On décrit le dosage du fer et de l'aluminium dans le filtrat après séparation du titane.

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APPLICATION OF CONSTANT CURRENT POTENTIAL LIMIT COULOMETRY TO CHEMICAL ANALYSIS

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Summary—Constant current potential limit coulometry has been examined as an alternative to controlled potential coulometry. It has been shown that the accuracy and precision obtainable by this new technique compare favourably with those obtained by controlled potential coulometry. Data are presented on its use in the determination of uranium^{VI}, cadmium^{II} and copper^{II} using various base electrolytes. The study of uranium has been extended to cover the presence of various impurities.

INTRODUCTION

Considerable developments in the analytical technique of coulometry have taken place in recent years and these have been reviewed by Lingane,[1,2] Delahay[3] and Smythe.[4] Coulometric methods of chemical analysis have many advantages over the more classical titrimetric techniques and amongst these are their inherent precision, accuracy, specificity and the ease of completely automatic instrumentation.

Two systems of coulometric analysis have been distinguished, firstly that described as "constant current coulometry" and secondly, "controlled potential coulometry". The instrumentation for accurate and precise coulometry is simpler and less expensive if based on the "constant current" system. A comparison between the two techniques shows, however, that the "controlled potential" system is more versatile and in a laboratory carrying out a wide variety of analysis it would therefore be more useful. No equipment was commercially available in United Kingdom for controlled potential coulometry and because the cost of developing an essentially constant current system would be less than a controlled potential system of the same overall accuracy, development work was concentrated on a variation of the former technique. Booman has suggested[5] that constant current potential limit (CCPL) coulometry is a valid alternative to controlled potential coulometry. It has the simplicity of a constant current system with the versatility of the controlled potential system.

This paper discusses the development of a CCPL system and its application to chemical analysis involving iron^{III}, cadmium^{II}, uranium^{VI} and copper^{II}.

CONSTANT CURRENT POTENTIAL LIMIT COULOMETRY

The equipment for this type of analysis consists essentially of (a) an instrument capable of delivering accurately known currents to an electrolyte via a working electrode, a method of measuring the potential of this electrode and a method of changing the current levels when the potential attains some predetermined value, and (b) an electrolytic cell with several electrodes. The technique of constant current

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potential limit coulometry operates as follows. Consider a solution containing various ions which can be reduced to lower valency states; then, if a known measured current is passed through this solution, the working electrodes will attain a potential which is governed by the potential characteristic of the most electropositive ion in the solution. As the ions of this type which are in the vicinity of the working electrode are reduced, migration of unreduced ions towards the working electrode will commence under the influence of the concentration gradient formed by this reduction process. If high levels of current are being passed, then the ions being reduced will no longer be able to carry all of the current and the potential of the working electrode will change until another type of ion begins to be reduced. The constant current potential limit coulometer, does not however, allow the potential of the working electrode to rise above that required to reduce the first type of ion; when the potential reaches this value (which has been set into the equipment) the instrument automatically switches to a lower current range. Now the speed of migration of ions is faster than the reduction, therefore, the potential does not rise to the limiting value until the reduction has proceeded further, when the instrument again "trips" and changes to a still lower current range, and so the process is repeated until the concentration of residual unreduced ions is very small compared with the original concentration. From the current levels, the time spent at these various levels and Faraday's Laws, the quantity of the species being reduced can be derived.

CCPL coulometer

The design parameters of a CCPL coulometer were formulated[6] at the Dounreay Experimental Reactor Establishment of the U.K.A.E.A. and, in conjunction with Electronic Instruments Limited (Richmond, Surrey, England), a prototype coulometer was built. A simplified diagram of the circuit of this coulometer is shown in Fig. 1.

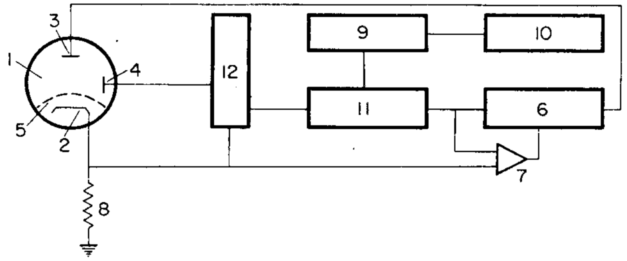

FIG. 1.—Circuit of C.C.P.L. coulometer:

1. Electrolytic Cell	7. Comparison Amplifier
2. Cathode	8. Cathode Resistor
3. Anode	9. Crystal Oscillator Timing Pulse Source
4. Reference Electrode	10. Electronic Ring Counter Register
5. Compartment Separator	11. Pulse Control Switch
6. Current Regulator	12. Potential Detector

The coulometric electrolytic cell (1) has three electrodes, the cathode (2), the anode (3) and the reference electrode (4) (for most of the work described in this paper the cathode has been the working electrode); a compartment separator (5) is used to separate the anode and cathode. Current, supplied to the anode from a current regulator (6), is varied by an error signal from a comparison amplifier (7). The inputs to this amplifier are derived from (a) the cell current as represented by a potential difference across a cathode resistor (8), and (b) a reference voltage from a standard cell. A crystal oscillator timing pulse source (9) passes pulses to an electronic ring counter register (10), which in common with the reference input to the amplifier (6) is controlled by a switch (11). This switch is operated by a

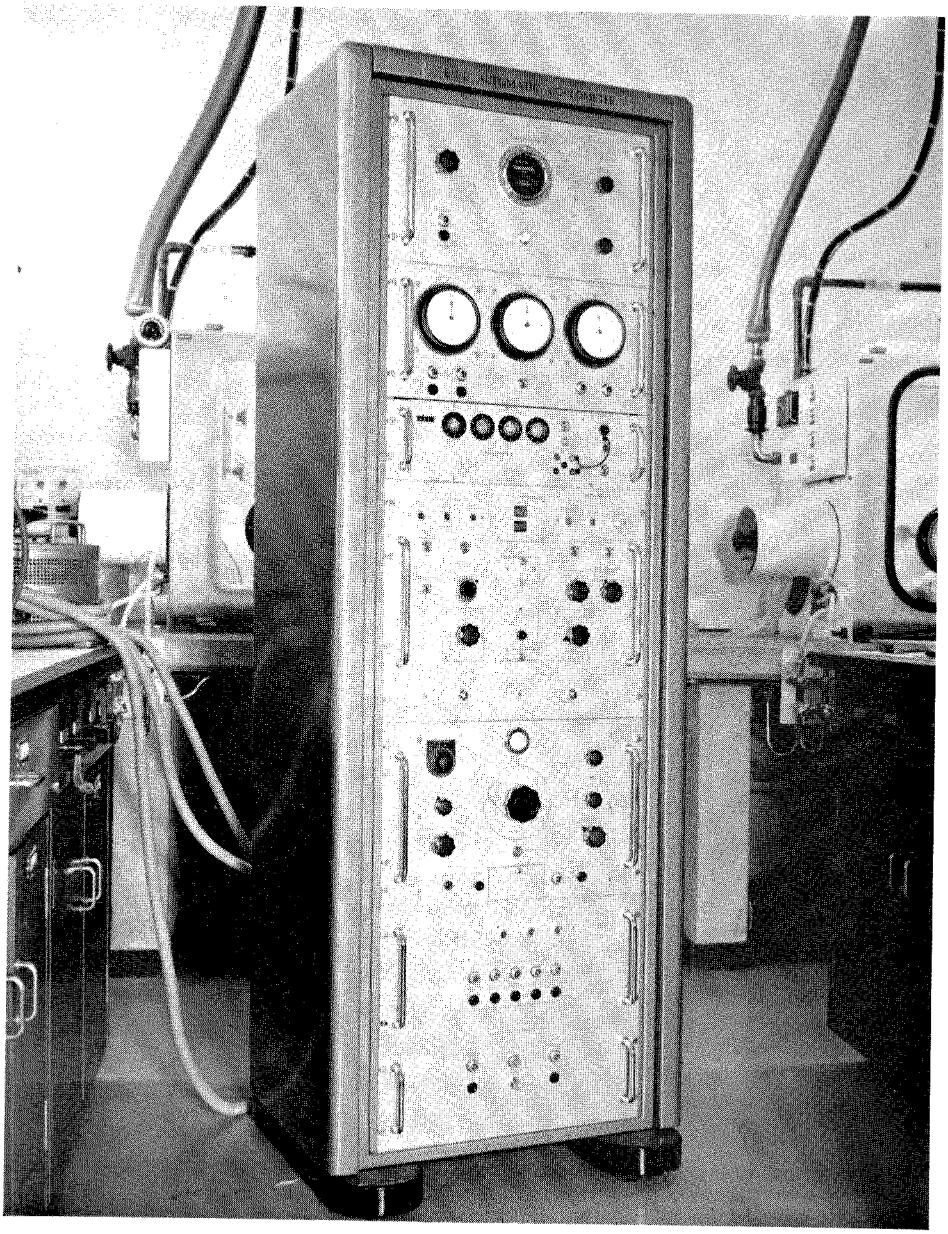

FIG. 2.—Constant current potential limit coulometer.

potential detector (12) connected to the reference electrode (4). The detector and switch are adapted to operate in the manner of overvoltage relays which, when a pre-set potential is reached by the reference electrode, causes a stepwise decrease on a binary scale of both the current and the timing pulse frequency.

The final prototype model of the coulometer which was developed is shown in Fig. 2. Data on the limiting potential, the prereduction potential and a "finish current" level are set into this instrument, the cell containing the ion under investigation in a suitable electrolyte is connected and then the titration started. The coulometer automatically goes through all of the current ranges, then presents, by display, the total number of coulombs used in the titration.

Electrolytic cell

The work on coulometry which is described in the following sections was done using a mercury pool as the working electrode. The cell used for this work (Fig. 3) represents the culmination of a considerable amount of experimentation. The results indicated that cell dimensions and type can have a marked effect on the accuracy, precision, titration time and background currents which are obtained in an analysis.

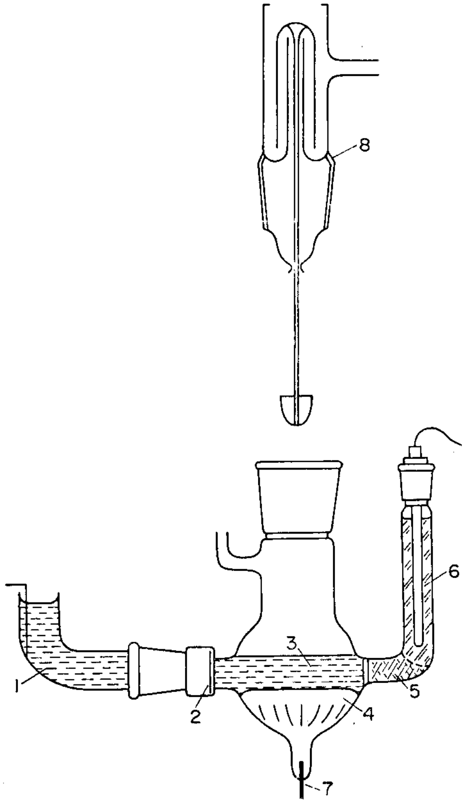

FIG. 3.—Electrolytic cell:

1. Anode Side Arm containing similar Solution to Main Cell
2. Permaplex Cation Exchange Membrane
3. Main Cell containing Electrolyte
4. Mercury Pool Cathode
5. Agar KCl Bridge
6. Reference Electrode Side Arm containing saturated Potassium Chloride Solution
7. Tungsten Wire Fused through Glass
8. Compressed Air Turbine Stirrer

The design of this cell was also conditioned by the requirement that it should be able to be operated remotely behind biological shielding when highly radioactive solutions were being analysed.

This cell, in common with others which have been described in the literature for use in controlled potential techniques, contained separate anode, cathode and indicator electrode compartments. A conventional porous glass sinter saturated with potassium chloride in agar-gel was used to separate the working electrode from the reference electrode. However, contrary to the technique of many other workers in this field, a glass sinter was not used between the anode and cathode compartments; instead, a low resistance ion-exchange membrane (Permaplex C.20) was preferred. The use of this membrane reduced the power ratings required in the transistor amplifier of the coulometer. The cell was also provided with indentation which Booman and Holbrook[7] claim is essential if good precisions are to be obtained.

"White Spot" grade nitrogen, used to remove oxygen from the solution being analysed, was introduced via a sintered glass disc. Satisfactory stirring was achieved using a four-bladed stirrer driven by compressed air, control of stirring rate being maintained by using a precision air pressure regulator connected to a manometer.

THE COULOMETER IN ANALYSES

The development of CCPL coulometric techniques for the determination of ions in solution by direct electroreduction and the recent work of Shults[8] where he electrogenerates a titrant utilising a controlled potential coulometer for the titration of plutonium have now made confusing the accepted use of the terms "constant or controlled potential coulometry" and "constant current coulometry" to describe a type of coulometric analysis. Coulometric techniques are probably better classified by the terms first or second order coulometry, and these can be defined as follows:

A first order coulometric technique is one in which the substance being determined is measured by the direct electroreduction or electro-oxidation at the working electrode of an electrolytic cell.

A second order coulometric technique is one in which the substance being determined is reacted (neutralised, oxidised, reduced, precipitated, *etc.*) with a titrant which is produced in the system by electrogeneration.

First order coulometry

First order coulometry has not been used to the extent that such an absolute method merits. This type of coulometry usually demands a relatively expensive controlled potential or potential limit instrument and this may well have limited its application. First order coulometric techniques must satisfy the following conditions:

(a) A 100% current efficiency for the analytical electrochemical reaction.
(b) The effects of secondary processes must be small.
(c) The electrode reaction must be carried out to virtual completion.

A 100% current efficiency is obtained in coulometric analysis by ensuring that no reducible (or oxidisable) species, which under the conditions of the electrolysis would compete at the electrode with the substance being analysed, are present. Any current resulting from such interference and that derived from the secondary processes is usually called "background current". This "background current" is defined as the difference between the total quantity of electricity actually consumed and the quantity calculated for the faradaic oxidation or reduction of the ion under investigation.

In an electrolytic cell of the type used for coulometric analysis the working electrode is normally separated from the other electrode of the two-electrode system by a potassium chloride-agar bridge. When current is passed through the cell the working electrodes would develop a potential, the magnitude of which depends on the reaction occurring at the electrodes. In an electrolytic reduction:

$$\mathrm{OX_1} + \mathrm{n_1e} \leftrightharpoons \mathrm{RED_1}$$

the potential of the system is governed by the modified Nernst equation, *viz*:

$$\mathrm{E_W} = \mathrm{E_{f_1}} + \frac{\mathrm{RT}}{\mathrm{n_1F}} \ln \frac{(\mathrm{OX_1})}{(\mathrm{RED_1})} + \mathrm{E_{Z_1}}$$

where $\mathrm{E_W}$ = working electrode potential,
$\mathrm{E_{f_1}}$ = formal electrode potential of the couple $\mathrm{OX_1/RED_1}$,
$(\mathrm{OX_1})$ = concentration of oxidised species in the vicinity of the electrode,
$(\mathrm{RED_1})$ = concentration of reduced species in the vicinity of the electrode,
$\mathrm{E_{Z_1}}$ = overpotentials,
$\mathrm{n_1}$ = number of electrons involved in the reaction,
while R, T and F have their usual thermodynamic significance.

As the concentration of the oxidised form decreases, transport of material to the working electrode decreases and hence the potential of the working electrode tends to become more cathodic and in a constant current system it would probably reach a value where $\mathrm{OX_2}$, another reducible species, could start being reduced. In the CCPL system, however, before the potential could reach that which reduced $\mathrm{OX_2}$, the instrument is "tripped" and the current is automatically halved and the reduction continues. This lower current requires a slower transport of material to the electrode. Again when the potential reaches the "pre-set" limit the current is halved; it has been found that after eleven such current steps, in the coulometer described earlier, the reduction is virtually complete. The known currents passing through these stages can readily be integrated and the total number of coulombs involved in the reaction determined. By suitable use of the potential limit system, the pre-reduction system, again at a limiting potential, and by varying the electrolyte, the technique can be made specific to one ion. In a controlled potential system, like the CCPL system, the potential is not allowed to drift above the pre-set "controlled potential"; however, in this case the instrument is designed so that it can integrate the exponentially decaying current.

Second order coulometry

This type of coulometry has been used to a greater extent than first order. It has been preferred probably because of the relatively simple and cheap instrumentation and because the electrogeneration of a titrant is equivalent to a classical chemical titrimetric procedure with very close control over the amount of titrant added. A representative list of applications, given by Delahay,[3] shows that it is relatively simple to transfer to second order coulometry the wealth of knowledge accumulated in titrimetric analysis, thus simplifying the problems of this relatively new analytical technique.

The CCPL instrument which is described in this paper has a function which enables second order titrations to be performed as readily as first order.

EXPERIMENTAL

The cell shown in Fig. 3 was assembled in the following manner. A piece of Permaplex cation exchange resin C.20 was washed several times with demineralised water. Using a No. 10 cork borer a disc was cut from this resin, care being taken to ensure that the disc was not cracked or pierced during the operation. The Quickfit B.19 cone on the side arm and the B.19 socket from the cathode compartment were cleaned and dried. The membrane disc was pushed to the end of the B.19 socket and firmly held in place with the B.19 cone. Hot "picien wax" was then used to seal the whole anode side arm in place. The effectiveness of the membrane as a liquid seal was tested by filling the anode compartment with demineralised water and leaving it for a few hr; no leakage was detected.

An agar-gel saturated with potassium chloride was made by adding 4 g of agar to 100 ml of a saturated solution of potassium chloride and slowly heated until boiling. After boiling for 5–10 min, this solution was transferred whilst hot into the reference side arm and allowed to solidify. A saturated solution of potassium chloride was then added and a standard calomel electrode fitted to the side arm.

Wire connections from the coulometer were soldered to the cell, hence completing the assembly. This preparation procedure was only necessary about once per month after the cell was dismantled for cleaning and changing of the membrane.

Standard solutions of all ions used for trials were made from spectroscopically pure metals or AnalaR grade chemicals dissolved in nitric or sulphuric acid. All electrolytes were made from AnalaR grade chemicals dissolved in demineralised water and were stored in large cells where they were electrolytically purified.

When the equipment was used to determine various redox ions the following procedure was adopted.

The titration cell was washed with approximately 4*M* nitric acid, then three times with demineralised water. Ten ml of triply distilled mercury were added to the cell to form the cathode, care being taken to see that the level of the mercury was below the membrane in the side arm. Seven ml of electrolytically purified electrolyte were then added to the cathode compartment. The anode side arm was filled with electrolyte, care being taken to prevent air bubbles becoming trapped between the membrane and the electrolyte. An aliquot of the sample was transferred to the cell together with any necessary pipette washings. The air turbine stirrer was fitted into the cell and the solution stirred. The stirrer was not rotated at too high a speed because this led to spray losses, high background currents and mercury splashing, all of which led to indifferent results; too slow a stirring rate made the titration time too long. Experience indicated that a cell should be calibrated to determine the most efficient stirring rate and it should be controlled thereafter by using a pressure regulator in conjunction with a mercury manometer. "White Spot" grade nitrogen was passed into the cell via the glass sinter at such a rate that spray losses were avoided.

Whilst the nitrogen was passing into the solution the controls on the coulometer were adjusted.

The start button was then pressed and the instrument was left to complete all of the operations automatically. Table I shows the settings for the determination of uranium in 1*M* sulphuric acid as the electrolyte.

TABLE I.—COULOMETER SETTINGS FOR URANIUM DETERMINATIONS IN 1*M* SULPHURIC ACID

Amount of uranium, *mg*	Pre-reduction potential, *mV*	Potential limit, *mV*	Set start, *mA*	Set stop, *μA*
200–100	−10	−250	256	64
100–20	−10	−250	128	32
20–10	−10	−250	64	32
10–2	−10	−250	16	15

The necessary data on limiting potentials and pre-reduction potentials were obtained from coulograms, *i.e.*, curves of total coulombs against working electrode potential limit. These were obtained as follows: the ions and the supporting electrolytes were placed in the cell and the equilibrium potential of the working electrode (with respect to the saturated colomel electrode) was measured. The initial limiting potential was then set 20 mV more cathodic than this, a suitable selection of current ranges chosen and a CCPL reduction undertaken. The total number of coulombs was recorded, the limiting potential made another 20 mV more cathodic and the whole process repeated. This was continued until it was clear that the ion under investigation was completely reduced. Figs. 4, 5 and 6 show typical coulograms which were recorded during this work.

In the development stages background currents in the cells were determined by using the constant potential circuit and the facility in the coulometer which allows a precision resistor to be placed in

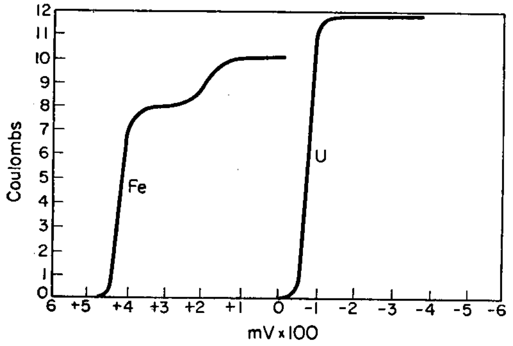

FIG. 4.—Coulograms in 1*M* sulphuric acid.

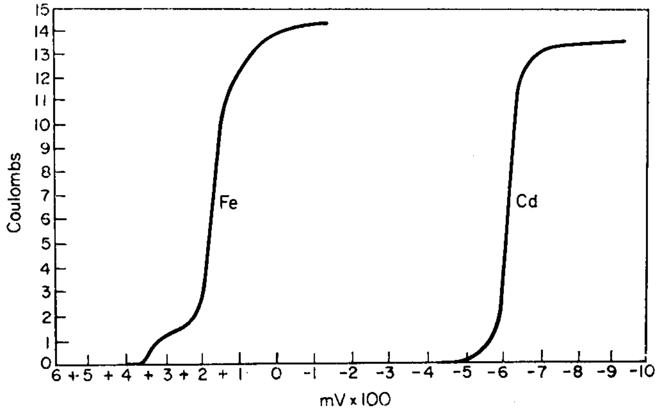

FIG. 5.—Coulograms in 0·5*M* sulphuric acid/0·5*M* potassium citrate.

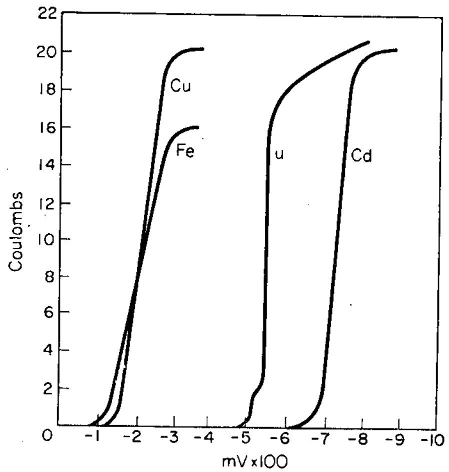

FIG. 6.—Coulograms in 1*M* potassium citrate.

series with the cell. The potential developed across this resistor is measured on a potentiometer with a highly damped galvanometer as the detector. Later this system was replaced by a Model VIII Universal Avometer.

DISCUSSION OF RESULTS

Coulograms of the ions uranium^{VI}, iron^{III}, copper^{II} and cadmium^{II} usually dissolved in 3*M* nitric acid were prepared using (a) 1*M* sulphuric acid, (b) 1*M* potassium citrate, and (c) 0·5*M* sulphuric acid/0·5*M* potassium citrate (Figs. 4, 5 and 6). The general trend was that the $E_{\frac{1}{2}}$ values for the ions were more anodic in the sulphuric acid electrolyte than in the potassium citrate. As would be expected, the reduction of uranium was slower in the potassium citrate medium than in the sulphuric acid. Close control of the pH is essential when using potassium citrate as an electrolyte (Table II). The final acidity of the solution in the cell results from the acid present in the original solution of the ion. Adjustment to the high pH ranges was accomplished by adding sodium hydroxide solution.

Table II.—Effect of hydrogen ion concentration on coulometric data in potassium citrate electrolyte

Element	pH	Pre-reduction potential, *mV*	Potential limit, *mV*
Uranium^{VI}	3·6	−100	−500
	6·4	−340	−600
	7·2	−430	−750
	9·5	−550	−800
Iron^{III}	3·6	+150	−200
	5·0	−25	−250
	6·3	−60	−350
	10·0	−425	−880
Copper^{II}	2·0	+100	−75
	3·5	+50	−150
	6·8	−150	−350
	8·2	−210	−430

A study was made of the magnitude of the background current in the three electrolytes. These experiments showed that 1*M* sulphuric acid can have a background current at −750 mV which is three times greater than for the potassium citrate/sulphuric acid electrolyte and some six times greater than the potassium citrate. Nitric acid solutions of the above mentioned ions are of particular interest at Dounreay and it was found that with 0·2*M* nitric acid in the 1*M* sulphuric acid electrolyte the background current increased six-fold. The presence of this amount of nitric acid in the other two electrolytes had no effect. The stirring rate also increased the background current (Table III); the increases were relatively unimportant for the system containing citrate, but quite important for sulphuric acid, especially when nitric acid was present. It is probable that this increase in background current was caused by dissolution and reduction of the mercury cathode; in some cases the reduction of the hydrogen overpotential of mercury, which has been observed in polarographic work, would also contribute.

Cell design was found to play an important part in background currents. A cell which was twice as large as the one used for this work and which had twice the surface area of cathode, gave rise to background currents which were four to six times greater than those shown in Table III.

TABLE III.—EFFECT OF STIRRING RATE ON BACKGROUND CURRENT.

Cell as shown in Fig. 3; stirrer had four triangular blades, apex of triangle at the centre spindle, distance of apex to base 1·6 cm, base 0·75 cm, and thickness 0·2 cm; 5 ml of electrolyte + 10 ml of mercury for the cathode.

(A) 1*M Sulphuric Acid*

Stirrer speed, *rpm*	Ib, *μA*			
	At −250 mV	At −450 mV	At −600 mV	At −750 mV
40	1	6	10	18
550	6	6	20	30
1150	10	14	22	43
1*M Nitric acid*				
40				4
550				60
1150				120
0·2*M Nitric acid*				
40				36
550				140
1150				275

(B) 0·5*M Sulphuric Acid* + 0·5*M Potassium Citrate*

Stirrer speed, *rpm*	Ib, *μA*			
	At −250 mV	At −450 mV	At −600 mV	At −750 mV
40	2	3	3	6
550	6	8	8	12
1150	13	15	13	26
0·2*M Nitric acid*				
40	3			5
550	8			8
1150	22			18

(C) 1*M Potassium Citrate*

Stirrer speed, *rpm*	Ib, *μA*			
	At −250 mV	At −450 mV	At −600 mV	At −750 mV
40	0·5	1	1	2
550	4	4	5	5
1150	5	4	6	8
0·2*M Nitric acid*				
40	1			1
550	5			2
1150	6			7

In general, the determination of copper, iron and cadmium took longer in the sulphuric acid medium than in the potassium citrate. For example, the time in 1*M* sulphuric acid for 4 mg of copper was about 60 min and for 10 mg of cadmium about 45 min, whereas in potassium citrate the time was about 25 min for both. With uranium the position was reversed, the titration time for 20 mg of uranium in potassium citrate was about 45 min, whilst in sulphuric acid it was about 25 min. This change in the pattern with uranium probably reflects the increased reversibility of the reaction in the acid medium.

Accuracy and precision data were obtained on the measurements of uranium, copper and cadmium dissolved in nitric acid by this technique of CCPL coulometry. These results showed (Table IV) that by suitable choice of electrolyte the bias could be reduced to less than 0·05 % for cadmium, less than 0·1 % for uranium and less than 0·2 % for copper whilst the corresponding coefficients of variation for the elements in the range 3–20 mg were 0·14 %, 0·19 % and 0·14 %, respectively. These results were based on between 20 and 30 determinations of the elements under study by three different operators. The addition of 20 % iron$^{\mathrm{III}}$ with respect to the uranium and 20 % iron$^{\mathrm{III}}$ plus 20 % chromium$^{\mathrm{III}}$, did not increase the bias when uranium was being determined coulometrically using 1*M* sulphuric acid as the supporting electrolyte. At a uranium level of 40 mg with both iron and chromium present, the coefficient of variation was about 0·23 %, slightly worse than without the added chromium and iron.

With 20 mg of uranium in the presence of 150 mR/hr of beta-gamma active fission products the coefficient of variation rose to 0·5 % and a positive bias of +0·8 % was found. Results from Zittel *et al.*[9] using controlled potential coulometry showed a positive bias of +3·0 % in a similar case because of the ruthenium species present.

Table IV.—Accuracy and precision measurements

Element	Approx. level, *mg*	E_p, *mV*	E_L, *mV*	Coefficient of variation, %	Bias, %
1*M Sulphuric acid*					
Cadmium	10	−475	−675	0·40	±0·01
Copper	4	+100	−75	1·0	−0·6
Uranium	15	±0	−250	0·20	0·1
	20			0·26	−0·3
	200			0·21	−0·4*
1*M Potassium citrate* (*pH* 6.4)					
Cadmium	12	−640	−800	0·30	−0·4
Copper	3	−150	−300	0·18	+0·4
Uranium	15	−340	−600	0·19	0·1
0·5*M Sulphuric acid*/0·5*M potassium citrate*					
Cadmium	10	−500	−700	0·14	0·05
Copper	8	+50	−150	0·14	0·2
Uranium		No experimental work			

* Based on a small number of determinations.

The technique of CCPL coulometry was used alongside normal titrimetric procedures for the determination of uranium in the enriched uranium product solution from the chemical processing plants at Dounreay. This showed that the overall accuracy and precision of the method was up to the standard predicted from the development work (Table V).

The only noticeable difference between these results and those that would have been anticipated from earlier work, was that coulometric titration times were slightly longer than expected. The reason for this is not fully understood but it is thought

TABLE V.—DETERMINATION OF HIGHLY ENRICHED URANIUM IN CHEMICAL PROCESSING STREAMS

Standard titrimetric analytical procedure, *mg/ml*	CCPL Coulometer, *mg/ml*		
	$1M$ Sulphuric acid	$0{\cdot}5M$ Sulphuric acid/ $0{\cdot}5M$ potassium citrate	$1M$ Potassium citrate
39·2	39·09	38·95	—
	39·05	—	—
34·4	34·33	34·37	—
33·3	33·25	33·18	33·20
29·9	29·87	30·10	29·99
16·4	16·42	—	—

to be caused by the presence of slight traces of organic materials carried through from the solvent extraction process in the chemical plants.

The results obtained by the technique of constant current potential limit coulometry compare very favourably with those obtained in controlled potential coulometry by workers such as Boyd and Menis,[10] Hobbs[11] and Stromatt and Conally,[12] and furthermore they show that this is a precise and accurate method of chemical analysis.

Zusammenfassung—Coulometrie bei konstantem Strom und begrenztem Potential wurde als Ersatz für Coulometrie bei kontrolliertem Potential untersucht. Es wurde gezeigt, dass Genauigkeit und Präzision der neuen Methode sehr gut mit der der alten konkurrieren kann. Daten über die Bestimmung von Uran, Cadmium und Kupfer in verschiedenen Elektrolyten werden mitgeteilt. Die Studie über Uran wurde ausgedehnt und schliesst Untersuchungen über verschiedene Verunreinigungen ein.

Résumé—La coulométrie à potentiel limite, à courant constant, se présente comme une variante de la coulométrie à potentiel controlé. La finesse et la précision du résultat sont comparables à celles que l'on obtient par coulométrie à potentiel contrôlé. Résultats concernant le dosage de l'uranium, du cadmium et du cuivre dans des électrolytes variés. L'étude concernant l'uranium s'étend à la recherche des diverses impuretés.

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SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF RARE EARTHS*

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Summary—At the present time arsenazo appears to be widely used for the spectrophotometric determination of rare earths. Unfortunately, the method is not selective. The separation of rare earths and yttrium from interfering elements has been studied, and the following method is proposed. Rare earths are precipitated as fluorides using calcium fluoride as the carrier. Thorium and zirconium are removed by extraction with thenoyltrifluoroacetone (TTA) in xylene at pH 1·3. Small amounts of residual aluminium, iron, *etc.*, are removed by extraction with 8-quinolinol-chloroform at pH 4·5. Rare earths are separated from calcium by TTA extraction at the same pH, then they are back-extracted into 1*M* nitric acid. After evaporation of the solution, the rare earths are determined spectrophotometrically with arsenazo.

INTRODUCTION

ALTHOUGH arsenazo is not particularly selective, it appears to be widely used for the spectrophotometric determination of the rare earths and yttrium at the present time. New reagents such as bromopyrogallol red,[1] salicylfluorone,[2] and arsenazo III[3] do not seem to be definitely more selective than arsenazo. Arsenazo III is, however, much more sensitive than arsenazo. Yttrium may be determined spectrophotometrically with pyrocatechol violet after a preliminary separation from iron, uranium, zirconium, thorium and molybdenum with tri-n-octylphosphine oxide.[4] However, the behaviour of rare earths and scandium remains to be established. Thus, a generally applicable method is needed for the separation of rare earths.

Arsenazo has been used for the determination of rare earths in uranium,[5,6] cast steels,[7] ores and rocks,[8] and soils.[9] A method was proposed for the successive determination of rare earths and thorium with arsenazo.[10]

Previously reported procedures have been developed for specific problems and are consequently somewhat limited in their applicability. For the purpose of extending the applicability of the spectrophotometric determination of rare earths with arsenazo, the separation of these elements from interfering elements has been studied.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Beckman Model DU spectrophotometer, using 1-cm cells. A Beckman Model G pH meter was used for pH measurements. For centrifugal separations, an International clinical centrifuge with 50-ml Lusteroid tubes was used. A shaking machine, Burrell shaker, with a time switch was used for extractions.

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Reagents

Calcium nitrate solution (10 mg of Ca/ml): 5·89 g of $Ca(NO_3)_2 \cdot 4H_2O$ in 100 ml of water.

0·5*M Thenoyltrifluoroacetone* (TTA) solution: 45 g in 400 ml of xylene.

5% 8-*Quinolinol solution:* Dissolve 5·0 g of 8-quinolinol in 10 ml of glacial acetic acid and dilute the solution to 100 ml with water.

3·5*M Ammonium acetate solution:* 135 g in 500 ml of water.

Acetic acid-sodium acetate solution: Mix 0·1*M* acetic acid and 0·1*M* sodium acetate (13·6 g of $NaC_2H_3O_2 \cdot 3H_2O$ in 1 litre of water) so that the pH of the mixture becomes 4·6 ± 0·1. Instead of sodium acetate, ammonium acetate may be used.

0·1% *Arsenazo solution:* 0·10 g in 100 ml of water.

Triethanolamine buffer solution: Mix 400 ml of 15% (w/v) triethanolamine solution, 330 ml of 1*M* nitric acid and 70 ml of water. Adjust the pH to 7·2 ± 0·1 with dilute nitric acid or aqueous ammonia.

Standard cerium solution (1·00 mg of Ce/ml): Add 10 ml of water, 10 ml of 70% perchloric acid and 1 ml of 30% hydrogen peroxide to 0·1228 g of previously ignited CeO_2. On heating, the oxide dissolves and the resulting solution is evaporated to dryness. Add 10 ml of 1*M* nitric acid and 1 ml of 30% hydrogen peroxide, and boil the solution for 5 min. After cooling, dilute the solution to exactly 100 ml with water.

Standard solutions of gadolinium (1 mg of Gd/ml) *and yttrium* (1 mg of Y/ml): The oxides are ignited and weighed. Dissolve them in a slight excess of nitric acid, and dilute the solutions to appropriate volumes with water.

Fluoride precipitation

Transfer the sample solution (0·5*M* in nitric acid and containing 20–100 μg of rare-earth metals or 10–60 μg of yttrium in a volume of approximately 50 ml) to a polyethylene beaker and add 1·0 ml of calcium nitrate solution and 10 ml of 48% hydrofluoric acid. Set the solution aside overnight.

Transfer the fluorides to a 50-ml Lusteroid centrifuge tube and separate at the full speed of the centrifuge for about 5 min. Carefully pour off the supernatant liquid. Wash the precipitate 3 times with 10-ml portions of 1:5 hydrofluoric acid Transfer the precipitate to a platinum dish with a minimum amount of 2*M* nitric acid. Add 2 ml of 70% perchloric acid and evaporate the solution to near dryness. (Note: If iron is present, it is important that the solution not be evaporated to complete dryness.).

TTA extraction at pH 1·3

Dissolve the residue in 7·0 ml of 0·1*M* nitric acid and transfer the solution to a 60-ml separatory funnel. Wash the dish with 7 ml of water. (If necessary, confirm that the pH of the solution is 1·3 ± 0·1). Shake the solution for 5 min with 10 ml of TTA solution. When the layers have separated, drain off the aqueous phase into a second separatory funnel. Discard the organic phase. Add 10 ml of TTA solution to the second separatory funnel. Shake the system for 5 min and discard the organic phase. Wash the aqueous phase by shaking it for 10 sec with 10 ml of xylene and discard the organic phase.

8-*Quinolinol extraction*

To the aqueous phase add 1·0 ml of 8-quinolinol solution, 1·0 ml of ammonium acetate solution and 1·0 ml of 0·7*M* ammonia solution. If the pH of the solution is not in the range 4·5 to 4·8, adjust with dilute nitric acid or aqueous ammonia. Add 20 ml of chloroform and shake the system for 1 min. When the layers have separated, drain off and discard the organic phase. Add 0·3 ml of 8-quinolinol solution and 20 ml of chloroform and equilibrate the phases for 1 min. Discard the organic phase. Wash the aqueous phase by shaking it for 10 sec with 20 ml of chloroform and discard the organic phase.

TTA extraction at pH 4·5

Shake the aqueous phase for 5 min with 15 ml of TTA solution. When the layers have separated, drain off the aqueous phase into a second separatory funnel. Add 15 ml of TTA solution to the second separatory funnel. Shake the system for 5 min and discard the aqueous phase. Combine the second extract with the first and wash the extracts by equilibrating them for 10 sec with 10 ml of acetic acid-sodium acetate solution. Discard the aqeuous phase.

Shake the organic phase for 5 min with 25 ml of 1*M* nitric acid. Transfer the aqueous phase to another separatory funnel. Discard the organic phase. Shake the aqueous phase for 10 sec with 10 ml of xylene. Transfer the aqueous phase to a 50-ml beaker and evaporate to dryness. To the residue add 1 ml of 70% perchloric acid and 1 ml of concentrated nitric acid. Evaporate the solution to dryness. Wash the sides of the beaker with a minimum amount of water and evaporate the solution to dryness.

Spectrophotometric determination of rare earths

Dissolve the residue in 1·0 ml of 0·1*M* nitric acid. Add 4 ml of water, mix, then add 2·0 ml of 0·1% arsenazo solution. Add 5·0 ml of triethanolamine buffer solution and 1·0 ml of 0·1*M* ammonia solution. Confirm that the pH of the solution is 7·2 ± 0·1. Transfer the solution to a 25-ml volumetric flask and dilute to the mark with water. Measure the absorbance of the solution in a 1-cm cell at 580 mμ, using water (or reagent blank) as the reference.

Construct a calibration curve by taking, for example, 0, 25, 50 and 75 μg of rare-earth metals or 0, 20, 40 and 60 μg of yttrium and carrying them through the entire procedure using water (or reagent blank) as the reference.

RESULTS AND DISCUSSION

Interference study

Kuznetsov[11] has reported that arsenazo forms coloured solutions or precipitates with the following ions in neutral media: rare earths, scandium, yttrium, uranium^{VI}, copper, aluminium, vanadium^{IV}, thorium, zirconium, gallium, indium, palladium, iron^{III}, titanium and chromium^{III}. Beryllium also[12] gives a colour. Because no quantitative data on interferences in the determination of the rare earths have been published, the absorbances of the solutions (pH 7·2, 25 ml) containing metal ions and arsenazo were measured at 580 mμ. The results are shown in Table I. Gadolinium was chosen to represent rare earths. Previous work[10] has shown that the absorbance of 20 μg of thorium is nearly the same as that of 16 μg of gadolinium. Among the elements studied, only thorium, uranium and zirconium gave straight-line calibration curves. The molar absorptivities for these elements were $2{\cdot}9 \times 10^4$, $2{\cdot}0 \times 10^4$ and $1{\cdot}3 \times 10^4$, respectively. Other elements showed deviations from Beer's law.

Fluoride precipitation

Sandell[13] has suggested the use of calcium salts or strontium salts as a carrier in the precipitation of small amounts of rare earths as fluorides or oxalates. Bornong

TABLE I.—COLOUR REACTIONS OF METALS WITH ARSENAZO

Metal, *mg*		Absorbance	Gd equal to absorbance, *μg*
Al^{III}	0·030	0·526	76
Ca^{II}	0·10	0·012	2
Cd^{II}	0·10	0·015	2
Co^{II}	0·10	0·087	13
Cr^{III}	0·10	0·32[a]	46
Cu^{II}	0·10	0·174	25
Fe^{III}	0·10	0·369	53
Mg^{II}	0·10	0·041	6
Mn^{II}	0·10	0·095	14
Mo^{VI}	0·20[b]	0·000	0
Ni^{II}	0·10	0·075	10
Pb^{II}	0·10[b]	0·007	1
Sc^{III}	0·050	0·678	98
U^{VI}	0·050	0·171	25
Zn^{II}	0·050	0·050	7
Zr^{IV}	0·10	0·563	81

[a] Absorbance increases with time. Measurement was made 25 min after addition of reagents.

[b] This amount of Mo or Pb does not interfere with the determination of 53 μg of Gd.

and Moriarty[7] used thorium as a carrier for the precipitation of rare-earth fluorides and oxalates. Because thorium is a more serious interference in the arsenazo method than is calcium, the latter was chosen as a carrier in the present work. The optimal conditions for the fluoride precipitation, as described in the procedure, gave 92–94% recovery of the gadolinium. Calcium was removed by TTA extraction at pH 4·5 prior to the gadolinium determination.

All of the recoveries in Tables II to V were calculated by referring to the calibration curve obtained without the separation of gadolinium, cerium, or yttrium. The recoveries from fluoride precipitation and TTA extraction are close to those from TTA extraction at pH 4·5 (Table III) indicating almost complete precipitation of gadolinium as fluoride.

Under the optimum conditions for the precipitation of gadolinium fluoride, 5 and 21 mg of iron^{III} gave absorbances corresponding to 15 μg and 14 μg of gadolinium, respectively. Ten mg of aluminium gave an absorbance of about 1·8; more than 0·1 mg of aluminium was, therefore, found in the fluoride precipitate.

8-Quinolinol–chloroform extraction

Because complete removal of iron and aluminium from rare earths was not effected either by fluoride precipitation or by TTA extractions, 8-quinolinol–chloroform extraction was examined. The following method was found to be applicable to at least 1 mg each of iron and of aluminium:

To a 10-ml aqueous solution, 1·0 ml of 5% 8-quinolinol in dilute acetic acid, 1·0 ml of 3·5M ammonium acetate solution and 3 ml of water were added. The pH of the solution was 4·8. Twenty ml of chloroform were added and the system was shaken for 1 min. After removal of the organic phase, 0·3 ml of 5% 8-quinolinol solution and 20 ml of chloroform were added and the system was shaken for 1 min. The organic phase was removed and the aqueous phase was shaken for 1 min with 20 ml of chloroform. The aqueous phase was evaporated to dryness. Three ml of concentrated nitric acid and 1 ml of concentrated hydrochloric acid were added and the solution was again evaporated to dryness. Gadolinium was then determined by the arsenazo method.

By this method, 53 μg of gadolinium were separated from the solutions containing 1 mg each of aluminium and of iron^{III}. The recovery of gadolinium was 98–99%.

At pH 4·5 the following ions will also be extracted into 8-quinolinol-chloroform: copper, gallium, indium, molybdenum^{VI}, niobium, nickel, tin^{IV}, titanium, thallium^{III} and vanadium.[13,14,15] Cobalt, manganese and lead will not be extracted.

TTA extraction at pH 1·3

Feldman and Ellenburg[16] separated a small amount (not specified) of thorium from rare earths by extraction with TTA in xylene at pH 1·0 and at 60°. The following experiments were conducted in order to know if complete removal of thorium would be achieved at room temperature (*ca.* 25°):

Aqueous phase: about 15 ml, pH 1·3 (0·05M in nitric acid).
Three extractions (5 min each) with 10-ml portions of 0·5M TTA solution in xylene.
The aqueous phase was washed with 10 ml of xylene and evaporated to dryness. After destruction of organic matter with nitric and perchloric acids, gadolinium was determined with arsenazo.

As shown in Table II, gadolinium can be separated from 10 mg of thorium. For less than 1 mg of thorium, two extractions are sufficient. The TTA extraction at pH 1·3 also removes copper, scandium and zirconium. Extractions of iron^{III} and uranium^{VI} are very incomplete.

TABLE II.—DETERMINATION OF GADOLINIUM AFTER TTA EXTRACTION AT pH 1·3

Addition, *mg*		Gd taken, *μg*	Gd found,[a] *μg*	Average recovery, %
—		—	0·7, 0·7	—
—		53·0	50, 50	94
Cu	1·0	—	0·0[b], 0·0[b]	—
Cu	1·0	53·0	50[b], 50[b]	94
Fe^{III}	0·10	—	17, 11	—
Fe^{III}	0·0125	—	1·0, 1·0	—
Fe^{III}	0·0125	53·0	49, 49	92
Sc	0·10	—	0·7, 1·0	—
Sc	0·10	53·0	48, 49	92
Th	10	—	1·5, 1·5	—
Th	10	53·0	50, 51	95
Th	20	—	4·5, 5·5	—
Th	20	53·0	49, 50	93
Th	5, 0·014 mmole Na_2SO_4	—	0·0, 0·0	—
Th	5, 0·014 mmole Na_2SO_4	53·0	50, 50	94
U^{VI}	0·10	—	23, 24	—
U^{VI}	0·10	53·0	48, 49	92
Zr	1·0	—	0·0, 0·0	—
Zr	1·0	53·0	50, 49	93

[a] Values obtained with 53 μg of Gd were corrected for respective blanks.
[b] Two TTA extractions.

TTA extraction at pH 4·5

After removal of thorium, Feldman and Ellenburg[16] extracted rare earths with TTA in xylene at pH 4·5 and at 60° and determined them spectrographically. Menis *et al.*[17] extracted lanthanum into TTA in 4-methyl-2-pentanone and determined it by a flame photometer. In the present work, the extraction of gadolinium at room temperature was studied under the following conditions:

Aqueous phase: about 10 ml, pH 4·5 (0·1*M* in acetate).

Two extractions (5 min each) with 10-ml portions of 0·5*M* TTA solution in xylene. The combined organic phase was washed with 10 ml of pH 4·5 solution (0·1*M* in acetate).

Back-extraction (5 min) of gadolinium with 15 ml of 1*M* nitric acid. The back-extract was washed with 10 ml of xylene.

The aqueous phase was evaporated to dryness. After destruction of organic matter, gadolinium was determined with arsenazo.

The results are shown in Table III.

TABLE III.—DETERMINATION OF GADOLINIUM AFTER TTA EXTRACTION AT pH 4·5

Addition	Gd taken, *μg*	Gd found,[a] *μg*	Average recovery, %
—	15·9	15, 15	94
—	53·0	50, 50	94
—	79·5	75, 75	94
1·0 mmole Na_2SO_4	53·0	49, 50	93
10 mg Mg	53·0	49, 50	93
10 mg Ca	53·0	51, 51	96
20 mg Ca	53·0	51, 51	96
1·0 mg Cd	53·0	50, 50	94

[a] Corrected for blanks which were in the range 1·0–2·5 μg of Gd.

Back-extraction of gadolinium with 2*M* nitric acid gave the same recovery, *i.e.*, 95% with 53 μg of gadolinium. Double back-extractions with 15 ml and 10 ml of 1*M* nitric acid did not improve the recovery, *i.e.*, 95% with 53 μg of gadolinium.

Positive interferences were observed with 1·0 mg of silver, 1·0 mg of molybdenum^{VI}, 1·0 mg of lead and 0·1 mg of zinc. It may be concluded that the TTA extraction at pH 4·5 is suitable only for the separation of rare earths from magnesium, calcium and probably strontium and barium.

By carrying out three TTA extractions at pH 1·3 and two TTA extractions at pH 4·5, 53 μg of gadolinium were separated from 10 mg each of thorium and of calcium. The recovery of gadolinium was 91%.

TABLE IV.—SEPARATION OF GADOLINIUM FROM OTHER ELEMENTS
(TTA extraction at pH 1·3 omitted)

Addition, *mg*		Gd taken, μg	Gd found,[a] μg	Average recovery, %
—		—	1·5, 1·7	—
—		53·0	51, 51	96
Al	20	—	0·7, 0·4	—
Al	20	53·0	50, 50	94
Co^{II}	1·0	—	0·7, 0·4	—
Co^{II}	1·0	53·0	51, 50	95
Cr^{III}	1·0	—	0·0, 0·0	—
Cr^{III}	1·0	53·0	50, 50	94
Cu (as $CuSO_4$)	51	—	1·0, 0·7	—
Cu (as $CuSO_4$)	51	53·0	50, 51	95
Fe^{III}	42	—	0·6, 1·3	—
Fe^{III}	42	53·0	50, 49	93
Fe^{III}	84	—	0·4, 1·3	—
Fe^{III}	84	53·0	50, 50	94
Mn^{II}	10	—	7·0, 7·5	—
Mn^{II}	10	53·0	50, 48	92
Mn^{II}	1·0	—	2·0, 2·5	—
Mn^{II}	1·0	53·0	51, 51	96
Mo (as ammonium molybdate)	20	—	1·6, 1·4	—
Mo (as ammonium molybdate)	20	53·0	51, 50	95
Nb	20	—	0·0, 0·0	—
Nb	20	53·0	50, 49	93
Ni	15	—	0·6, 0·3	—
Ni	15	53·0	50, 51	95
P (as KH_2PO_4)	10	—	0·0, 0·0	—
P (as KH_2PO_4)	10	53·0	51, 51	96
Pb	5·0	—	110, 110	—
Pb	0·10	—	2·4, 2·1	—
Pb	0·10	53·0	50, 49	93
Ti	20	—	0·2, 0·6	—
Ti	20	53·0	51, 50	95
U^{VI}	10	—	32, 32	—
U^{VI}	0·20	—	2·5, 2·0	—
U^{VI}	0·20	53·0	51, 51	96
V^{V}	5·0	—	0·9, 0·0	—
V^{V}	5·0	53·0	51, 50	95
W^{VI}	10	—	1·9, 1·4	—
W^{VI}	10	53·0	50, 50	94
Zn	2·0	—	2·2, 1·9	—
Zn	2·0	53·0	51, 51	96

[a] Values obtained with 53 μg of Gd were corrected for respective blanks.

Procedure in the absence of thorium

When thorium and zirconium are absent from the sample, the TTA extraction at pH 1·3 can be omitted. If the sample contains microgram amounts of thorium, the method described previously by Onishi *et al.*[10] can be applied. The procedure that consists of fluoride precipitation, 8-quinolinol-chloroform extraction at pH 4·5–4·8 and TTA-xylene extraction at the same pH provides for the presence of many elements (Table IV). The separation of milligram amounts of lead and uranium from rare earths is not satisfactory. Lead was precipitated almost completely as fluoride, and further purification steps did not remove lead. Methods for the separation of rare earths from uranium[5,6] have previously been published. The work of Young, White and Ball[4] suggests that an extraction with tri-n-octylphosphine oxide might very well be used to remove uranium, thorium, and zirconium.

General procedure

Results obtained in applying the proposed procedure are collected in Table V.

In the presence of 1 mg of zirconium, an emulsion was formed during the TTA extraction at pH 1·3. It was found that evaporation of the perchloric acid solution of calcium and zirconium to dryness caused this emulsion formation. From Table V it is seen that 10 mg of thorium are not so effective as 10 mg of calcium as a carrier for gadolinium.

The average recovery of the last 4 experiments in Table V is 90%. This value is very close to the average of 91% for the first 5 experiments in the same table, and the construction of the calibration curve through the entire procedure is justified.

TABLE V.—SEPARATION OF RARE EARTHS FROM OTHER ELEMENTS BY GENERAL PROCEDURE

Addition, *mg*				Rare earth			Average recovery, %
					Taken, *μg*	Found,[a] *μg*	
—				—	—	0·0–0·6[b]	—
—				Gd	21·2	20, 19	92
—				Gd	53·0	48, 48	91
—				Gd	79·5	71, 72	90
—				Ce	58·0	52, 52	90
—				Y	39·0	35, 35	90
Th	10			—	—	1·1[c], 1·1[c]	—
Th	10			Gd	53·0	40[c], 40[c]	75
Th	10			—	—	1·9[d], 1·7[d]	—
Th	10			Gd	53·0	46[d], 46[d]	87
Sc	1.0			—	—	2·4, 2·4	—
Sc	1·0			Gd	53·0	47, 47	89
Zr	0·10			—	—	0·0, 0·3	—
Zr	0·10			Gd	53·0	47, 47	89
Th	1·0			—	—	0·6, 0·4	—
Th	1·0			Gd	53·0	48, 49	92
Fe^{III}	42	Th	1·0	—	—	0·9, 0·9	—
Fe^{III}	42	Th	1·0	Gd	53·0	47, 48	90

[a] Values obtained with rare earths were corrected for respective blanks.

[b] Av. of 10 experiments = 0·2 μg.

[c] Fluoride precipitation without Ca; three TTA extractions at pH 1·3.

[d] Three TTA extractions at pH 1·3.

It may be mentioned that the method of Bornong and Moriarty[7] for the determination of rare earths in cast steels gave an average recovery of 89%, with a coefficient of variation of 7%. The present method gives more reproducible results.

Excluding the time of digestion of the fluoride precipitates, a complete analysis requires 8 to 10 hrs.

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Zusammenfassung—Gegenwärtig scheint Arsenazo weite Verbreitung als Reagens zur photometrischen Bestimmung der seltenen Erden zu finden. Leider ist die Methode nicht selektiv. Daher wurde die Abtrennung der S.E. und des Yttriums von störenden Elementen untersucht und die folgende Methode entwickelt. Die S.E. werden als Fluoride gefällt wobei Calciumfluorid als Fänger dient. Th und Zr werden durch Extraktion mit Theonyltrifluoroazeton (TTA) in Xylol bei pH 1·3 entfernt. Kleine Mengen an verbleibendem Al, Fe usw. werden durch eine Oxinextraktion in Chloroform bei pH 4·5 entfernt. Die Trennung der S.E. von Calcium geschieht mittels TTA-Extraktion bei dem gleichen pH-Wert. Nach Eindampfen der Lösungen werden die S.E. mit Arsenazo spektrophotometrisch bestimmt.

Résumé—A l'heure actuelle les arsenazo sont très utilisés dans le dosage spectrophotométrique des terres rares. Cependant, cette méthode n'est pas sélective. L'étude de la séparation des éléments des terres rares et de l'yttrium des éléments gênants, permet de proposer la méthode suivante. Les éléments des terres rares sont précipités sous forme de fluorures par le fluorure de calcium. On élimine le thorium et le zirconium par extraction au moyen de la thenoyltrifluoracétone (TTA) dans le xylène à pH 1,3. Des petites quantités résiduelles d'aluminium, de fer, etc... sont éliminées par extraction au 8-quinolinol-chloroforme à pH 4,5. Les terres rares sont alors séparées du calcium par extraction au TTA dans les mêmes conditions de pH et finalement extraites par l'acide nitrique 1*M*. Après évaporation du solvant, on dose les terres rares par spectrophotométrie avec les arsenazo.

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DETERMINATION OF COPPER IN HIGH-PURITY NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN METALS WITH BATHOCUPROÏNE*

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Summary—A spectrophotometric method for determining 0·0005–0·125% of copper in high-purity niobium, tantalum, molybdenum and tungsten metals is described. After sample dissolution and reduction of copper to the univalent state with ascorbic acid, the yellow complex formed by copper^I and bathocuproïne (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) is extracted into n-amyl alcohol and the absorbance of the resulting extract is determined at 476 mμ. Other impurities present in the four high-purity metals described do not interfere in the proposed method.

INTRODUCTION

AN analytical project involving the determination of impurities in high-purity niobium, tantalum, molybdenum and tungsten metals is currently being conducted at the Mines Branch laboratories. As part of this project, the present investigation was undertaken to develop a suitable spectrophotometric procedure for determining trace amounts of copper that would be applicable to all four metals.

Several spectrophotometric procedures have previously been applied to the determination of small amounts of copper in matrices of the above metals,[1–7] but none of these methods were directly applicable to all four metals under consideration without some modifications.

Recently, Penner and Inman[8] reported a method for the determination of iron in the above metals. It was considered that the dissolution procedure and solution preparation described in this method would be easily adaptable to a procedure for copper in which the copper was extracted as a coloured complex with an organic solvent. Bathocuproïne was chosen as the chromogenic reagent in this investigation because of its sensitivity, reported specificity, and the solubility of its copper^I complex in various organic solvents.[9,10,11] It is the most sensitive of the three cuproïne reagents; its copper^I derivative has a molar extinction coefficient of 14,160 compared to 6,220 for cuproïne and 7,950 for neocuproïne.[10] Smith and Wilkins[9] first investigated its analytical potential and applied it to the determination of copper in iron.

This paper describes the successful use of bathocuproïne in determining copper in high-purity niobium, tantalum, molybdenum and tungsten metals. Moderate amounts (5 mg) of cobalt, cadmium, chromium, nickel, manganese and zinc do not interfere in this method.

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EXPERIMENTAL

Apparatus

Spectrophotometer: Beckman Model DU.
pH meter: Leeds and Northrup.
Centrifuge: Clinical type.
Teflon (tetrafluoro-ethylene) beakers, 250 ml: Dynalab Corp., Rochester, N.Y.

Reagents

Water: De-ionised by passing distilled water through a column of Dowex 50W-X8 resin.

Standard copper solution: Dissolve 0·1000 g of pure copper in 10 ml of 1:1 nitric acid. Add 5 ml of concentrated perchloric acid and evaporate to fumes of perchloric acid. Cool, dilute to 500 ml with water and store in a polyethylene bottle. Dilute 5 ml of this stock solution to 200 ml with water. Prepare fresh as needed (1 ml of this diluted solution = 5 μg of copper).

Bathocuproïne, 0·002M solution: Dissolve 0·360 g of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (G. Frederick Smith Chemical Co.) in 500 ml of ethyl alcohol and store in a polyethylene bottle.

Ammonium tartrate, 25%, copper-free solution:* Dissolve 125 g of ammonium tartrate and 1 g of hydroxylamine hydrochloride in approximately 350 ml of water. Add 20 ml of bathocuproïne solution, allow to stand for 1 hr, then extract three times with 15-ml portions of a 3:1 mixture of chloroform and n-amyl alcohol. Extract the copper-free solution three times with chloroform to remove excess n-amyl alcohol. Filter, dilute to 500 ml with water and store in a polyethylene bottle.

*Boric acid, 5%, copper-free solution**: Dissolve 50 g of boric acid in approximately 800 ml of hot water. Cool, dissolve 1 g of hydroxylamine hydrochloride in this solution, then add 30 ml of bathocuproïne solution and allow to stand for 1 hr. Extract with chloroform and n-amyl alcohol as described for the ammonium tartrate solution. Filter, dilute to 1 litre with water and store in a polyethylene bottle.

Ascorbic acid, 10%, copper-free solution: Dissolve 10 g of ascorbic acid (Analytical Reagent, British Drug Houses Ltd.) in approximately 60 ml of water. Add 5 ml of bathocuproïne solution and allow to stand for 5 min. Extract twice with 8-ml portions of a 3:1 mixture of chloroform and n-amyl alcohol, then three times with chloroform to remove excess n-amyl alcohol. Filter and dilute to 100 ml with water. Prepare a fresh solution every second day.

n-Amyl alcohol: Analytical Reagent, obtained from Mallinckrodt Chemical Works.

Chloroform: Analytical Reagent, obtained from Fisher Scientific Co.

Procedure

Calibration curve: Pipette 20 ml of 25% ammonium tartrate solution, 40 ml of 5% boric acid solution and 20 ml of 10% ascorbic acid solution into a 250-ml beaker. Using a pH meter, adjust the resulting "base" solution to pH 5·5 with concentrated ammonia solution and dilute to volume with water in a 200-ml volumetric flask. Add a 20-ml aliquot of this solution to each of six 60-ml separatory funnels that are marked at 25 ml, then, by burette, add to the last five funnels 1, 2, 3, 4 and 5 ml, respectively, of standard copper solution (*i.e.*, 1 ml = 5 μg of copper). The first funnel contains the blank. Dilute the contents of each funnel to the 25-ml mark with water and swirl to mix. (Because n-amyl alcohol is soluble to a certain extent in water, *i.e.* 2·19% by weight at 25°, the total volume should be kept relatively constant). Add to each funnel 2 ml of 0·002*M* bathocuproine solution, mix and allow to stand for 10 min, then add, by pipette, 10 ml of n-amyl alcohol, stopper and shake for 2 min. Allow 5 min for the layers to separate, then drain off and discard the lower aqueous layer. Drain the n-amyl alcohol extracts into 15-ml centrifuge tubes and centrifuge for 30 sec. Determine the absorbance of each extract against the blank as the reference solution, using 2-cm cells in a Beckman DU spectrophotometer, at a wavelength of 476 mμ. Plot μg of copper *vs.* absorbance.

Procedure for Niobium, Tantalum, Molybdenum and Tungsten Metals; In the following procedure a reagent blank is carried along with the samples.

Transfer a 0·5000-g sample of the powdered metal to a 250-ml Teflon beaker, add 2 ml of hydrofluoric acid (plastic pipette) and cover the beaker with a Teflon watch glass. Through the lip of the beaker add concentrated nitric acid slowly, 10 drops at a time, until all of the metal is in solution. Usually 1 or 2 ml is sufficient. If a small portion of the sample remains undissolved at this stage, heat gently on the hot plate until in solution. Remove the Teflon cover and wash down the sides of the beaker with a small amount of water. (For molybdenum metal and a separate reagent blank, add at this point, 2 ml of concentrated hydrochloric acid and heat until the dark brown colouration disappears and the solution becomes pale yellow.) Add 3 ml of formic acid to destroy excess nitric acid and heat

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* The use of hydroxylamine hydrochloride rather than ascorbic acid is recommended as reducing agent in the preparation of the solution because ascorbic acid produces a dark yellow colouration in 1 week.

gently until the evolution of brown oxides of nitrogen ceases. Wash down the sides of the beaker with a minimum amount of water and evaporate to approximately 5 ml. Add 10 ml of water and 10 ml of 25% ammonium tartrate solution, and heat gently without boiling for 5 to 10 min, at which point the solution should be clear. Add 20 ml of 5% boric acid solution and allow to stand for 20 min. (If the copper determination cannot be completed the same day, allow to stand overnight at this point.) Add 10 ml of 10% ascorbic acid solution, mix, then using a pH meter adjust the pH to 5·5 with concentrated ammonia solution. Transfer to a 100-ml volumetric flask and dilute to volume. (At this point, slightly low results, *i.e.*, 0·002% at the 0·1-% level, are obtained if the samples are allowed to stand for more than 2 hr before the extraction and subsequent determination of the copper.) Transfer a suitable aliquot (4–20 ml) of both sample and blank solutions, depending on the copper content of the sample, to 60-ml separatory funnels. Dilute to the 25-ml mark with water and proceed with the copper extraction as described for the calibration curve. Measure the absorbance of the sample against the reagent blank and determine the copper content of the aliquot by reference to the calibration curve. When 20-ml aliquots of sample solution are taken:

$$1\ \mu g \text{ of copper} = 0{\cdot}001\,\%.$$

RESULTS

Extraction of the coloured complex

Although the copper^{I}-bathocuproïne complex can be extracted into various organic solvents,[9,10,11] n-amyl alcohol was chosen for the present work because of its ready availability.

In preliminary experiments with pure copper solutions, up to 50 μg of copper contained in 25 ml of solution could be extracted quantitatively in a single stage with 10 ml of n-amyl alcohol. Larger amounts (100 μg) could also be extracted with approximately 99·5% efficiency, but this was not feasible in the present investigation because of the high optical density of the resulting extract.

Reduction of copper

In the method previously described for determining iron in high-purity niobium, tantalum, molybdenum and tungsten metals with bathophenanthroline,[8] reduction of iron was achieved with a mixture of ascorbic acid and hydroxylamine hydrochloride. Colour fading was observed in the n-amyl alcohol extract of the iron^{II}-bathophenanthroline complex when ascorbic acid alone was employed as reductant. This was attributed to insufficient ascorbic acid being extracted into the organic phase to prevent air oxidation of the complex.

In the present investigation, tests performed with ascorbic acid alone showed that reduction of copper in sample solutions of each of the four metals, prepared according to the described procedure, and to which standard additions of copper had been made, was rapid and complete. The colour of the extract was stable for at least 3 days.

These results indicate that the copper^{I}-bathocuproïne complex is less subject to atmospheric oxidation than the corresponding iron^{II}-bathophenanthroline complex.

Effect of pH

A search of the literature did not reveal references to methods for determining copper with bathocuproine in which the optimum pH range for the complete formation of the complex has been defined. Therefore, in order to determine this range, the following procedure was used with a series of "base" solutions (described under *Calibration Curve*) of increasing pH.

A known amount of pre-reduced copper (ascorbic acid) was added to a 20-ml aliquot of each of the above "base" solutions and the resulting "test" solutions were each diluted to 25 ml with water. (Reduction of the copper prior to addition to the aliquot of "base" solution ensures that all of the copper will be present in the reduced form at the given pH). Then, 2 ml of 0·002*M* bathocuproïne solution were added and, after a 10-min interval to allow for colour development, the copper complex was extracted with 10 ml of n-amyl alcohol. The absorbance of each extract was measured in a 2-cm cell against its corresponding blank, prepared by carrying a second 20-ml aliquot of each "base" solution (without added copper) through the same procedure.

Because the dilution of a 20-ml aliquot of "base" solution to 25 ml with water prior to the addition of bathocuproïne solution and extraction of the copper complex is accompanied by a small variation in pH, the initial pH adjustment of each "base" solution was, therefore, only an approximation, and the exact pH at which the copper complex was formed in the "test" solutions was determined by measuring the pH of the aqueous phase after the copper complex was extracted. (The pH of the "test" solution is not altered by the extraction step and therefore the measured pH is that of the solution prior to extraction.) The results of these tests (Table I) show that colour development is complete in the pH range 1·45 to 6·25.

TABLE I.—EFFECT OF pH ON THE FORMATION OF THE COPPER^{I}-BATHOCUPROÏNE COMPLEX

pH of aqueous phase	Optical density of extract
0·85	0·539
1·45	0·562
2·45	0·570
4·05	0·569
4·75	0·566
5·35	0·567
5·70	0·563
6·25	0·559
6·60	0·501
7·75	0·265

Copper present: 15 μg.

During the above tests it was observed that the rate of colour formation at pH 0·85 was quite slow; therefore, if a longer time interval was allowed after the bathocuproïne addition, complete colour development would probably be obtained at this pH.

Experiments to determine the effect of pH on the formation of the copper complex in solutions of the high-purity metals were performed with molybdenum solutions only, because it was considered that the optimum conditions for determining copper in molybdenum metal would also be applicable to the other three metals. In these experiments, synthetic molybdenum samples containing 0·10% of added copper were prepared as described under *Procedure* and the final pH of these solutions was varied from 0·5 to 7·0. The results of these tests showed that complete colour development, indicated by total recovery of the added copper, was obtained over the same pH range described above for test solutions.

Because the method for iron[8] required a final sample solution pH of approximately 5·5, this pH was also chosen for the present work; copper and iron could then be determined on aliquots of the same sample solution. Tests carried out at pH 5·5 on synthetic niobium, tantalum and tungsten samples also indicated complete formation of the copper-bathocuproïne complex.

Effect of diverse metal ions

The reported specificity of bathocuproïne for copper was investigated by testing separately the effect of 5-mg quantities of the various impurities (cobalt, cadmium, nickel, manganese and zinc) that occur in small amounts in samples of the four high-purity metals on a known amount (15 μg) of copper. The effect of chromium^{III} [added as $CrK(SO_4)_2.12H_2O$] was also tested, because this cation was found to interfere in the determination of copper with the related neocuproïne reagent (2,9-dimethyl-1,10-phenanthroline).[12]

The results of these tests showed that none of the ions tested interfered in the copper determination. Iron also does not interfere when complexed with citrate or tartrate.[9,10]

Application to synthetic niobium, tantalum, molybdenum and tungsten samples for copper contents up to approximately 0·1%

In order to determine its accuracy, the proposed method was applied to the analysis of a series of synthetic samples in which the added copper varied from 0·005 to 0·10%. The standard copper solution was added after the formic acid treatment. The results obtained are given in Table II.

TABLE II.—RECOVERY OF COPPER BY THE PROPOSED METHOD FROM SYNTHETIC NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN SAMPLES

Sample	Total Cu present, %	Cu found, %	Sample	Total Cu present, %	Cu found, %
Nb + 0·005% Cu	0·0054	0·0055	Ta + 0·005% Cu	0·0051	0·0050
Nb + 0·010% Cu	0·0104	0·0103	Ta + 0·010% Cu	0·0101	0·0098
Nb + 0·025% Cu	0·0254	0·0253	Ta + 0·025% Cu	0·0251	0·0249
Nb + 0·050% Cu	0·0504	0·0502	Ta + 0·050% Cu	0·0501	0·0502
Nb + 0·100% Cu	0·1004	0·0993	Ta + 0·100% Cu	0·1001	0·1004
Mo + 0·005% Cu	0·0052	0·0052	W + 0·005% Cu	0·0050	0·0050
Mo + 0·010% Cu	0·0102	0·0102	W + 0·010% Cu	0·0100	0·0098
Mo + 0·025% Cu	0·0252	0·0254	W + 0·025% Cu	0·0250	0·0249
Mo + 0·050% Cu	0·0502	0·0505	W + 0·050% Cu	0·0500	0·0499
Mo + 0·100% Cu	0·1002	0·1009	W + 0·100% Cu	0·1000	0·1001

Duplicate determinations of copper in the above Nb, Ta, Mo and W metals by the proposed method gave average results of 0·0004, 0·0001, 0·0002% and none detected, respectively.

DISCUSSION

Table II shows that the results obtained by the proposed bathocuproïne method agree favourably with the total calculated percentage of copper present in the range of values up to approximately 0·1%.

In the proposed procedure, the formation and subsequent extraction of the copper^{I}-bathocuproïne complex takes place under essentially the same conditions previously described for the formation and extraction of the iron-bathophenanthroline complex.[8] Therefore, both copper and iron can be determined in the same sample using separate aliquots of sample solution prepared as described in the method for iron, provided that de-ionised water and both copper- and iron-free reagents are used throughout the procedure.

The method presented in this paper is suitable for samples containing between 0·0005 and 0·125% of copper, but copper contents below 0·0005% can be determined fairly accurately because the reagent blank contains approximately 1 μg or less of copper. Materials containing more than 0·125% of copper can also be successfully analysed by reducing the initial sample weight. The method is extremely sensitive, the technique required is simple, and results are reproducible under routine conditions.

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Zusammenfassung—Eine spektralphotometrische Methode zur Bestimmung von 0·0005 bis 0·125% Kupfer in hochgereinigtem Nb, Ta, Mo und W wird beschrieben. Nach Lösen der Probe wird Kupfer reduziert (Ascorbinsäure) und mittels Bathocuproin (2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolin) in der Form eines gelben Komplexes in n-Amylalkohol ausgeschüttelt. Der Extrakt wird bei 476 mμ photometriert. Andere Verunreinigungen in den oben erwähnten Metallen stören bei der Methode nicht.

Résumé—Description d'une méthode de dosage du cuivre en concentration de l'ordre de 0·0005 à 0·125% dans des échantillons de niobium, tantale, molybdène et tungstène très purs. On dissout l'échantillon et l'on réduit le cuivre à l'état cuivreux au moyen de l'acide ascorbique; le complexe jaune formé par le cuivre cuivreux et la bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phénanthroline) est extrait par l'alcool n-amylique et l'on détermine l'absorption de cet extrait à 476 μ. Les autres impuretés présentes dans les échantillons des métaux purs cités, ne gênent pas le dosage.

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THE PREPARATION OF FORTIFIED 70–80% PERCHLORIC ACID EMPLOYING ANHYDROUS MAGNESIUM PERCHLORATE AS DESICCANT

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Summary—The preparation of 73·6% perchloric acid, $HClO_4 \cdot 2H_2O$, by a new procedure is described; this is the vacuum distillation of commercially available 70–71% acid to which anhydrous magnesium perchlorate has been added. The process can be extended to the preparation of 75–80% perchloric acid concentrations, for which there exists commercial demand. The processes involved are described in detail.

INTRODUCTION

PERCHLORIC acid of commerce is 70–71%, (b.p. 200–201° at 750–760 mm pressure.) The water-azeotrope, of which the composition is 72·5% acid and 27·5% water (b.p. 203°), results from the concentration of the commercially available acid by boiling at ordinary barometric pressure. By vacuum distillation[1] of 70–71% acid at a pressure of 2–7 mm, one obtains a 40–50% yield of the dihydrate, $HClO_4 \cdot 2H_2O$, which has been established as a primary standard in acidimetry. A number of processes have been described[2] for the preparation of anhydrous acid (f.p. approximately −110°.) By combining equimolecular proportions of the anhydrous acid with the dihydrate, there results the monohydrate, $HClO_4 \cdot H_2O$ (m.p. 49·905°) containing 84·80% acid. This crystalline form is permanently stable at ambient temperature. By vacuum distillation at 50 mm pressure it may be dissociated to regenerate the anhydrous acid, leaving, as still-pot acid, the dihydrate. The anhydrous acid cannot be stored at ordinary temperatures for more than a few hundred hr without resultant violent decomposition, caused by degradation products formed progressively soon after preparation. The acid anhydride,[3] Cl_2O_7, is explosive under heat and percussion. Perchloric acid anhydride has been prepared by vacuum distillation of mixed perchloric acid dihydrate and 60% fuming sulphuric acid.[4] Deuterium perchlorate has also been synthesised.[5]

FORTIFICATION OF 71% STOCK ACID

Commercially available "anhydrous" magnesium perchlorate retains 5–6% residual water. American Chemical Society specifications require less than 10%. The lowest hydrate, $Mg(ClO_4 \cdot 2H_2O$, contains 14·66% water. By heating the commercially supplied desiccant at 225–250° *in vacuo* at 1–5 mm pressure, complete dehydration results without fusion or decomposition. Such material was used in the procedures to be described. Its porosity is estimated to be 40–50% of its bulk volume.

All metallic perchlorates (K, Rb, and Cs excepted) are very soluble in water and in most organic solvents including alcohols, esters, ketones and polyhydric alcohols (such as glycerol and ethylene glycol). Concentrated perchloric acid is another excellent solvent. The coefficients of increase in solubility with increase in temperature are high.

Concentrated (70–80%) perchloric acid is a good solvent for magnesium perchlorate at ordinary temperatures. At 100–110°, the solubility has increased by a factor of 4- or 5-fold. The anhydrous desiccant has its maximum dehydration efficiency at a minimum of 180–190°. Conversion from the anhydrous form to the dihydrate involves absorption of 14·66% by weight of water. As has been shown by Trussel and Diehl,[6] anhydrous $Mg(ClO_4)_2$ is a much more satisfactory desiccant than P_2O_5 both in efficiency and in capacity. The combination of these properties is ideal for the present process.

APPARATUS

Apparatus for the preparation of fortified 73·6–80% perchloric acid is shown in Fig. 1.

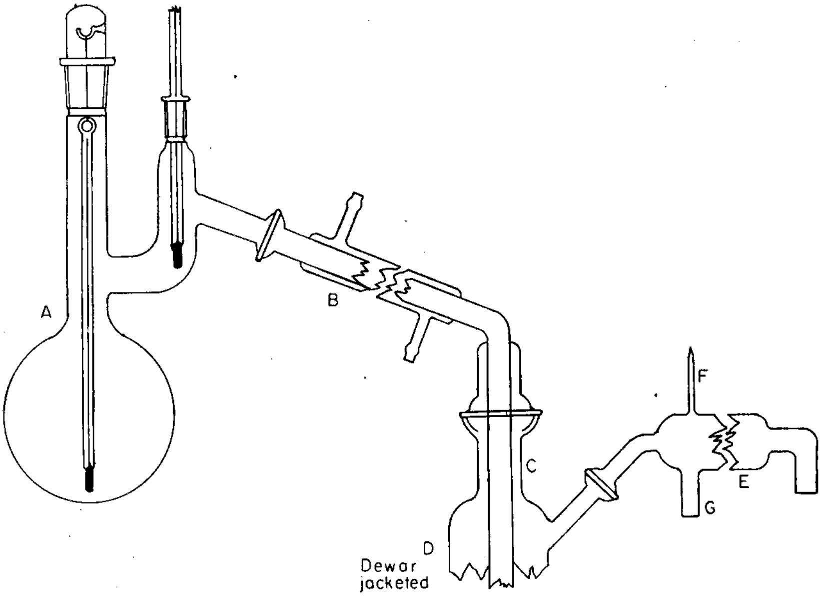

Fig. 1

The 1000-ml Claissen flask, A, serving as still-pot is provided with thermometers to indicate the temperatures of the distilling acid and of the vapour phase passing into the condensers. Both a water-cooled condenser, B, and a cold-finger condenser, C, are provided. The latter is cooled employing dry ice using a large Dewar, D, as immersion container. It is essential that an effective acid-absorbing protection tube, E, be employed between the distillate receiver and the oil-containing vacuum pump. All connections between the units A and E should be ground-glass.' A still-pot electric heating-mantle and accompanying variable power-stat is to be recommended, although a wire gauze and gas burner heating assembly may be employed. Any type of oil-operated vacuum pump capable of providing pressures of a fraction of a mm of mercury is suitable. A miniature type McLeod vacuum gauge covering the range 0–5 mm is connected in the system at G. A small appendix tube, F, provides for periodic opening of the apparatus assembly to atmospheric pressure. This vent tube is closed by fusion of the tip using a small hot gas flame. The inner tube of the water condenser, B, should be at least of 15-mm bore. Receiver C is used without dry ice for cooling in the preparation of acid of not more than 73·6%. For the preparation of stronger acid dry ice must be employed in D.

ACID FORTIFICATION OF 68–71% PERCHLORIC ACID

Commercially available 68–71% acid serves as stock acid to be fortified. A weight of anhydrous magnesium perchlorate equal to 10% of the weight of the stock acid is placed in the still-pot of the distillation assembly. The stock acid is then added, and the distillation train put under vacuum. For this fortification tap water only is used for cooling. The pressure should be in the range 0·1–1·5 mm. The application of heat should be moderate and slowly intensified. The desiccant, under vacuum, evolves air from its highly porous structure, and rises to the surface of the still-pot acid. With slight elevation of temperature it readily dissolves. At 85–90° distillation begins. The temperature of the vapour phase is generally 6–10° lower than that of the liquid phase, This indicates the extent to which super-heating results. Some "spitting" type ebullition results from the out-gassing of the still-pot acid. By limiting the differential between the liquid phase and gas phase to 10° the distillation process proceeds continuously without any ebullition.

TABLE I.—FORTIFICATION OF STOCK 68–71% PERCHLORIC ACID IN PREPARATION OF $HClO_4 \cdot 2H_2O$

Sample wt, *g*	$HClO_4$ conc'n, %	$Mg(ClO_4)_2$ added, *g*	Distillation fraction, wt, *g*, and $HClO_4$, %					
			1	2	3	4	5	Still Pot
661	67·92	66	133·5 64·8	163 72·7	161·5 73·4	105 73·3		156
839	70·98	84	83·5 71·6	162 73·25	166 73·73	165·5 73·63	75 73·3	255·5

The results from two distillations are shown in Table 1. After 70–80% of the starting acid has been collected, the still-pot acid is clear and colourless. At this point the still-pot acid holds in solution approximately 50% of its weight of hydrated magnesium perchlorate at a temperature of 85–90°. Four to five fractions of distilled acid were collected. The strength of the stock acids was determined titrimetrically. The strength of distilled fractions was determined by density measurement at 25°/4° and is accurate to ±0·25% in acid content.

The results in Table I indicate that the recovery of $HClO_4 \cdot 2H_2O$ is 40% of the weight of starting acid. The recovery of distilled acid is 85%. The still-pot acid desiccant is recovered and neutralised using magnesium oxide; $Mg(ClO_4)_2 \cdot 6H_2O$ is then reclaimed for reprocessing to form the anhydrous starting material. This procedure, as compared with simple vacuum distillation,[1] gives fortified acid more rapidly, and provides the dehydrated acid in the distillate rather than in the still-pot acid.

CONVERSION OF PERCHLORIC ACID DIHYDRATE TO 74–80% PERCHLORIC ACID

The stock acid for this process is prepared by the procedure described as giving the values in Table I (by titration 73·42% acid). The same apparatus and procedure are again used. The distillate receiver is cooled by immersion in dry ice. The most concentrated acid is found in the first fraction distilled. For this reason the water-cooled condenser is not operative in the early part of the distillation. The inner tube of the cold finger must not become clogged by solidified distillate. To prevent this, the portion of the cold finger receiver above the dry ice may require to be heated using a soft brush gas flame, so that the inner tube is warmed sufficiently to avoid clogging. As the distillate accumulates, its acid strength decreases. When approximately 50% of the distillation is complete, the water-cooled condenser is brought into use. Typical results are given in Table II.

As already mentioned, Smith and Goehler[6] have shown that by the vacuum distillation of perchloric acid dihydrate at a pressure of as low as 20 mm the vapour phase can be fractioned employing a cascade of "in line" condenser stages, collecting progressively the following perchloric acid hydrates:

$$HClO_4{\cdot}3H_2O,\ HClO_4{\cdot}H_2O \text{ and anhydrous } HClO_4.$$

The still-pot acid in a simultaneous multiple separation of this type is the dihydrate $HClO_4{\cdot}2H_2O$.

TABLE II.—THE FORTIFICATION OF $HClO_4{\cdot}2H_2O$ TO PREPARE 74–80% PERCHLORIC ACID

Stock acid, *g*	Desiccant added, *g*	$Mg(ClO_4)_2$ added, %	Distillate		Still-pot residue, *g*	Final vapour-phase temp. and pressure
			g	% acid		
568·5	17	3	473·5	74·04	—	76° at 1·0 mm
521·5	26	5	384·5	74·69	158	73° at 0·65 mm
498·3	37·4	7·3	421·5	75·31	109	80·5° at 1·5 mm
570·5	57	10·0	416·25	80·12	206	103° at 3·5 mm

Since the anhydrous acid portion of the acid in this distillation process is the last condensed of the three vaporised acid forms, being preceded in turn by the monohydrate and the trihydrate, these acids are obviously more volatile the less their degree of hydration. Hence the second fortification process described above provides the strongest acid in the first fraction collected.

This 80% acid is approximately the strongest acid that can be prepared without obtaining a product which would deposit crystalline $HClO_4{\cdot}H_2O$ at ordinary temperatures.

No hazardous manipulations were involved in the studies herein described.

Zusammenfassung—Die Herstellung von 73·60% iger Perchlorsäure, $HClO_4{\cdot}2H_2O$, mittels eines neuen Verfahrens wird beschrieben. Die Vakuumdestillation von komerzieller 70–71% iger Säure wird nach Zugabe von Magnesiumperchlorat durchgeführt. Der Prozess kann auch zur Herstellung von 75–80% iger Säure herangezogen werden, für die kommerzieller Bedarf existiert. Detaillierte Angaben über die Verfahren werden gemacht.

Résumé—Description d'un nouveau procédé de préparation de l'acide perchlorique à 73,60%, ($ClO_4H{\cdot}2H_2O$). La solution habituelle de ce problème, consiste en la distillation sous vide de l'acide commercial à 70–71% auquel on ajoute du perchlorate de magnésium anhydre. Le procédé peut être étendu à la préparation d'acide à 75–80% pour lequel il existe un besoin commercial. Les détails relatifs aux procédés mis en jeu sont en conséquence indiqués.

REFERENCES

[1] G. Frederick Smith and W. W. Koch, *Ind. Eng. Chem., Analyt.*, 1931, **3**, 52.
[2] O. E. Goehler and G. Frederick Smith, *ibid.*, 1931, **3**, 55.
G. Frederick Smith, *J. Amer. Chem. Soc.*, 1953, **75**, 184; *Talanta*, 1961, **7**, 212.
[3] A. Micheal and W. T. Cohn, *Amer. Chem. J.*, 1900, **23**, 444.
[4] In the author's laboratory.
[5] G. Frederick Smith, Feigl Anniversary Symposium, Birmingham, England, April 1962. Elsevier Publishing Co., Amsterdam, in press.
[6] G. Frederick Smith and O. E. Goehler, *Ind. Eng. Chem., Analyt.*, 1931, **3**, 61.

Talanta, 1963, Vol. 10, pp. 417 to 420. Pergamon Press Ltd. Printed in Northern Ireland

PRELIMINARY COMMUNICATIONS

Coulometric reduction of iridium^{IV} in perchloric acid media

(*Received* 24 *December* 1962)

PAGE[1] has recently reported on the polarographic and coulometric reduction of iridium^{IV} in a variety of acidic media. At potentials sufficiently negative to prevent the oxidation of mercury, iridium^{IV} was found to be smoothly reducible to iridium^{III} in dilute solutions of hydrochloric acid. In perchloric acid solutions, however, the apparent value of n, the number of electrons involved in the electrolysis, was variable and greater than one. Page attributed this behaviour to prior chemical oxidation of iridium^{IV} by perchloric acid.

We have investigated the iridium^{IV}-perchloric acid system spectrophotometrically and coulometrically and find no evidence for oxidation of iridium^{IV} by dilute solutions of perchloric acid at room temperature, yet also note apparent n values greater than one for controlled-potential reductions carried out under these conditions. Similar observations[2] encountered during the coulometric reduction of ruthenium^{IV} prompted us to investigate the possibility of a secondary chemical reaction to account for the anomalies observed during the electrolytic reduction of iridium^{IV}.

EXPERIMENTAL

The controlled-potential electrolyses were carried out using a Model 600 electronic potentiostat (Duffers Associates, Inc., Troy, N.Y.). The current passed was integrated by means of a SI-100 solion-type integrator (Texas Research and Electronic Corp., Dallas, Texas). Electrolyses were carried out using a mercury cathode and platinum anode in a double diaphragm cell similar to that described by Meites.[3] The mercury cathode was stirred mechanically and by the continuous passage of purified and solvent-presaturated nitrogen through the electrolyte. A Leeds and Northrup saturated calomel electrode served as a reference; for electrolyses in perchlorate solutions an intermediate bridge containing chloride-free electrolyte was used with the reference electrode. The entire electrolysis cell was immersed in a thermostatic bath held at 30 ± 0·2°. The potential of the working electrode was continuously monitored, as an added precaution, using a Model 620 DC-potentiometric voltmeter (Houston Instruments Corp., Bellaire, Texas), and the electrolysis current was measured with an external precision meter. K_2IrCl_6 (Johnson, Matthey and Co.) was used as a source of iridium^{IV}. All other chemicals were of reagent grade. Spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer.

RESULTS AND DISCUSSION

The results of controlled-potential electrolyses carried out at $-0{\cdot}35$ v *versus* the saturated calomel electrode are summarised in Fig. 1. Curve A corresponds to the reduction of a solution which was $5 \times 10^{-4}M$ in iridium^{IV} and $0{\cdot}2M$ in perchloric acid; curve B indicates the current-time behaviour observed for the same reduction carried out in $0{\cdot}2M$ hydrochloric acid solution. It will be noted that the current-time behaviour observed is similar for both electrolytes during the early portion of the electrolysis, but that the current levels off at a relatively high value in the perchloric acid medium. Residual currents measured during pre-electrolyses of the solvents alone have been subtracted from all experimental points. From the slopes and intercepts of the initial straight line portions of these log current-time plots, using the technique of MacNevin and Baker,[4] n was calculated to be equal to one for both electrolyses. The initial electrolysis product is, therefore, some form of iridium^{III} in both perchloric and hydrochloric acid media.

The high steady-state current observed in perchloric acid media, however, indicates the occurrence of some secondary reaction[5] which is regenerating additional reducible material. The small, but finite, steady-state current observed in hydrochloric acid solution may be attributed to catalytic hydrogen ion reduction, since its magnitude appears to be potential dependent. The secondary process in the perchloric acid medium might involve an interaction between iridium^{III} and any reducible species present in the electrolyte. Test of the electrolysis solution showed, however, that chloride ion is produced during electrolyses in perchloric acid media; this would seem to indicate that the chemical interaction is between iridium^{III} and perchlorate ion. This hypothesis is further supported by the fact that when more perchlorate is added to the electrolyte, additional iridium^{IV}, as indicated by spectrophotometric measurements, is produced. We feel, therefore, that the apparent n values greater than one which are observed during electrolyses of iridium^{IV} in perchloric acid media are the result of a primary reduction to iridium^{III} followed by a chemical interaction between the electrolysis product and perchlorate ion to regenerate iridium^{IV} and produce, eventually, chloride ion. The kinetics and mechanism of this secondary reaction are at present under investigation, and will be reported on in a later paper.

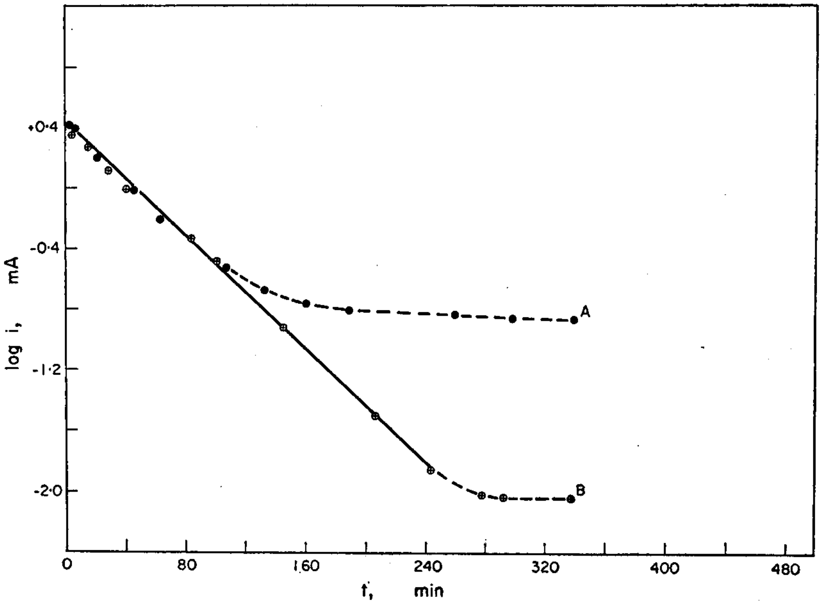

FIG. 1.—Reduction of 5 × $10^{-4}M$ iridium^{IV} at −0·35 v *vs.* S. C. E.
A—Reduction in 0·2M $HClO_4$:
B—Reduction in 0·2M HCl.

Acknowledgement—The financial support of the Laboratory for Research on the Structure of Matter is gratefully acknowledged.

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Summary—The anomalous behaviour of iridium^{IV} during electrolysis in perchloric acid media has been investigated by controlled-potential coulometric techniques. The observed variation in apparent n values is attributed to a chemical interaction between the initial electrolysis product, iridium^{III}, and perchlorate ion, to regenerate iridium^{IV}.

Zusammenfassung—Das anomale Verhalten von Iridium^{IV} bei der Elektrolyse in überchlorsauren Lösungen wurde mit coulometrischen Methoden bei kontrollierter Spannung untersucht. Die beobachteten Unterschiede der scheinbaren n-Werte werden einer chemischen Reaktion zwischen dem Primärprodukt der Elektrolyse, Iridium^{III} und Perchlorat-Ion zugeschrieben, wobei Iridium^{IV} zurückgebildet wird.

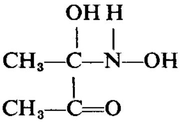
Résumé—Le comportement anormal de l'iridium IV au cours de l'électrolyse en milieu acide perchlorique, a été étudié par coulomètrie à potentiel contrôlé. La variation que l'on observe dans les valeurs apparentes de "n" est attribuée à l'interaction chimique entre le produit initial d'électrolyse, l'iridium III, et l'ion perchlorate qui restitue l'irridium IV.

REFERENCES

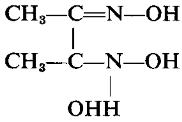
[1] J. A. Page, *Talanta*, 1962, **9**, 365.
[2] G. A. Rechnitz, *Inorg. Chem.*, 1962, **1**, 953.
[3] L. Meites, *Analyt. Chem.*, 1955, **27**, 1116.
[4] W. M. MacNevin and B. B. Baker, *ibid.*, 1952, **24**, 986.
[5] G. A. Rechnitz and H. A. Laitinen, *ibid.*, 1961, **33**, 1473.

The reactions of biacetyl, hydroxylamine and metal ions to form chelates

In continuing studies on the oximation of biacetyl,[1] the following additional reaction intermediates have been found:



$$\begin{array}{ccccl} & & OH & & H \\ & & | & & | \\ CH_3 & — & C & — & N—OH \\ & & | & & \\ CH_3 & — & C & = & O \end{array}$$



$$\begin{array}{ccccl} CH_3 & — & C & = & N—OH \\ & & | & & \\ CH_3 & — & C & — & N—OH \\ & & & & | \\ & & OH & & H \end{array}$$

Spectroscopic evidence indicates that biacetyl disappears almost immediately upon its addition to an aqueous solution containing hydroxylamine; the reaction products, *i.e.*, biacetyl monoxime and dioxime, are slowly formed from the above intermediates. Similar results were obtained when biacetyl monoxime and hydroxylamine were used in the starting mixture. Preliminary numerical analysis of the kinetic results indicates the plausibility of the above reaction intermediates.

The effect of the presence of nickel^{II} or palladium^{II} on the reaction mechanism is also being studied. The results will shortly be reported in Talanta.

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Summary—Two additional reaction intermediates in the reaction between biacetyl and hydroxylamine (E. D. Salesin, E. W. Abrahamson and Louis Gordon, *Talanta*, 1962, **9**, 699) are reported. The effect of the presence of Ni^{II} or Pd^{II} on the course of the reaction is being studied.

* On study leave from The Queen's University, Belfast, Northern Ireland.

Zusammenfassung—Es wird über zwei weitere Zwischenstufen der Reaktion zwischen Biacetyl und Hydroxylamin berichtet (E. D. Salesin, E. W. Abrahamson und Louis Gordon, *Talanta* 1962, **9**, 699). Der Einfluß von Ni^{II} und Pd^{II} auf den Reaktionsverlauf wird untersucht.

Résumé—Description de deux intermédiaires dans la réaction d'addition du biacétyle sur l'hydroxylamine (E. D. Salesin, E. W. Abrahamson et Louis Gordon. *Talanta*, 1962, **9**, 699). Etude de l'influence du Ni^{II} ou du Pd^{II} sur l'évolution de la réaction.

REFERENCE

[1] E. D. Salesin, E. W. Abrahamson and Louis Gordon, *Talanta*, 1962, **9**, 699.

Talanta, 1963, Vol. 10, pp. i to xiv. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

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

CANADA

Monday–Wednesday 16–18 *September* 1963: **Tenth Ottawa Symposium on Applied Spectroscopy:** *Canadian Association for Applied Spectroscopy.* Ottawa, Canada.

Papers are invited in all fields of applied spectroscopy, including emission, X-ray fluorescence and diffraction, flame emission and absorption, ultraviolet, visible and infrared absorption, nuclear magnetic resonance and mass spectroscopy.

Titles and brief abstracts of papers should be submitted before 3 June to Mr. John Kelly, Steel Company of Canada Ltd., Metallurgical and Chemical Laboratory, Wilcox Street, Hamilton, Ontario, Canada.

GERMANY

Mittwoch–Samstag 24–27 *April* 1963: *Gesellschaft Deutscher Chemiker, Fachgruppe „Analytische Chemie"* **Einladung** zur Gemeinsamen Tagung mit dem *Deutschen Ausschuss für Spektrochemie* und der *Arbeitsgruppe Massenspektroskopie* im Verband Deutscher Physikalischer Gesellschaften in Erlangen.

Vortragsprogramm

Mittwoch, 24 *April* 1963

Plenarvortrag

Quantitative spektroskopische Plasma-Analyse.	W. Lochte-Holtgreven

Diskussionsvorträge-Emissionsspektralanalyse

Der Einfluß der Gas-Dampf-Zusammensetzung auf die Linienintensitäten spektrochemischer Lichtquellen.	H. Krempl
Kritische Bemerkungen zum Corlissbogen.	W. Keßler und D. v. Dobeneck
Quantitative spektrochemische Untersuchungen mit hochfrequenten Plasmaflammen.	W. Tappe und J. van Calker
Beobachtungen und Untersuchungen an Hf-Plasmaflammen.	U. Jecht und W. Keßler
Quantitative spektrochemische Analyse mit kondensierten Funkenentladungen hoher Folgefrequenz.	J. Lensing und J. van Calker
Über den Einfluß dritter Partner bei der Emissionsspektralanalyse von Gläsern.	W. Flessa und W. Keßler
Kriterien für ein universelles Puffersystem für die Emissionsspektralanalyse von dielektrischen Proben.	W. Keßler
Systematische Untersuchungen an Preßelektroden für die Emissionspektralanalyse dielektrischer Proben.	W. Keßler
Die spektrochemische Bestimmung von Phosphor im Kupfer nach dem Kugelbogenverfahren.	O. Werner
Untersuchungen über die Anregung der kurzwelligen ultravioletten Spektren von Schwefel, Kohlenstoff und Phosphor in Stahllegierungen.	J. van Calker und H. Steiner
Beobachtungen über chemische Reaktionen in borhaltigen Graphitpreßlingen im Gleichstrombogen.	H. Nickel
Über die Anwendung thermochemischer Reaktionen in der emissionsspektrographen Spurenanalyse und ihre Bedeutund für den Carrier-Effekt.	E. Schroll
Quantitative spektrochemische Untersuchungen mit Lichtbogenanregung an biologischen Analysenmaterialien.	J. van Calker und B. Wischgoll

Versuche zur Überwachung des Thomasprozesses mit Hilfe kontinuierlicher spektrochemischer Analyse des Blasstaubes.	W.-D. Hagenah und K. Laqua
Die Anwendung der Röntgenspektrometrie bei der Analyse von Siliciumlegierungen.	F. Wagner

Fachdiskussionen

Donnerstag, 25 *April* 1963

Plenarvorträge

Analytische Anwendungen der Fluoreszenspektroskopie.	F. Dörr
Methoden der Konformationsanalyse.	M. Hanack

Diskussionsvorträge-Molekülspektroskopie

Bemerkungen zur Lichtabsorption des Stilbens.	H.-H. Perkampus
Identifizierung und Bestimmung polycyclischer, aromatischer Kohlenwasserstoffe durch Fluoreszenspektren fester Lösungen bei tiefen Temparaturen.	H.-J. Eichhoff und M. Köhler
Quantitative IR- und UV-Analyse.	G. Bergmann
Zur Konstitutionsabhängigkeit niedrig frequenter Schwingungen bei organischen Verbindungen.	G. Kresze
Ramanspektroskopie von geringen Mengen fester und flüssiger Substanzen.	B. Schrader
Die Infrarotspektren von ungesättigten Steroiden im CH-Valenzschwingungsbereich.	B. Hampel
Ultrarotspektroskopische Untersuchungen an Alkylverbindungen von Gallium, Indium und Antimon.	F. Oswald
Ultrarotspektroskopische Studien an O-Heterocyclen. 1.3-*Dioxan-Derivate.*	K. D. Ledwoch

Plenarvortrag

Strukturuntersuchung organischer Verbindungen mit Hilfe der Massenspektrometrie.	G. Spiteller

Parallelsitzungen

A. Diskussionsvorträge-Massenspektrometrie organischer Substanzen

Massenspektrometrischer Untersuchungen an Verbindungen aus der Pyrolyse von Methylchlorsilanen.	F. Aulinger und W. Reerink
Massenspektrometrie monocyclischer Ketone.	J. Seibl und T. Gäumann
Analytische Anwendungsmöglichkeiten des Feldionen-Massenspektrometers.	H. D. Beckey und G. Wagner
Die Bestimmung von ^{15}*N-Überschußkonzentrationen in Aminosäuren unmittelbar aus ihren Mischungen.*	G. Deffner
Negative Ions Produced by Electron Impact in Mono-, Di- and Tri-Methylamine.	H. Branson, H. Ebinghaus und K. Kraus
Fortschritte in der Anwendung von Massenspektrometern als spezifisch anzeigende Ionisationsdetektoren für die Gaschromatographie.	C. Brunnée, L. Jenckel und K. Kronenberger

B. Diskussionsvorträge-Optische Spektralgeräte

Untersuchungen über eine neue Methode zur Auswertung photographischer Meßgrößen.	J. van Calker und H. Kasselmann
Zur Ausleuchtung des Zwei-Gitter-Spektrographen der Firma Bausch & Lomb.	H. R. Kleinhanß und J. van Calker
Neue Gesichtspunkte bei der Ebert-Aufstellung als Spektrograph und Monochromator für die spektrochemische Analyse.	O. Vierle
Über die bestmögliche Ausnutzung von Spektralgeräten für die optische Analyse.	H. Krempl
Verwendung sehr hochauflösender Gitterspektrographen für die Emissions-Spektralanalyse von Mineralien.	E. Preuss

Fachdiskussionen

Feitag, 26 *April* 1963

Plenarvortrag

Preparation and Analysis of Silicon and Germanium Hydrides and of Derivatives of Borazole.	C. PHILLIPS

Diskussionsvorträge

Die Bestimmung von metallischen zweiwertigem und dreiwertigem Fe nebeneinander in Eisenhüttenprodukten.	G. KRAFT und J. FISCHER
Zur Schnellbestimmung von Metallspuren in Reaktorwässern.	F. A. POHL
Photometrische Wolframbestimmung in Wolframerzen und Ferrowolfram.	H. HARTKAMP
Untersuchungen zur Mitfällung an Wolframoxidhydrat.	W. GEBAUHR
Empfindlichkeitssteigerung photometrischer Bestimmungen durch Verwendung borhaltiger Chelate.	F. UMLAND und D. THIERIG
Zur exakten stufenweisen Titration von Calcium und Magnesium mit ÄDTA.	H. BALLCZO und A. KOSAK

Plenarvorträge

Determination of Impurities in Solids by Spark Source Mass Spectrometry.	R. D. CRAIG
Spuren- und Phasenanalyse mit kristalloptischen Methoden.	TH. ERNST

Parallelsitzungen

A. Diskussionsvorträge-Chemische Analyse anorganischer Substanzen

Die Anwendung der Röntgenspektralanalyse in Verbindung mit absoluten Altersbestimmungen (Rubidium-Strontium-Methode).	P. HAHN-WEINHEIMER
Untersuchungen zur polarographischen Bestimmung von Pertechnetat neben Perrhenat.	L. ASTHEIMER und K. SCHWOCHAU
Die analytische Aussagemöglichkeit von Diffusionsmessungen.	H. J. ANTWEILER

B. Diskussionsvorträge-Massenspektroskopie anorganischer Substanzen und massenspektroskopische Apparate

Erfahrungen mit der massenspektrometrischen ^{15}N-Analyse in biologischen Versuchen.	R. HÜSER
Ein modifiziertes Lecksuch-Massenspektrometer für Atemluftanalysen und allgemeine Betriebskontrollaufgaben.	C. BRUNNÉE und L. DELGMANN
Massenspektrometrische Analysen mit einer neuen Quelle zur Feldionenerzeugung an dünnen Drähten oder Metallschneiden.	H. D. BECKEY
Fehlermöglichkeiten bei der massenspektrographischen Festkörperanalyse bei Verwendung von Hochfrequenzfunken zur Ionenerzeugung.	J. FRANZEN und H. HINTENBERGER
Abreißfunke als Ionenquelle.	F. RAU und H. EWALD
Massenspektroskopische Festkörperanalysen bei Verwendung eines Gleichstromabreißfunkens zur Ionenerzeugung.	K. D. SCHUY und H. HINTENBERGER

Fachdiskussionen

Samstag, 27 *April* 1963

Plenarvortrag

Neuere Ergebnisse zur Bestimmung der Zusammensetzung extrahierter anorganischer Verbindungen.	H. SPECKER

Diskussionsvorträge-Analytische Trennmethodenm, chemische Analyse organischer Substanzen

Extraktiv-photometrische und gravimetrische Trennverfahren für Kupfer, Quecksilber und Gold von anderen Übergangsmetallen.	M. ZIEGLER

Kationen-Trennung und Identifizierung in wasserfreier Essigsäure als Lösungsmittel.	H. D. Hardt und M. Eckle
Coulometrische und radiometrische Mikrobestimmung von Ionenaustauschkapzitäten.	B. Sansoni
Leitfähigkeitsmessungen mit der RC-Methode und ein Beitrag zur Kinetik im System Trifluoressigsäurephenylester-Methanol-Wasser.	K. Cruse
Gas-Adsorptions-Chromatographie mit dem Hydrierungskatalysator Chrom(III)-oxid.	H. W. Kohlschütter und W. Höppe
Die Analyse durch Kombination von katalytischer Hydrierung und Titration in wasserfreiem Medium: Bestimmung von Nitrilen in Gegenwart von Säureamiden.	W. Huber
Die Analyse hochfluorierter Kohlenwasserstoffe demonstriert am Beispiel des n-Hexans.	H. Martin und K. Abraham
Gaschromatographische Trennung der Inhaltsstoffe des technischen Divinylbenzols.	E. Blasius

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Wednesday–Wednesday 19–26 *June* 1963: **Sixth World Petroleum Congress.** Frankfurt (Main).

The following papers in *Section V, Composition-Analysis-Testing* may be of interest to analytical chemists:

Analyses d'identification de polymeres et de copolymeres de propylene et de butenes.	R. Leonard et J.-C. Loewenguth
Applications analytiques de la spectrométrie de masse a ionisation moderee.	D. Joly
Analyse d'un residu de power-forming, pyrolyse et radiolyse, par spectrométrie de masse en basse tension et par spectrométrie infrarouge.	J. Ulrich, A. Copet, P. Bedague et A. Cornu
Separation of compound mixtures difficult to separate by distillation by a continuous process under the conditions of gas elution chromatography.	H. Pichler, H. Schultz and B. Firnhaber
Some applications of the electron probe microanalyser in the petroleum industry.	R. J. Bird
Continuous plant analysers.	S. A. Berridge, C. J. Pearce and E. N. White
Composition of crude oils by gas chromatography: Geological significance of hydrocarbon distribution.	R. L. Martin, J. C. Winters and J. A. Williams
High speed mass spectrometer as a gas chromatography detector in determination of crude oil composition.	V. F. Gaylor, C. N. Jones, J. H. Landerl and E. C. Hughes
New developments in hydrocarbon type characterisation using nuclear magnetic resonance.	R. B. Williams and N. F. Chamberlain
Information concerning hydrocarbon structure and physical properties from nuclear magnetic resonance.	W. B. Moniz and J. A. Dixon
Automatic procedures in analysis of petroleum stocks by neutron activation.	J. T. Gilmore, D. E. Hull and B. A. Fries
A rapid and comprehensive activation analysis method using fast and slow neutrons: Applications in the petroleum and petrochemical industries.	V. P. Guinn, R. A. Johnson and G. C. Mull

Further information may be obtained from the Congress Secretary General, Frankfurt (Main), Postfach 7, Germany.

UNITED KINGDOM

Thursday–Friday 18–19 *April* 1963: Symposium on **Analysis of Calcareous Materials:** *Society of Chemical Industry, Road and Building Materials Group.* Imperial College of Science and Technology, London S.W.7.

The programme is as follows:

Thursday 18 *April, Morning*

Section I—Sampling

The Efficiency of a Sampling Table.	B. H. Kaye
Efficient Sample Reduction by Means of a Riffle Sampler.	B. H. Kaye

Section II—Gravimetric, Volumetric and Colorimetric Methods of Analysis

Review of the Determination of Iron in Calcium Carbonate.	M. L. RICHARDSON
Determination of Fatty Acid Coatings on Coated Calcium Carbonate, Whitings, etc.	M. L. RICHARDSON
Determination of Fluorine in Cements.	S. R. BOWDEN
Determination of Strontium in Calcareous Materials.	S. R. BOWDEN
An Ion-exchange Method for Determination of Sulphates in Cements and Ground Waters.	T. P. LEES
Determination of Fatty Acid Content of Coated Whiting.	D. C. SOUL

Thursday 18 *April, Afternoon*

Section II (continued)

Analysis of Chalk and Other Limestones for Geochemical Studies.	R. M. S. PERRIN
Cement Analysis by Complexometric Techniques.	R. G. BLEZARD

Section III—Physical Methods of Determination of Content of Element and Radical

Determination of Trace Elements in High 'Luminescent' Quality Calcium Carbonate by Cathode Ray Polarography.	M. L. RICHARDSON
Flame Photometric Determination of Magnesium in Presence of Calcium, Aluminium and Phosphorus.	S. GREENFIELD and C. T. BERRY
Determination of Magnesium by Flame Spectrophotometry.	S. R. BOWDEN
Determination of the Original Total Water: Cement Ratio of Hardened Concrete with the Aid of a Thermogravimetric Technique.	C. J. KEATTCH

Friday 19 *April, Morning*

Section III (continued)

Application of X-Ray Fluorescence to the Analysis of Raw Materials in Cement Works.	R. ALÈGRE
Analysis of Iron and Steel Making Slags by Optical Emission and X-ray Fluorescence Spectroscopy.	W. JOHNSON
Survey of Some of the Instrumental Techniques as Applied to Calcareous Materials.	G. F. REYNOLDS

Section IV—Methods of Determination of Compound Content

Use of Digital Techniques to aid in the Phase Analysis of Portland Cement by X-Ray Diffraction.	G. J. C. FROHNSDORFF and P. H. HARRIS
Determination of the Major Compound Contents of Portland Cements by X-Ray Diffraction.	D. L. KANTRO, C. H. WEISE, S. BRUNAUER and L. E. COPELAND
Identification and Determination of Alite in Portland Cement Clinker.	H. G. MIDGLEY, K. E. FLETCHER and A. G. COOPER
A Comparison of Results obtained for the Compound Composition of Portland Cement by X-Ray Diffraction, Microscopy and Wet Chemical Methods.	A. E. MOORE
Application of X-Ray Powder Diffraction Analysis to Agricultural Fertilisers containing Calcium Compounds.	R. V. COATES

Friday 19 *April* 1963, *Afternoon*

Section IV (continued)

Vacuum Thermogravimetric Analysis of Calcareous Materials	D. R. GLASSON

Determination of Calcium Oxide, Calcium Hydroxide and Carbonate by Thermogravimetry.	J. A. Forrester
Differential Thermal Analysis and Study of Calcareous Materials.	J. E. Kruger and T. L. Webb
Precision of Standard Cement Analysis and its Effect on the Calculated Compound Composition.	J. A. Forrester, T. P. Lees and A. E. Moore
The Compound Composition of Hydrated Lime.	G. E. Bessey and H. N. Lee

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Wednesday 1 *May* 1963: **The Use of Magnetic Resonance Measurements in Chemistry:** Professor R. S. Nyholm: *Society for Analytical Chemistry.* University College, Gower Street, London W.C.1.

Wednesday 22 *May* 1963: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group. The Feathers,* Tudor Street, London E.C.4. 6.30 p.m.

Friday 10 *May* 1963: Symposium on **Modern Aspects of Electroanalytical Chemistry:** *Society for Analytical Chemistry, Scottish Section.* I.C.I. Ltd., Nobel Division, Stevenston, Ayrshire (see *Talanta,* 1963, **10,** No. 3, i).

Wednesday–Friday 17–19 *July* 1963: **Microchemistry Group Summer Meeting:** *Society for Analytical Chemistry.* School of Pharmacy, Brunswick Square, London W.C.1.

This meeting will follow the XIXth I.U.P.A.C. Congress. The following programme has been arranged:

Wednesday 17 *July, Afternoon*

Future Possibilities in Microanalysis.	A. J. P. Martin
Methods of Organic Microanalysis: A Comparative and Critical Study.	R. Levy

Thursday 18 *July, Morning*

Mass Spectrometry and Microanalysis.	A. Quayle
Infrared and Microchemistry.	D. M. W. Anderson

Thursday 18 *July, Afternoon*

Choice of visits to microchemical laboratories near London.

Thursday 18 *July, Evening*

Concurrent Discussion Meetings:
- (a) *Organic Microanalytical Techniques*
- (b) *Inorganic and Physical Microanalytical Techniques*

Friday 19 *July, Morning*

Some Recent Developments in Functional Group Analysis on the Micro Scale.	S. Veibel
The Status of Microgram Analysis.	R. Belcher

Friday 19 *July, Afternoon*

Discussion Meeting on *Instrumental Methods for Determination of Carbon and Hydrogen* (Introductory speakers include H. Malissa, W. Simon, W. R. Nall and G. Ingram)

Sunday–Saturday 19–25 *July* 1964: **Third International Congress of Polarography:** *Polarographic Society.* Southampton University.

The Congress will be under the Chairmanship of Professor G. J. Hills. Further information may be obtained from Dr. D. A. Pantony, Imperial College of Science and Technology, Royal School of Mines, Prince Consort Road, London S.W.7.

Monday–Friday 7–11 *September* 1964: **International Conference on Magnetism:** *Institute of Physics and Physical Society* on behalf of *I.U.P.A.P.* and *National Committee for Physics.* University of Nottingham.

The conference will follow the main lines of earlier conferences at Grenoble and Kyoto and will deal with all fundamental aspects of the magnetism of solids. It is not proposed to arrange for the discussion of the applications of magnetic materials. The main sessions so far proposed will include:

Theories of Magnetism
Crystal Field Effects
Mutual Interaction between Magnetic Carriers (Ferromagnetic and Anti-Ferromagnetic)
Metals and Alloys
Magnetic Resonance and Relaxation Processes
Domain Structure and Magnetisation Processes
Magnetic Applications of Neutron Diffraction

It is hoped that each main session will be introduced with an invited review paper. Other sessions to be run in parallel will be arranged.

Registration is necessary. Attendance will be limited and a selection may have to be made by the Organising Committee. Further information may be obtained from the Deputy Secretary, Institute of Physics and Physical Society, 47 Belgrave Square, London S.W.1.

At the **Nineteenth Annual General Meeting** of the *Microchemistry Group* of the *Society for Analytical Chemistry*, Friday, 22 February, 1963, the following Officers of the Group were elected for the forthcoming year:

Chairman: Mr. D. W. Wilson
Vice-Chairman: Mr. R. Goulden
Secretary: Mrs. D. E. Butterworth, National Chemical Laboratory, Teddington, Middlesex.
Treasurer: Mr. G. Ingram

At the **Annual General Meeting** of the *Society for Analytical Chemistry*, Friday, 8 March, 1963, the following were elected Officers and Members of Council for the forthcoming year:

President: D. C. Garratt
Past Presidents serving on Council: A. J. Amos, R. C. Chirnside, J. H. Hamence, K. A. Williams.
Vice-Presidents: S. G. Burgess, R. E. Stuckey.
Hon. Treasurer: D. T. Lewis.
Hon. Secretary: S. A. Price.
Hon. Asst. Secretaries: C. A. Johnson, D. W. Wilson.
Ordinary Members of Council: L. Brealey, H. E. Brookes, P. F. S. Cartwright, B. S. Cooper, J. F. Herringshaw, A. G. Jones, E. Q. Laws, R. M. Pearson, F. C. J. Poulton, A. A. Smales, S. G. E. Stevens, C. Whalley.
Ex-Officio Members of Council: C. J. House, R. A. Chalmers, F. H. Pollard, W. H. Stephenson, D. W. Wilson, W. Cule Davies, W. A. Broom.

UNITED STATES OF AMERICA

Monday 29 *April–Wednesday* 1 *May* 1963: **Ninth Annual ISA Analysis Instrumentation Division Symposium on Analytical Methods of Instrumentation.** Rice Hotel, Houston, Tex.

Tuesday 14 *May* 1963: **Joint Meeting** of *New York* and *Delaware Valley Sections, Society for Applied Spectroscopy*. James Jorrestal Research Centre, Princeton University, Princeton, N.J.

The meeting will consist of a tour of the Plasma Physics Research Laboratories, then a paper on **Spectroscopy on the C-Stellarator** by J. Hirschberg.

Monday–Thursday 20–23 *May* 1963: **Fourteenth Annual Mid-America Spectroscopy Symposium:** *Society for Applied Spectroscopy, Chicago Section,* Chicago.

The programme is as follows:

Monday 20 *May*

Morning Session—Electron Microprobe Analysis
Microprobe Analysis of Minerals and Segregates. I. Adler

Industrial Applications of Microprobe Analysis.	B. R. Banerjee and N. S. Blake
Applications of the Electron Microprobe to the Operation of an Industrial Plant.	W. W. Welbon and R. J. Debeer
Use of a Multichannel Analyser for Electron Probe Microanalysis.	L. S. Birks and A. Batt
Development and Use of a Semimicro X-Ray Fluorescence Attachment.	W. J. Wittig

Morning Session—Infrared and Raman Spectroscopy

Raman Sources other than Mercury Arcs.	E. R. Lippincott
Gas Maser Spectroscopy in the Infrared.	W. L. Faust, R. A. McFarlane, C. K. N. Patel and C. G. B. Garrett
Infrared and Raman Spectra of Xenon Compounds.	H. H. Claussen, J. G. Malm and C. Shernick
Infrared Determination of Oil in Phosphotur.	A. Davis, H. M. Joseph and L. E. Tufts

Afternoon Session—X-Ray Spectroscopy in Process Control

Process Stream Analysis by X-Ray Spectroscopy.	R. H. Munch
Auxiliary Equipment for X-Ray Process Control Installations.	J. W. Kemp
X-Ray Fluorescence Applied to On-Stream Analysis.	W. R. Kiley
A Digital Computor for Optical and X-Ray Quantometers.	W. E. Fowler and A. J. Hartwick
Use of Digital Techniques to Aid in the Phase Analysis of Portland Cement by X-Ray Diffraction.	G. J. C. Frohnsdorff and P. H. Harris

Afternoon Session—Infrared and Raman Spectroscopy

Infrared Analysis in Biomedical Research.	D. S. Erley
Use of Thin-Layer Chromatography with Infrared Spectroscopy.	J. G. Grasselli and M. K. Snavely
Infrared Spectra of Pesticides Recorded at Microgram Levels.	W. W. Morris, Jr. and E. O. Haenni
Characterisation of Saturated Aliphatic Esters in the 15-40 *Micron Region.*	J. J. Lucier and F. F. Bentley

Tuesday 21 *May*

Morning Session—Infrared and Raman Spectroscopy

The Urey-Bradley Potential Function.	K. Nakamoto
Applications of Normal Co-ordinate Treatments.	S. Sundaram
The Urey-Bradley Force Constants of Triginal Bipyramidal XY_5-Type Molecules.	R. A. Condrate and K. Nakamoto
Normal Co-ordinate Treatments of 1,2-*Dihalo Alkenes.*	R. Krupp

Morning Session—X-Ray Emission Spectroscopy

Practical Methods of Solving Absorption and Enhancement Problems in X-Ray Emission Spectroscopy.	E. L. Gunn
X-Ray Fluorescence Control Analysis in the Manufacture of Magnetic Alloys.	J. P. Kapetan
X-Ray Spectrometric Analysis of Alloyed Copper.	T. J. Cullen
X-Ray Spectroscopy in Biology and Medicine: Microtechniques and Instrumental Sensitivity.	J. C. Mathies and P. K. Lund
Assay of Iodine Content of Thyroid Extraction by X-Ray Absorption Edge Analysis.	D. E. Flick

Afternoon Session—Infrared and Raman Spectroscopy

Examples of Fermi Resonance and Coupling Involving N-D Vibrations.	C. Curran
Raman Spectral Studies of Aqueous Solutions of Selenic Acid.	G. E. Walrafen

Afternoon Session—X-Ray Emission Spectroscopy

Recent Progress in Soft X-Ray Spectroscopy in the Wavelength Region 13-150 Å.	J. E. Holliday

Panel Discussion—Panelists: I. Adler, L. S. Birks, V. E. Buhrke and E. L. Gunn

Wednesday 22 *May*

Morning Session—Flame Emission Spectroscopy

Physiochemical Processes in Flame Spectroscopy.	W. D. Cooke
Flame Photometry: An Investigation of Some Factors Affecting the Emissivity of Metals when Solutions of their Chelates in Organic Solvents are Aspirated into a Flame.	H. C. Eshelman and J. Armentor
Mutual Interference Effects of Certain Group III-A Ions with Calcium in Flame Photometry.	M. E. Doty and W. G. Schrenk
Flame Photometric Detection of Toxic Volatile Compounds.	R. S. Bramen and W. A. Loseke

Morning Session—Nuclear Magnetic Resonance Spectroscopy

An Empirical Approach to the Interpretation of NMR Spectra.	R. Bible
Proton Magnetic Resonance Spectra of Substituted Pyridines and the Effect of Protonation.	C. Bell, R. S. Egan and L. Bauer
Hydrogen-Deuterium Exchanges in Organic Molecules by NMR Spectroscopy.	R. Mattoon and R. Kriese

Morning Session—Visible-Ultraviolet Spectroscopy

What We Don't Know about Electronic Spectra.	D. S. McClure
Indirect Spectrophotometric Determination of Metals in their Metal Oxides by Reduction of the Nitrite Ion.	H. F. Combs and E. L. Grove
Absorption in Chromium(VI) Oxide.	J. Anysas

Afternoon Session—Flame Emission Spectroscopy

New Developments in Practice and Technique of Flame Spectroscopy.	J. A. Dean
Some Spectrophotometric Observations of Hydrogen Arc-Jets.	R. L. Fox
Characterisation of Chemical Species in Plasma.	E. Raisen, R. A. Carrigan, V. Raziunas and E. L. Grove

Afternoon Session—Electron Spin Resonance Spectroscopy

Electron Spin (Paramagnetic) Resonance Spectroscopy in Biological Systems.	J. Heise
Electron Spin Resonance Spectra of Gamma Radiolysis Products of Solid Acetonitrile.	D. Dunbar, D. Hale, L. Harrah R. Rondeau and S. Zakanycz

Afternoon Session—Visible-Ultraviolet Spectroscopy

Properties of Broad Optical Bands Associated with Imperfections.	J. J. Markham
Optical Spectrum of $HI_3.2C_6H_5CONH_2$*: A Model of the Starch-Iodine Complex.*	M. B. Robin

Thursday 23 *May*

Morning Session—Arc-Spark Emission Spectroscopy

The RF Discharge at Atmospheric Pressure and Its Use as an Excitation Source in Analytical Spectroscopy.	R. Mavrodineanu and R. C. Hughes
Spectrographic Determination of Trace Impurities in High Purity Gold.	A. J. Lincoln and J. C. Kohler
Spectroscopy in Astronomy.	R. Johnson
An Application of the Stallwood Jet DC-Arc to the Analysis of Air Contamination in Inert Gases.	W. A. Loseke and E. L. Grove

Morning Session—Gas Chromatography

High Temperature Gas Chromatographic Separation of Inorganic Compounds.	R. S. Juvet, Jr. and F. Tivin
Application of Gas Chromatography to Phosphorous Containing Compounds.	A. Davis, A. Roaldi, J. G. Michalovic and H. M. Joseph
Some Experiments in Gas Chromatography.	H. A. Szymanski
Factors Affecting the Efficiency of Gas Chromatography of Steroids.	M. D. Whittier, L. Mikkelson and N. Armstrong
Recent Advances in Preparative Chromatography.	K. P. Dimick

Afternoon Session—Arc-Spark Emission Spectroscopy

Controlled Atmosphere Spectroscopy.	W. A. Gordon

Panel Discussion—Panelists: J. F. Woodruff, J. A. Norris, A. Goldblatt, H. Plagge and J. R. Churchill

Afternoon Session—Gas Chromatography

Recent Advances in Column Theory.	D. DeFord
An Application of Gas Chromatography to Solid State Physics: Determination of Gases Evolved when Coloured Potassium Chloride Dissolves.	F. Phelps
Studies on the Detection of Narcotics in Human Urine by Gas-Liquid Chromatography.	J. Ressner
A Broad Range Ionisation Detector.	W. Barbour and D. R. Rushneck

Further information may be obtained from the Symposium Publicity Chairman, John E. Murphy, Borg-Wagner Research Centre, Wolf and Alonquin Roads, Des Plaines, Illinois, U.S.A.

Monday–Thursday 20–23 *May* 1963: **International Symposium on Humidity and Moisture: Measurement and Control in Science and Industry.** Sheraton Park Hotel, Washington, D.C., U.S.A.

The following parts of the technical programme may be of interest to analytical chemists:

Monday, May 20

PRINCIPLES AND METHODS OF MEASURING HUMIDITY OF GASES— Electric Hygrometry. 2.00 p.m.

Review of Lithium Chloride Radiosonde Hygrometer Elements.	D. A. Mathews
A Resistance-Humidity Relationship for Sensors of the Dunmore Type.	C. P. Hedlin
A Study of the Accuracy of Dunmore Type Humidity Sensors.	G. O. Handegord, C. P. Hedlin and F. N. Trofimenkoff
On the Aging Effect of an Electrolytic Hygrometer.	J. Kobayashi and Y. Toyama
An Investigation of the Accuracy and Response Rate of a Lithium Chloride Heated Electrical Hygrometer.	C. P. Hedlin and F. N. Trofimenkoff
A Small Electrical Hygrometer for Microclimate Measurements.	M. N. Rogers
An Application of the Dunmore Electric Hygrometer to Humidity Measurement at Low Temperatures.	G. O. Handegord and C. E. Till
Experimental Apparatus for the Determination of Equilibrium Relative Humidity in the Temperature Range of 0 *to* −30°C.	L. Szalai
A Relative Humidity Sensor Based on the Capacitance Variation of a Plastic Film Condenser.	D. E. Nelson and E. J. Amdur
Humidity Meter Using Cerium Titanate Elements.	S. R. Duggan and C. E. Johnson, Jr.
A Ceramic Relative Humidity Sensor.	E. J. Amdur, D. E. Nelson and J. C. Foster

PRINCIPLES AND METHODS OF MEASURING MOISTURE IN LIQUIDS AND SOLIDS—Physical and Chemical Methods: 2.00 p.m.

Gas Chromatography in the Determination of Moisture in Grain.	E. L. Weise and J. K. Taylor
Hygrometric Method of Measuring Moisture Contents in Porous Materials.	Manuel Rocha and Elda de Castro
A Thermocouple Psychrometer for Measuring the Relative Vapour Pressure of Water in Liquids or Porous Materials.	L. A. Richards
Direct Spectrophotometric Determination of Moisture Content of Solids.	K. H. Norris and J. R. Hart
Improved Apparatus for Moisture Extraction from Friable Materials.	K. Kostyrko and T. Plebanski
Non-Steady-State Method for Determination of Moisture-Content in Structures.	B. H. Vos
Moisture Balance.	Kamekichi Shiba and T. Ichinose
Determination of Water in Rocket Propellants: A Comparison of Several Analytical Techniques.	Anthony Nudo and W. L. Clark
An Infrared Instrument for Measurement of Quality of Steam.	Melvin Greenberg
Infrared Analysis of Water.	W. M. Trippeer

Tuesday, May 21

PRINCIPLES AND METHODS OF MEASURING HUMIDITY OF GASES—Electric Hygrometry: 9.00 a.m.

Some Research on Lithium Chloride Radiosonde Hygrometer Elements and a Guide for Making Them.	D. A. Mathews
A Method of Measuring the Moisture Content of Air Directly in Grains Per Pound of Dry Air.	E. E. Stanley
Carbon Humidity Elements: Manufacture, Performance and Theory of Operation.	S. L. Stine
Transient Behaviour of Carbon Humidity Element.	R. M. Marchgraber
A Hygrometer Utilising Anodic Oxide Film of Aluminium	H. Watari and A. Miyata
Mode of Operation of Saturation Temperature Hygrometers Based on Electrical Detection of a Salt-Solution Phase Transition.	D. E. Nelson and E. J. Amdur
Accurate Hygrometry with Ionic Single Crystals.	R. G. Wylie
Analysis of Response Data from Radiosonde Flights of the Barium Fluoride Film Hygrometer Element.	F. E. Jones
Poly-Electrolytic Resistance Humidity Elements.	R. C. Musa and G. L. Schnable

PRINCIPLES AND METHODS OF MEASURING MOISTURE IN LIQUIDS AND SOLIDS—Dielectric, Resistance and Capacitance Methods: 9.00 a.m.

Measurement and Control of Moisture Content by Microwave Absorption.	Alec Watson
Improvement of Moisture Determination by Dielectric Constant through Density Correction.	F. J. Hughes, J. L. Vaala and R. B. Koch
A Portable Electronic Moisture Detector for Reinforced Plastics and Its Application.	J. O. Outwater
Conductimetric Determination of Surface Moisture of Building Materials.	Geza Szük
Plaster of Paris Block as an Electrical Measuring Unit for Making a Continuous Measurement of Soil Moisture under Field Conditions.	G. J. Bouyoucos
Use of Capacitance Methods for Determining Quantities of Materials in Mixtures.	J. E. Fletcher
Electric Measurement of Soil Porosity or Moisture Content.	H. Cambefort and C. Caron

Determination of Moisture Content in Canadian Grain by Electric Moisture Meter.	V. Martens and I. Hlynka
Moisture Measurement by High Frequency Currents.	Robert Leroy
Continuous Moisture Measurement in Solids.	R. M. Green

PRINCIPLES AND METHODS OF MEASURING HUMIDITY OF GASES— Spectroscopic Hygrometry: 2.00 p.m.

Absorption of Radiation by Water Vapour.	J. W. Johns
Theoretical Bases for Spectroscopic Determination of Humidity.	W. S. Benedict
Infrared Absorption Hygrometer.	W. F. Staats, L. K. Foskett and H. P. Jensen
The Infrared Hygrometer: Its Application to Difficult Humidity Measurement Problems.	R. C. Wood
A Special Hygrometer for Measuring Total Precipitable Water.	N. B. Foster, D. T. Volz and L. W. Foskett
A Long-Path Infrared Hygrometer.	W. G. Tank
The NRL Lyman-Alpha Humidiometer.	D. L. Randall, T. E. Hanley and O. K. Larison
Measurement of Water Vapour Density by Absorption of Vacuum Ultraviolet Radiation.	J. E. Tillman

PRINCIPLES AND METHODS OF MEASURING MOISTURE IN LIQUIDS AND SOLIDS—Nuclear Methods: 2.00 p.m.

Nuclear Magnetic Resonance as a Technique for Measuring Moisture in Liquids and Solids.	W. L. Rollwitz
Application of Nuclear Magnetic Resonance to Measurement of Moisture Content in Coals and Cokes.	W. R. Ladner
Field Determination of Moisture and Density in Soils by the Nuclear Method.	J. Huet
A Statistical Correlation of Neutron Scattering by Proton Interaction for Determining Moisture Content.	Seha Senturk
Measurement and Control of Moisture in Raw Materials Used in Iron Making Processes by Neutron Moderation.	Yoshio Miyashita
Neutron Scattering Measurement of Soil Moisture: Development and Current Status.	C. H. M. Van Bavel
Calibration of a Neutron Soil Moisture Meter.	K. N. Burn
Measurement of Moisture Content of Soil by Radio-Isotopes.	E. E. de Beer and E. H. G. Goelen

PRINCIPLES AND METHODS OF MEASURING HUMIDITY IN GASES— Chemical Hygrometry and Other Methods: 2.00 p.m.

A Technique for the Continuous Indication of Medium-Low Water Vapour Pressures.	R. G. Wylie, W. A. Caw and N. W. Bryant
Interaction of Water Vapour with a Thin Liquid Layer: Applications to Gas Chromatography and Hygrometry.	R. J. Charlson
Detection and Measurement of Humidity and Moisture by the Hygrophotographic Technique. Chemical Humidity Indicators Used in Military Storage.	B. G. Blinn
Continuous Absorption Hygrometry with a Pneumatic Bridge Utilising Critical Flow.	W. A. Wildhack, T. A. Perls and C. W. Kissinger
Measurement of Relative Humidity in Confined Spaces.	J. E. Kennedy and L. E. Machattie
Characteristics of Human Hair Affecting Design and Performance of Humidity Sensing Instruments.	F. K. Davey
A Sensitive Thermoelectric Water Vapour Recorder.	G. C. Flumerfelt
A Water Vapour Partial Pressure Meter.	S. H. Smith, Jr.

Wednesday, May 22

PRINCIPLES AND METHODS OF MEASURING HUMIDITY OF GASES—

Psychrometry: 9.00 a.m.

A Critical Review of Tables and Charts Used in Psychrometry.	H. H. Bindon
Laminar Boundary Layer Calculation for a Flat-Plate Wet-Bulb Element.	Tamami Kusuda
Experimental Results of the Psychrometer Constant.	M. Yoshitake and I. Shimizu
An Integrating Temperature and Humidity Gradient Recorder.	B. G. Collins
Response of a Psychrometer to Fluctuations in Vapour Pressure.	R. J. Taylor
A Thermocouple Recording Psychrometer for Measurement of Relative Humidity in Hot Arid Atmosphere.	Lee Richardson
A Proposed Technique for Measuring Relative Humidity at Below Freezing Temperatures.	C. I. Branton

PRINCIPLES AND METHODS OF MEASURING HUMIDITY OF GASES—

Psychrometry: 2.00 p.m.

Proposal for an Experimental Triple-Tubed Adiabatic Saturator to Measure Thermodynamic Wet-Bulb Temperature as a Limit Approached during the Saturation Process.	L. P. Harrison
Design and Calibration of a Thermocouple Psychrometer Utilising the Peltier Effect.	J. E. Box, Jr.
Wet-and-Dry-Plate Dew Point Hygrometer.	Kamekichi Shiba and Tatsumi Tozawa
Psychrometric Determination of Relative Humidity in Air with Dry Bulb Temperature Exceeding 212°*F.*	R. W. Worrall

PRINCIPLES AND METHODS OF MEASURING HUMIDITY OF GASES—

Coulometric Hygrometry: 2.00 p.m.

Mixing Ratio Indicator.	P. B. MacCready, Jr.
Adaptation of the Electrolytic Moisture Detector to Atmospheric Humidity Measurement.	Michael Czuha, Jr.
Additional Performance Data on a New Electrolytic Hygrometer Cell.	R. H. Jones and Arne Peterson
Detection of Parts Per Million Moisture in Refrigerants.	C. M. Finlay and John Shaffer

Thursday, May 23

PRINCIPLES AND METHODS OF MEASURING HUMIDITY OF GASES—

Dewpoint Hygrometry: 9.00 a.m.

The Dew or Frost Point Hygrometer.	A. W. Brewer
The Basic Process of the Dewpoint Hygrometer.	R. G. Wylie and D. K. Davies
Two New Hygrometers—Dewpoint Hygrometer and Frost Point Hygrometer.	K. M. Greenland and S. Martin
Measurement of Humidity by High Altitude Aircraft.	C. H. Hinkel
A Recording Dewpoint Hygrometer.	Einar Brendeng
Design Features of the NYU Dewpoint Hygrometer.	A. M. Nathan
An Automatic Frost Point Hygrometer Using Radioactive Detection.	J. G. Ballinger

STANDARDS—Humidity Generators and Calibration Chambers: 9.00 a.m.

The NBS Standard Hygrometer.	ARNOLD WEXLER and R. W. HYLAND
A Pneumatic Bridge Hygrometer for Use as a Working Humidity Standard.	LEWIS GREENSPAN
Two-Pressure Relative Humidity Standards.	E. J. ADMUR and R. W. WHITE
An Intercomparison between the NBS Two-pressure Humidity Generator and the NBS Standard Hygrometer.	S. HASEGAWA, R. W. HYLAND and S. RHODES
An Atmosphere Producer for Laboratory Use.	J. D. WENTZEL
The Gilbarco Moisture Generator.	J. KERTZMAN
Moisture Monitor Testing and Calibration.	C. D. MONTGOMERY
Mixing Hygrostat for Calibration of Hygroscopic Hygrometers.	VILHO VÄISÄLÄ
Testing Techniques for the Carbon Humidity Element.	P. A. ROGERS

PRINCIPLES AND METHODS OF MEASURING HUMIDITY OF GASES— Dewpoint Hygrometry: 2.00 p.m.

Hygrometer Developments at U.S. Naval Research Laboratory.	R. E. RUSKIN
Design and Applications of High Performance Dewpoint Hygrometers.	LOUIS PAINE and H. R. FARRAH
Dewpoint Apparatus of High Accuracy.	J. L. CHAMBERLIN, J. L. HARTLEY and W. D. HUFF
Direct Measurement of Dewpoint Temperature with Semiconducting Thermoelements.	VICTOR ARMSTRONG
Improvements in Dewpoint Measurements of Gases by Use of Peltier Devices.	O. J. LEONE
An Automatic Dewpoint Hygrometer with Thermoelectric Cooling.	D. J. BEAUBIEN and C. C. FRANCISCO

STANDARDS—Calibration and Test Chambers. Fixed Points: 2.00 p.m.

Thermohygrostatic Chamber.	K. KOSTYRKO, J. CZERNIK and T. PLEBANSKI
A New Apparatus for Study of Moisture Sorption by Starches and Other Food Stuffs in Humidified Atmospheres.	P. R. SMITH
Automatic Relative Humidity Test Chamber.	LOREN KREUGER
Control of Conditioning Atmospheres in Small Sealed Chambers.	K. M. GREENLAND and S. MARTIN
Properties of Water-Salt Systems in Relation to Hygrometry.	R. G. WYLIE
Relative Humidities over Saturated Solutions of Nine Salts in the Temperature Range from 0 to 90°F.	C. P. HEDLIN and F. N. TROFIMENKOFF
Vapour Pressures of Saturated Salt Solutions.	D. T. ACHESON
Control of Atmospheric Humidity by Aqueous Sulphuric Acid Solution.	KOJI KAWASAKA and KYOICHI KANOU

Enquiries about the Symposium in general should be addressed to any of the sponsoring organisations—*American Society of Heating, Refrigerating and Air-Conditioning Engineers, American Meteorological Society, Instrument Society of America,* and *National Bureau of Standards*—or directly to the Meetings Secretary, ASHRAE, 345 East 47 Street, New York 17, N.Y., U.S.A.

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BOOK REVIEW

Methods of Forensic Science, Volume I: Edited by FRANK LUNDQUIST, Interscience Publishers, 1962. Price £7 10 0d.

THE use of scientific methods in crime investigation is steadily increasing, but the literature on the subject is scattered throughout a wide range of books and periodicals which are often difficult to obtain when required. There is, therefore, a growing need for a standard methodology to which the forensic scientist can refer when some procedure is required, or has to be devised, to solve a specific problem. The book under review is the first of a series of volumes designed to meet this need. Each chapter will be contributed by one or more outstanding workers in the field and will include a short review of the subject followed by a detailed description of recommended procedures. As chapters become out of date or new and important methods appear these latest developments will be included in subsequent volumes.

The first volume gets the series off to a good start, and contains eight chapters. The first, on the isolation and detection of alkaloids, illustrates the increasing complexity of modern toxicology, as it lists no fewer than four hundred and fifty one alkaloids. Reference is made to the use of chromatography to narrow the field of investigation of an unknown alkaloid, followed by crystal tests for positive identification. Where necessary, spectrophotometry, melting point and other determinations may be employed as confirmatory tests.

In the second chapter, on the detection and identification of bloodstains, the various standard and proved methods are described together with more recent techniques, such as paper chromatography, electrophoresis and polarography. The references do not extend beyond 1959, no doubt because of the necessity of meeting editorial requirements, and do not therefore include the important recent advances made by Coombs and his associates.

The chapter on the determination of the source of origin of biological stains deals with the various problems associated with the serological investigation of stains found on a wide range of materials. Some of the more recent methods are described together with their limitations. A few errors in terminology were noted in this chapter; thus activated carbon or charcoal is referred to as "medical coal".

The next chapter, which deals with the examination of materials such as metal fragments, minerals, paint, soil and glass, would be better entitled "The Identification of Traces of Non-biological Origin". This chapter describes standard methods widely used in most forensic science laboratories. It suffers from the fact that it lacks the copious references which are characteristic of the other chapters in the book.

In view of the increasing number of deaths from derivatives of barbituric acid it is appropriate that the first volume of the series should contain a chapter on the detection and estimation of this class of compounds. This chapter describes all the standard methods of separation and identification, and includes more recently used techniques such as thin layer chromatography. There are a number of very clear photographs of crystals, and graphs illustrating the effect of pH on the shape of the ultraviolet absorption spectrum, and there are over 500 references.

Another common cause of death is poisoning by carbon monoxide, and a chapter is devoted to its quantitative determination. A particularly useful feature of this chapter is the section on the physiological effects of carbon monoxide.

The final chapter deals with the various procedures adopted in the study of firearms and ammunition.

This book is well produced, the print is easy to read, the diagrams and photographs are clear. It is recommended in spite of the somewhat high price to forensic scientists, and to all those concerned with the application of science to crime investigation. The editor is to be congratulated on the production of what will undoubtedly become a standard work of reference, and it is to be hoped that the other volumes to be published in this series will maintain the standard set by the first volume.

A. J. HOWARD

Talanta, 1963, Vol. 10, p. xvi. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

The complexometric analysis of pyro- and triphosphates—I: Stability constants of the proton and metal complexes of the acids: AXEL JOHANSSON and ERKKI WÄNNINEN. (30 *January* 1963)

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