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devoted to the application of microtechniques in all branches of science

Editor: Al Steyermark

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Microchemical Journal, Volume 18, Number 4, August 1973

Briefs

Trace Determination of Tin(II) and Tin(IV) in Different Solvents (H_2O, CH_3OH) by Anodic Stripping Voltammetry. V. FANO AND L. ZANOTTI, *Laboratorio Maspec del C.N.R., Parma, Italy.*

A method for the analysis of tin(II) and tin(IV) traces by stripping voltammetry in aqueous medium and in methanol is reported. The advantages of using methanol as a solvent are illustrated. In this medium, it is possible to perform the silmultaneous determination of traces of tin(II) and other cations which have more negative dissolution potentials.

Microchem. J. **18,** 345 (1973).

The Use of Platinum in the Perkin–Elmer 240 Elemental Analyzer: The All-Platinum Ladle. J. F. ALICINO, *The Squibb Institute for Medical Research, Princeton, New Jersey 08540.*

An all-platinum ladle, for use in the CHN Analyzer, is described, which in effect provides a second combustion and gives more accurate results. No change is made in the programmed sequence of the instrument.

Microchem. J. **18,** 350 (1973).

Marine Adhesives. IV. Hexosamine Content of *Balanus eburneus* Adhesive. ALAN F. KRIVIS AND MICHAEL D. MARTZ, *Department of Chemistry, The University of Akron, Akron, Ohio 44325.*

The adhesive secreted by the barnacle, *Balanus eburneus,* was studied because of its excellent adhesive characteristics. Two hexosamines, glucosamine and galactosamine, were isolated.

Microchem. J. **18,** 354 (1973).

Complexometric Estimation of Glutamic Acid by Titration with Standard Cadmium Acetate Solution Employing 4-(2-Thiozolyl Azo) Resorcin. KRISHAN BAHADUR AND INDRA SAXENA, *Chemical Laboratories, University of Allahabad, Allahabad, India.*

Glutamic acid is titrated with cadmium acetate using 4-(2-thiozolyl azo) resorcin as the indicator. Titrations are carried out at pH 9.0.

Microchem. J. **18,** 358 (1973).

Microdetermination Techniques for H_2O_2 in Irradiated Solutions. B. L. GUPTA, *Directorate of Radiation Protection, Bhabha Atomic Research Centre, Trombay, Bombay-85, India.*

Ferric-xylenol orange and H_2O_2-titanium-xylenol orange complexes are used for the determination of hydrogen peroxide in irradiated solutions.

Microchem. J. **18,** 363 (1973).

Microdetermination of Tartaric and Malic Acids Present Together. P. K. JAISWAL, *Department of Chemistry, M.M.M.V. Bhat Par Rani, Deoria, India.*

Tartaric acid is oxidized by Ag(III), whereas both tartaric and malic acids are oxidized by Cu(III).

Microchem. J. **18,** 375 (1973).

Extraction of Radiozinc, Radioiron, and Radiomanganese from Alcoholic and Acetonic Acidic Solutions. A. ALIAN, *Nuclear Chemistry Department, Analytical Division, Atomic Energy Establishment, Cairo, U. A. R.*

The extraction of the radiometals with a xylene solution of tridodecylamine (TDA) and tributyl phosphate (TBP) in the absence of acetone and water-miscible alcohols is reported.

Microchem. J. **18,** 377 (1973).

Microdetermination of Naturally Occurring Nodososide from *Cassia nodosa,* Using Chlorauric Acid as Oxidizing Agent in Alkaline Medium. S. J. RAI, P. C. GUPTA, AND O. C. SAXENA, *Chemical Laboratories, University of Allahabad, Allahabad, India.*

Nodososide, from the flowers of *Cassia nodosa,* is subjected to alkaline hydrolysis followed by oxidation, resulting in the formation of sodium formate and sodium acetate.

Microchem. J. **18,** 393 (1973).

Titrimetric Microdetermination of Chromotrope 2R: Ceric Sulfate as Oxidizing Agent. S. A. I. RIZVI, *Chemical Laboratories, University of Allahabad, Allahabad, India.*

The determination is based on the reaction in which forty equivalents of ceric sulfate are used and the end product is formic acid.

Microchem. J. **18,** 398 (1973).

Direct Titrimetric Microdetermination of Tropeolin OO. I. Oxidation of Tropeolin OO with Ceric Sulfate. O. C. SAXENA, *Chemical Laboratories, University of Allahabad, Allahabad, India.*

Two methods are described. One is by direct titration with ceric sulfate resulting in the formation of a salt in the ratio of 1:2. The other method is an oxidation in which 51 equivalents of ceric sulfate are used to give an end product of formic acid.

Microchem. J. **18,** 401 (1973).

Synergism in the Solvent Extraction of Samarium by Thenoyltrifluoroacetone and Triphenyl or Trioctyl Phosphine Oxide Mixture. HISHAM F. ALY AND HASSAN A. EL-NAGGAR, *Nuclear Chemistry Department, U.A.R. Atomic Energy Establishment,* Cairo, U.A.R.

A systematic investigation of the extraction of samarium with solvents was carried out. From the distribution data obtained, the formula of the extracted complex was shown to be composed of one molecule of samarium salt to two molecules of complexing agent.

Microchem. J. **18,** 405 (1973).

Spectrophotometry of Iron Chelates with 2-Hydroxy-5-methylpropiophenone Oxime. SHRI PRAKASH, YAG DUTT, AND R. P. SINGH, *Department of Chemistry, University of Delhi, Delhi-7, India.*

2-Hydroxy-5-methylpropiophenone oxime forms two complexes with ferric iron, the formation of which is dependent upon the pH. A blue colored complex is formed at low pH values, having a composition of one ferric iron to one oxime. At higher pH values, a brown-red chelate is formed with a composition of one ferric iron to three oximes.

Microchem. J. **18,** 412 (1973).

Microdetermination of Arsenic(III) and Osmium(VIII) Through Osmium–Thiourea Reaction. P. P. NAIDU AND G. G. RAO, *Department of Chemistry, Andhra University, Waltair, India.*

The osmium–thiourea reaction is catalyzed by arsenic(III), which forms the basis of the determinations of these metals.

Microchem. J. **18,** 422 (1973).

Applications Involving the Iodine Ion. VII. Determination of Small Amounts of Cerium (IV) and Analysis of Its Mixtures with Some Metal Ions. H. KHALIFA AND B. N. BARSOUM, *Faculty of Science, Cairo University, Giza U.A.R.*

Excess iodide is added and the mixture then is titrated with mercury(II), using a silver amalgam electrode.

Microchem. J. **18,** 428 (1973).

Applications Involving the Iodide Ion. VIII. Direct and Indirect Determination of Mercury(I) and Analysis of Mixtures. Analysis of Chromium(VI)–Chromium(III) Mixtures. Determination of Hypochlorite. H. KHALIFA AND Y. M. ISSA, *Faculty of Science, Cairo University, Giza, U.A.R.*

Mercury(I) is determined by direct titration with iodide or by back-titration of the excess of iodide with mercury(II) using silver amalgam as the indicating electrode. Analysis of chromium(VI)–chromium(III) mixtures involves potentiometric back-titration of excess iodide and of excess EDTA separately with mercury(II). Back-titration is also applied to the determination of hypochlorite.

Microchem. J. **18,** 436 (1973).

MICROCHEMICAL JOURNAL 18, 345–349 (1973)

Trace Determination of Tin(II) and Tin(IV) in Different Solvents (H_2O, CH_3OH) by Anodic Stripping Voltammetry

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Laboratorio Maspec del C.N.R., Parma, Italy

Received March 20, 1973

The determination of tin(IV) by stripping voltammetry has been reported in the literature. The peak has been seen in NH_4SCN solution in the presence of both pyrogallol at pH 1 (*1*) and in hydrochloric acid solution (*3*). In the present work we have verified that tin(II) can also be determined in aqueous solution of hydrochloric acid at pH values which prevent its precipitation. Nevertheless, when low pH values and very negative potentials are used, the study of the simultaneous presence of cations with many more electronegative electrodissolution potentials, such as Mn^{2+}, Zn^{2+} is very difficult because of the presence of a strong residual current. In this work we show that the determination of tin(II) and tin(IV) is also possible in nonaqueous solutions such as methanol. By using sodium chloride as a supporting electrolyte in such a medium, it is possible to work with still more negative preelectrolysis potentials than −1.5 V vs SCE. The use of this medium is particularly indicated in the determination of tin(II) and tin(IV) even when preelectrolysis potentials more negative than −1 V vs SCE are required.

APPARATUS AND REAGENTS

The polarograph, with hanging mercury drop electrode, that has been used for the measurements is described in (*2*). The polarograph cell was equipped with a thermostat. All of the polarographic measurements were made at 18°C with a sweep rate of 4.3 mV/sec. All of the examined cation solutions were prepared at the time of analysis by dissolving the respective chlorides in methanol (with the exception of lead for which nitrate was used). All of the materials were reagent grade and were used without further purification; only methanol had been purified by means of repeated distillations. The degassing time was fixed at 10 min. Operating under these conditions (temp, 18°C, degassing time, 10 min) the volume variation due to the evaporation of methanol was able to be controlled. If longer degassing times and stronger nitrogen fluxes are used and if the variation in the volume obtained is kept in mind the result can be easily corrected.

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THE USE OF METHANOL IN STRIPPING VOLTAMMETRY FOR THE DETERMINATION OF Cu^{2+}, Cd^{2+}, Sn^{4+}, Zn^{2+}, Mn^{2+}

The use of methanol as a solvent in substitution of water can be extended to the determination of many cations which are usually of major interest in stripping voltammetry analysis. In fact, methanol contains some important characteristics such as: it dissolves compounds, such as sodium chloride, in a large enough quantity to be used as supporting electrolytes; it is a good solvent of halides ($ZnCl_2$, $CdCl_2$, $CuCl_2$, $SnCl_2$) and of salts such as $PbNO_3$. Since the donor action of alcohol is similar to the donor action of water, it also dissolves many acceptor halides such as $SbCl_5$ or $SnCl_4$.

In the present work we have found that saturated sodium chloride solution of methanol, as a supporting electrolyte, allows one to find microtraces of Cu^{2+}, Pb^{2+}, Cd^{2+}, Sn^{4+}, Zn^{2+}, Mn^{2+} (Fig. 1). In such a medium, the electrodissolution potentials of the examined cations are about equal to those measured in NaCl aqueous solutions vs SCE., while peaks heights are usually lower (Table 1). The preelectrolysis potentials were -1.3 V vs SCE for all of the examined cations with the exception of Mn^{2+} for which -1.75 V was necessary. In the trace analysis of Mn^{2+}, if the base electrolyte proposed by us is used, the peak heights must be measured on the left side. Since the peak is so wide, it is impossible to measure its height on the right side, that is at more negative potentials, as is generally used.

DETERMINATION OF TIN(II)

In this work we have shown that it is also possible, with a good degree of precision, to determine traces of tin(II) in an aqueous solution, if the solution is acid enough to prevent the formation of hydroxides. In Fig. 1 the results of the analysis of tin(II) in 0.1 *N* hydrochloric acid are reported. However, when working in such a medium,

TABLE 1
CATIONS PEAKS HEIGHTS IN DIFFERENT MEDIA[a]

Cation	Peak height (cm)	
	In saturated sodium chloride solution of methanol	In 0.1 *N* sodium chloride aqueous solution
Zn^{2+}	12	38.5
Cd^{2+}	19.6	45
Cu^{2+}	10.1	14
Mn^{2+}	5.8	45.5

[a] Cation concn: 12.5 μg/ml $\times 10^2$; preelectrolysis time: 5 min; preelectrolysis potentials: 1.3 V, sveep rate: 4.3 mV/sec.

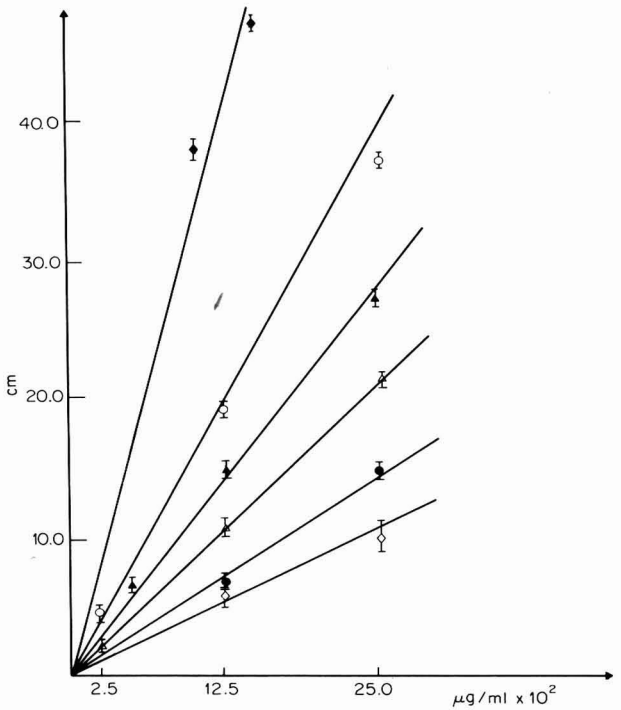

FIG. 1. Polarographic peak heights as a function of cation concentrations: (○) Cd^{2+}, (▲) Pb^{2+}, (△) Zn^{2+}, (●) Cu^{2+}, (◇) Mn^{2+} in sodium chloride solution of methanol; (◆) Sn^{2+} in 0.1 *N* hydrochloric acid aqueous solutions.

a residual current appears which makes impossible the simultaneous analysis of tin(II) and of other cations having more negative electrodissolution potentials than −1 V vs SCE. Also in this case it is advisable to use a NaCl saturated solution in methanol. In this medium the tin(II) peak manifests itself at −0.6 V vs SCE, and not every residual current appears even when it is necessary to work at more negative potentials than −1.5 V vs SCE.

However when performing stripping voltammetry analysis in solutions in which the oxidation state of the same element may vary, as in the case of tin(II) which can pass to tin(IV), the effect of the various valence states on peak heights must always be verified. In the case of tin, the polarogram obtained in the stripping process, involves only the oxidation of the tin amalgam to the stannous state. Nevertheless, the complete analysis process is made up of some stages, the first of which is the free diffusion of ions to the electrode surface. Therefore this stage may generally critically influence the entire process for each oxidation state of the cation under examination. In such a case, the influence of the variation of the cation oxidation state in solution must

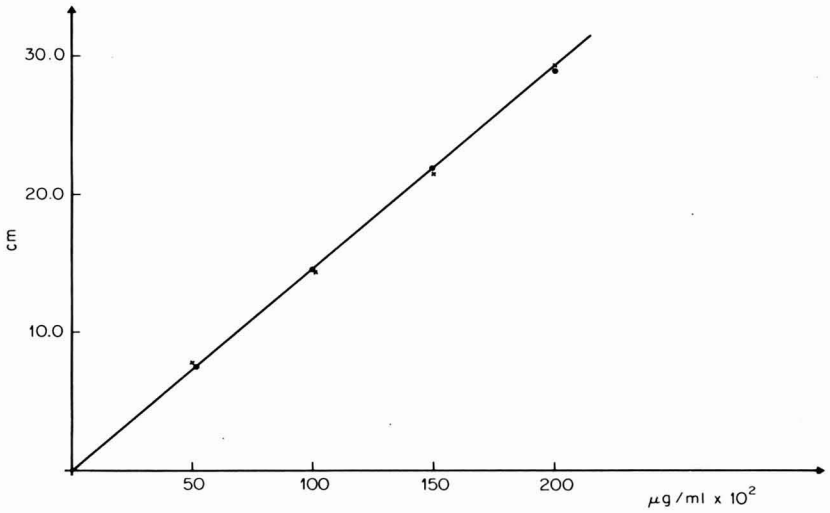

FIG. 2. Polarographic peak heights of (+) tin(II) and (●) tin(IV) as a function of concentration, in sodium chloride solution of methanol.

be analyzed. At first, therefore, the real valence of the ions in solution has to be verified, and it was seen that the oxidation process of tin(II) to tin(IV) in an alcoholic solution was very limited. For this reason, colorimetric titration was carried out on tin solutions in methanol for concentrations equal those used in polarographic analysis. For this purpose, we have used hematoxylin following the technique reported in (*4*), where methanol is substituted for water. We could then verify that only 1% of total quantity of tin(II) in methanol was oxidated to tin(IV), after 10 hr (more than the time required to carry out the polarographic measurements). In addition, by the results shown in Fig. 2 we can see that equal tin(II) and tin(IV) concentration solutions reveal equal polarographic peak heights. Thus, it follows that eventual variations in the oxidation states, in any concentration ratio, do not influence the determination of the total quantity of tin.

SUMMARY

In this work, a method for the analysis of tin(II) and tin(IV) traces by stripping voltammetry in an aqueous medium and in methanol is reported. The advantages of using methanol as a solvent, which does not leave any residual current even at very negative potentials, are illustrated. Thus, in this medium, it is possible to perform the simultaneous analysis of traces of tin(II) and other cations which have much more negative dissolution potentials.

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MICROCHEMICAL JOURNAL 18, 350–353 (1973)

The Use of Platinum in the Perkin–Elmer 240 Elemental Analyzer: The All-Platinum Ladle

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INTRODUCTION

The Perkin–Elmer 240 Elemental Analyzer has functioned well in these laboratories for a number of years. The instrument has been made more automatic by the installation of an Infotronic CRS-30 and a novel sample-entry device. In addition, we modified the composition of the combustion-tube filling. Slightly less than the recommended amounts of tube filling were employed in order to accommodate a longer length (30–40 mm) of platinum gauze of a slightly heavier mesh than that recommended in the Perkin–Elmer manual. This change, which is in line with a recommendation made more than 30 years ago for a more efficient combustion of organic compounds by the Pregl methods (*1*, *2*), is of even greater importance now with the use of rapid-combustion techniques (*4*, *6*).

DISCUSSION

A serious drawback to the use of the Perkin–Elmer analyzer was, in our opinion, the use of the quartz ladle. Objections to the quartz ladle include: (*1*) discoloration of the quartz after limited use; (*2*) contamination of the ladle and combustion tube by catalytic aids, metal oxides, or decomposition products; (*3*) breakage; (*4*) faulty seals; and (*5*) the need for frequent replacement, which increased operating costs. The addition of fine platinum wire, wound around a section of the quartz rod, helped somewhat, but still gave low results on refractory compounds. Eventually, we came to desire a one piece, all-platinum ladle that would meet the objections to the quartz ladle and would accelerate the decomposition of compounds that were combustible only with difficulty without the need for catalytic materials. It is recommended however, that compounds containing alkali or alkali earth metals be still mixed with a small portion of tungstic oxide before combustion.

MATERIALS

The first model of an all-platinum ladle (*3*) was not completely satisfactory. The rod connecting the boatholder end to the magnet end

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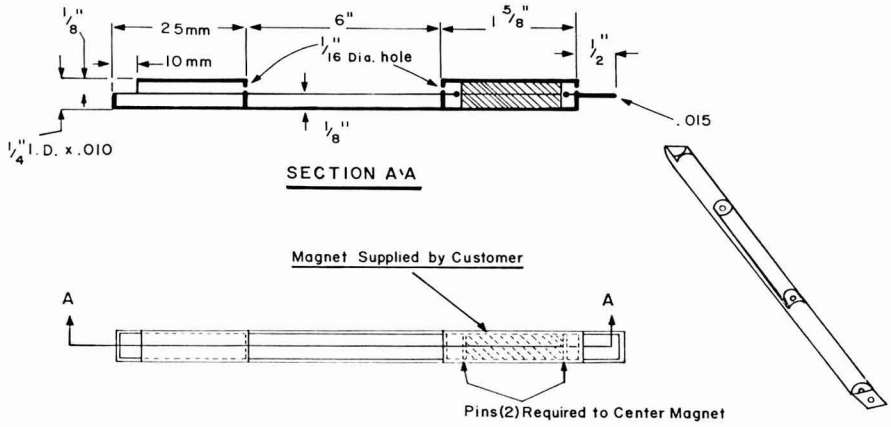

FIG. 1. Boat holder. Material: platinum–20% rhodium, 0.010 thick.

was of solid platinum and heavy, causing the ladle to be somewhat unwieldy and costly. This shortcoming was corrected by asking the manufacturer to construct a one-piece device from a semi-cylindrical length of platinum (20% Rhodium) of proper thickness. This ladle was light enough to be moved easily by the magnet. Rather than trying to make the magnet end of the ladle completely air tight as is done in the quartz ladle (previous failure to do so had caused errors in the nitrogen signal resulting from trapped air) we had to change slightly this section of the ladle. We, therefore, designed a "flowthro" system for this portion of the ladle, somewhat similar to that for the boat end. The design for the improved ladle is represented in Fig. 1. Actually, this new model resembles a platinum "tray" rather than a ladle.

More than a year after the successful use of our ladle, Thomas and Robinson (*7*) pointed out the difficulties inherent in the use of the conventional quartz ladle and described a novel metal ladle substitute. The platinum ladle has been used for thousands of analyses and still appears unchanged. Overall, we find that it is less costly than the many quartz ladles formerly used. Its weight is approximately 1.5 oz, worth about $150, but the fabricator will accept scrap platinum metal as credit towards the amount of platinum required for the ladle, thus reducing the overall cost.

Six compounds of a refractory nature were analyzed by use of the platinum ladle, without the addition of metal catalyst to any of the samples. The same compounds, shown in Table 1, previously had been analyzed by use of the quartz ladle.

TABLE 1

ANALYSIS OF ORGANIC COMPOUNDS WITH THE PERKIN–ELMER ELEMENTAL ANALYZER USING A QUARTZ AND ALL-PLATINUM LADLE

		C	H	N
$C_{31}H_{34}O_4SN_2$	Calculated	70.17	6.46	5.28
With Quartz Ladle	Found	69.67	6.38	5.20
With Pt Ladle	Found	70.22	6.37	5.33
$C_{17}H_{33}O_5SN_3$	Calculated	62.35	10.16	12.83
With Quartz Ladle	Found	61.69	10.11	12.64
With Pt Ladle	Found	62.41	10.30	12.78
$C_{15}H_{23}O_6N_3$	Calculated	52.77	6.79	12.31
With Quartz Ladle	Found	52.13	6.88	12.11
With Pt Ladle	Found	52.64	6.81	12.27
$C_{18}H_{13}O_3SN_3$	Calculated	61.54	3.73	11.96
With Quartz Ladle	Found	60.76	3.67	11.59
With Pt Ladle	Found	61.61	3.88	11.81
$C_{14}H_{11}O_5N_5$	Calculated	51.06	3.37	21.27
With Quartz Ladle	Found	50.51	3.22	21.04
With Pt Ladle	Found	50.97	3.42	21.21
$C_{16}H_{23}O_3$	Calculated	70.29	8.48	15.37
With Quartz Ladle	Found	69.61	8.32	15.02
With Pt Ladle	Found	70.23	8.55	15.29

CONCLUSION

We believe that, for the analysis of difficult combustible compounds, an added surface of platinum results in a more efficient combustion. Indeed, the use of platinum as a catalyst for the combustion of organic compounds goes as far back as Dennstadt in 1897 for macroanalysis and more recently Hazenberg (*5*) employed thin platinum sheets incorporated in his "long path" combustion tube in his modified rapid combustion method. After the initial 60-sec combustion in the Perkin–Elmer instrument, the high temperature auxiliary furnace is activated. At this moment, some of the sample decomposition products which might have escaped complete combustion are now subject to a heated section of the platinum ladle. In effect, we are dealing with a second combustion over an additional 150 mm of heated platinum catalyst, without changing the programmed sequence of the instrument. In the course of several hundred combustions, we find virtually no visible carbon deposits in the section of the combustion tube outside of the auxiliary furnace. This was not always the case in our experience with the quartz ladle.

ACKNOWLEDGMENTS

Acknowledgments are due Mr. Gerald Liberti, Mr. Joseph Hydro and Mrs. Mary Young for their assistance in this work.

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MICROCHEMICAL JOURNAL **18,** 354–357 (1973)

Marine Adhesives. IV

Hexosamine Content of *Balanus eburneus* Adhesive

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Received April 13, 1973

INTRODUCTION

Several of the papers in this series (*4–7*), as well as other sources (*2, 3, 8*), have described in detail the various favorable attributes of the adhesives secreted by a number of marine organisms such as the mussel and the barnacle. Suffice it to say, the marine adhesives bond strongly, are applied under water, and cure rapidly at ambient temperatures. This brief list alone would be ample explanation as to why there has been a great deal of interest in the characterization of these adhesives. The ultimate aim, of course, is synthesis and production of the adhesive.

Although several of the reports of studies on the composition of the barnacle adhesive agree on the presence of various amino acids, the presence or absence of one or more hexosamines is a point of contention (*2–5, 8*). In a study of the mussel adhesive (*5*), it was found that degradation of the hexosamines during hydrolysis of the sample would cause loss of these components. The results then would erroneously indicate an absence of hexosamines, as had been reported by several groups of workers. The present report details the evidence which confirms the presence of two hexosamines in the barnacle adhesive.

EXPERIMENTAL METHODS

Sheets of polymethylmethacrylate plastic (*ca.* 25 × 25 cm) were immersed in the Atlantic Ocean at Miami Beach, Florida (Miami Marine Test Station) and allowed to become covered with marine fouling. The fouled sheets with *Balanus eburneus* attached were shipped via airplane, in a moist condition, to our laboratories. Upon receipt, the plates were carefully and gently scrubbed to remove plant fouling, crabs, worms, etc., but not damage the barnacles. The plates with the barnacles attached were immersed for a period of time in a decalcification solution to effect removal of the barnacles; several solutions including EDTA solution, NH_4Cl solution and dilute HCl (pH 2) could be utilized. After decalcification, the plates were rinsed

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thoroughly and the animals removed carefully, leaving the microscopically thin layer of adhesive attached to the plastic plates. The plates containing the ringlets of adhesive were rinsed and dried. The adhesive was removed from the plate by very careful scraping. Care was taken to avoid scratching the plates and contaminating the adhesive with scraped plastic. A visual examination of each site was made, after scraping, in order to make certain that no gouging had occurred. The amount of adhesive at each attachment site was small. About 150 barnacles were needed to produce less than 1 mg of dried adhesive.

Milligram amounts of adhesive were hydrolyzed either in a sealed tube in 4 *M* HCl at 92°C, or under a nitrogen atmosphere in 2 *M* HCl at 96°C. After removal of most of the residual HCl, a portion of the hydrolyzed material was taken up in a minimum of distilled water and chromatographed using a thin-layer chromatographic method which was developed to separate hexosamines (*7*). Another portion of the hydrolyzate was first chromatographed by means of an ion-exchange column (*1*) and aliquots of eluate fractions which were expected to contain hexosamines then were chromatographed by means of the tlc procedure previously mentioned (*7*).

RESULTS AND DISCUSSION

Thin-layer chromatograms of aliquots of hydrolyzed barnacle adhesive (Fig. 1) indicated the presence of both glucosamine (Spot No. 2) and galactosamine (Spot No. 1), in addition to several other materials. A partial separation of the hexosamines from some of the other components in the adhesive was carried out using an ion-exchange procedure. An eluate fraction which was thought to contain the hexosamines was analyzed by means of the tlc procedure mentioned previously. The resulting chromatogram (Fig. 2) indicated the presence of both glucosamine and galactosamine. Additional corroboration for the presence of hexosamines was obtained by use of a tlc procedure which separates hexosamines from amino acids (*6*); chromatograms indicated the presence of hexosamines.

On the basis of these data, it is apparent that both glucosamine and galactosamine are components of the *Balanus eburneus* adhesive.

The reasons for the disagreement between laboratories regarding the presence or absence of the hexosamines in barnacle adhesive seem to be quite similar to those which caused difficulties concerning the mussel adhesive (*4, 5*). The hexosamines in both types of marine adhesive are quite sensitive to the conditions used to hydrolyze the materials; elevated temperatures and/or extended hydrolysis times can degrade either and/or both glucosamine and galactosamine. In the present case, by increasing the temperature, it was possible to destroy

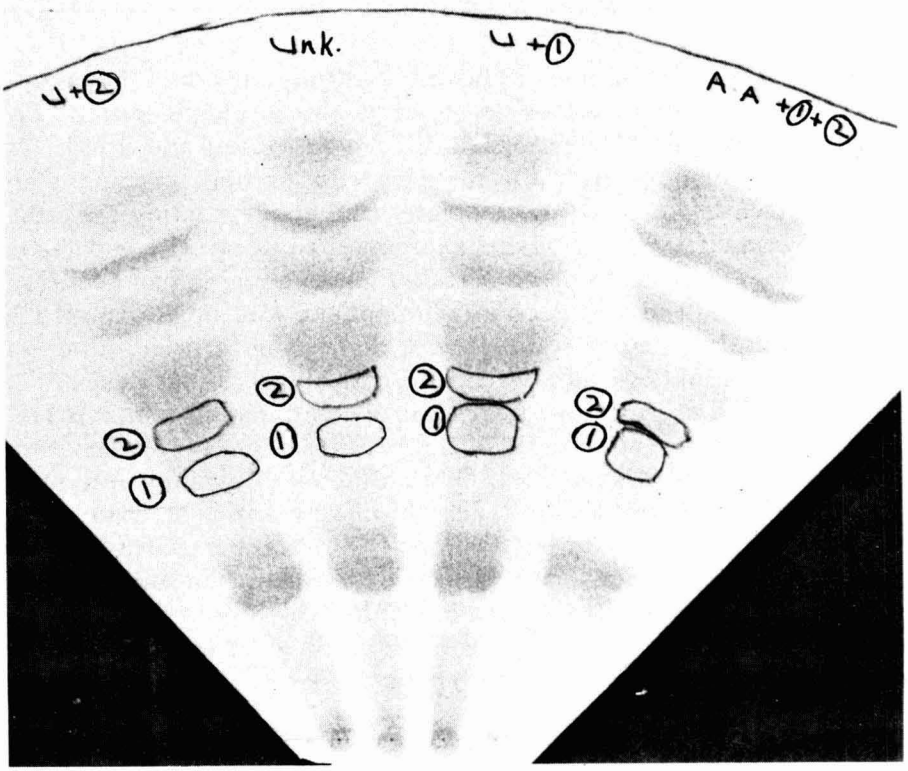

FIG. 1. Thin-layer chromatogram of hydrolyzed barnacle adhesive (Unk.). Spot number 1 is galactosamine and spot number 2 is glucosamine.

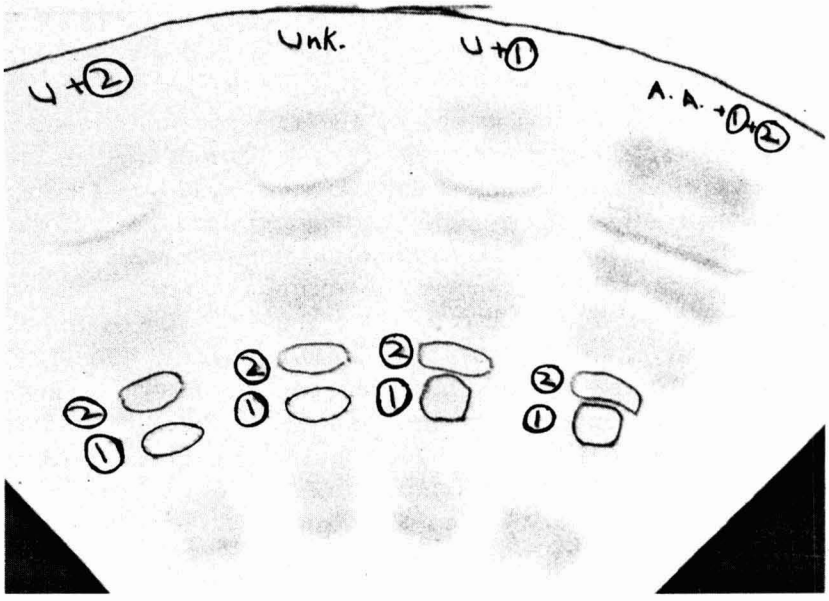

FIG. 2. Thin-layer chromatogram of ion-exchange eluate fraction of barnacle adhesive (Unk.). Spot number 1 is galactosamine and spot number 2 is glucosamine.

galactosamine alone, or glucosamine and galactosamine. By relatively minor changes in hydrolysis conditions, it was thus possible to find no hexosamines, one hexosamine, or both hexosamines. Therefore, variations in hydrolytic conditions can be account for the disparities in the published articles concerning the hexosamine content of barnacle adhesive.

SUMMARY

The adhesive secreted by the barnacle, *Balanus eburneus,* has been demonstrated to contain two hexosamines, glucosamine and galactosamine. Degradation of the hexosamines during hydrolysis of the adhesive appears to be the reason why previous studies of the adhesive have indicated the absence of hexosamines, or the presence of only one hexosamine.

ACKNOWLEDGMENT

The authors thank the National Institute of Dental Research for support through Contract PH-43-67-1172.

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MICROCHEMICAL JOURNAL 18, 358–362 (1973)

Complexometric Estimation of Glutamic Acid by Titration with Standard Cadmium Acetate Solution Employing 4-(2-Thiozolyl Azo) Resorcin

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Cohen (*1*) in 1939 suggested a method for the estimation of glutamic acid by the oxidation of glutamic acid to succinic acid. Opsahl and Arnow (*2*) estimated glutamic acid by conversion to pyrolidone carboxylic acid in 1942. In 1943, Schramm separated glutamic acid and aspartic acid from the neutral and basic amino acids by adsorption on Al_2O_3. Cannan (*3*) in 1944, suggested the estimation of dicarboxylic amino acids in protein hydrolysates. Schales and Schales (*4*), in 1946, suggested an enzymatic decarboxylation of glutamic acid. Drake estimated glutamic acid and aspartic acid by adsorption on ion exchange resins. Takahashi and co-workers (*5*) suggested volumetric analyses of amino acids.

So many methods have been suggested by different scientists from time to time for the estimation of glutamic acid but still there appears to be no procedure for the direct titration of glutamic acid in presence of other natural amino acids. This paper reports a complexometric procedure of such a direct titration of glutamic acid in micro amounts separately and also in the presence of other natural amino acids.

It was observed that at pH 9.0 glutamic acid combines with cadmium quantitatively. It was further observed that 4-(2-thiozolyl azo) resorcin (TAR) combines with cadmium, forming a complex of pink color. However, if in a mixture containing a buffer of pH 9.0 4-(2-thiozolyl-azo) resorcin as indicator and glutamic acid, cadmium acetate solution is added, no TAR–Cd complex is formed till all the glutamic acid has reacted with cadmium. After this reaction the excess of cadmium reacts with TAR and forms a pink complex. This change of color has been used to judge the end point; and it was observed that the titration can be carried out within 0.001 to 0.02 *M* glutamic acid with 0% error. The presence of other natural amino acids, in the reaction mixture does not interfere with the titration.

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EXPERIMENTAL METHODS

Glutamic acid (E. Merck) 0.01, 0.001, and 0.02 *M* glutamic acid was prepared in glass distilled water.

Cadmium acetate (A.R.) 0.01 *M* of $Cd(CH_3COO)_2$ was dissolved in glass distilled water.

4-(2-Thiozolyl azo) resorcin: 0.001 g was dissolved in absolute alcohol and made up to 50 ml.

Buffer solution: 0.02 *M* boric acid and 0.05 *M* borax buffer solution was made in glass distilled water; pH 9.0 was used.

Procedure

The titration was carried out by employing semi micropipettes and burettes with minimum divisions up to 0.01 ml.

Two-ml samples of buffer solution of pH 9.0 were placed in different beakers, and to each, 0.05 ml of the dye (TAR) was added as indicator. Different volumes of known standard amino acid were added in the beakers (a change of color was observed which is due to alkaline pH range of the buffer used). A standard solution of cadmium acetate was added in each mixture from a microburette until a sharp change in color (from yellow to pink) was observed at the end point. The experiments were also carried out on 0.001 and 0.02 *M* glutamic acid at the same pH value (Tables 1–3).

The pH values ranging from 2.0 to 9.0 had also been tried, but the best results were obtained at pH 9.0.

Further experiments were performed to determine the micro amount of glutamic acid together with the mixture of different amino acids (one from each group of amino acids) i.e., DL-methionine, L-histidine HCl, DL-tryptophan, DL-serine, DL-valine, DL-alanine, and L-proline. The

TABLE 1

TITRATION OF 0.001 *M* GLUTAMIC ACID AGAINST 0.01 *M* CADMIUM ACETATE USING TAR AS INDICATOR

Glutamic acid (ml)	Cadmium acetate (ml)	Amount of glutamic acid		Error (%)
		Observed	Calculated	
1.00	0.08	0.000147	0.000147	0.0
2.00	0.16	0.000294	0.000294	0.0
3.00	0.24	0.000441	0.000441	0.0
4.00	0.32	0.000588	0.000588	0.0
5.00	0.40	0.000735	0.000735	0.0

TABLE 2

TITRATION OF 0.01 *M* GLUTAMIC ACID SOLUTION WITH 0.01 *M* CADMIUM ACETATE USING TAR AS INDICATOR

Glutamic acid (ml)	Cadmium acetate (ml)	Amount of glutamic acid		Error (%)
		Observed	Calculated	
1.00	0.72	0.00147	0.00147	0.0
2.00	1.44	0.00294	0.00294	0.0
3.00	2.18	0.00441	0.00445	0.00004
4.00	2.88	0.00588	0.00588	0.0
5.00	3.60	0.00735	0.00735	0.0

mixture of amino acids does not interfere. The results are shown in Tables 4 and 5.

Discussion:

Table 1 shows that glutamic acid is estimated by direct titration against a standard solution of cadmium acetate using TAR as indicator in buffer medium at pH 9.0, within a fairly wide range of concentration of glutamic acid. The titration of glutamic acid can also be carried out in presence of the mixture of DL-methionine, L-histidine HCl, DL-tryptophan, DL-serine, DL-valine, DL-alanine, and L-proline (Table 4 & 5). It has been observed that these amino acids do not interfere in the titration. A complex is formed with the ratio of cadmium ion:glutamic acid, 5:7.

The data suggested that the probable structure of the complex will be as follows: Five atoms of cadmium and six molecules of glutamic acid

TABLE 3

TITRATION OF 0.02 *M* GLUTAMIC ACID WITH 0.01 *M* CADMIUM ACETATE USING TAR AS INDICATOR

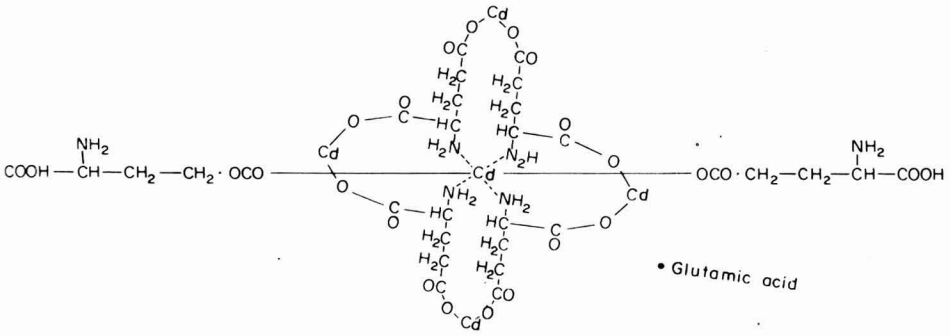
Glutamic acid (ml)	Cadmium acetate (ml)	Amount of glutamic acid		Error (%)
		Observed	Calculated	
1.00	1.44	0.00294	0.00294	0.0
2.00	2.88	0.00588	0.00588	0.0
3.00	4.32	0.00882	0.00882	0.0
4.00	5.76	0.01176	0.01176	0.0
5.00	6.20	0.01470	0.01470	0.0

TABLE 4

TITRATION OF VARYING QUANTITIES OF GLUTAMIC ACID IN PRESENCE OF OTHER AMINO ACIDS AGAINST CADMIUM ACETATE SOLUTION

Mixture of amino acids (ml)	Glutamic acid 0.01 *M* (ml)	Cadmium acetate (ml)	Amount of glutamic acid		Error (%)
			Observed	Calculated	
1.00	1.00	0.72	0.00147	0.00147	0.0
1.00	2.00	1.44	0.00294	0.00294	0.0
1.00	3.00	2.18	0.00441	0.00445	0.00004
1.00	4.00	2.88	0.00588	0.00588	0.0
1.00	5.00	3.60	0.00735	0.00735	0.0

combine to produce a complex which form a salt with one molecule of glutamic acid: $Cd_5 \cdot Glu_6 \cdot Glu$.



It has been reported that cadmium combines with histidine. We used histidine together with other amino acids as DL-tryptophan, DL-serine, L-histidine, DL-methionine, L-proline, DL-alanine, and DL-valine, different concentration in the mixture with a certain fix concentration of glutamic acid and observed that in this concentration also glutamic acid

TABLE 5

TITRATION OF GLUTAMIC ACID IN PRESENCE OF VARYING QUANTITIES OF OTHER AMINO ACIDS AGANIST STANDARD CADMIUM ACETATE

Mixed amino acids solution (ml)	Glutamic acid (0.01*M*) (ml)	Cadmium acetate 0.01 *M* (ml)	Amount of glutamic acid		Error (%)
			Observed	Calculated	
1.00	1.00	0.72	0.00147	0.00147	0.0
2.00	1.00	0.72	0.00147	0.00147	0.0
3.00	1.00	0.72	0.00147	0.00147	0.0
4.00	1.00	0.72	0.00147	0.00147	0.0
5.00	1.00	0.72	0.00147	0.00147	0.0

TABLE 6

TITRATION OF 0.01 *M* SOLUTION OF HISTIDINE WITH STANDARD CdAc SOLUTION AT pH 9.0 USING TAR AS INDICATOR

Histidine (ml)	Cadmium acetate (ml)	Amount of Histidine		Error (%)
		Observed	Calculated	
1.00	0.04	0.002095	0.002095	0.0
2.00	0.08	0.004190	0.004190	0.0
3.00	0.12	0.006285	0.006285	0.0
4.00	0.16	0.008380	0.008380	0.0
5.00	0.20	0.010475	0.010475	0.0

can be accurately estimated. 0.01 *M* of histidine solution was then prepared and titrated it against cadmium acetate employing TAR as indicator, and using boric acid–borax buffer at pH 9.0. The results are shown in Table 6. The results show that though histidine, when added in equal concentration, can cause an interferance of about 6%, a small concentration of 2–3% of histidine in the mixture, which is an unusual concentration of this amino acid in the protein hydrolysate, will not interfere in this titration.

SUMMARY

Glutamic acid can be titrated quantitatively against standard cadmium acetate using 4-(2-thiozolyl azo) resorcin as indicator in presence of boric acid–borax buffer at pH 9.0. Small concentrations of other natural amino acids do not interfere with the titration. However the presence of an equivalent molar concentration of histidine can cause an error of about 6%.

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MICROCHEMICAL JOURNAL 18, 363–374 (1973)

Microdetermination Techniques for H_2O_2 in Irradiated Solutions

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Makoto Otomo (*10*) has reported the formation of different complexes of ferric ions with xylenol orange. His results show that in acidic medium, Fe^{3+} reacts with excess of xylenol orange (XO) to form 1:1 and 1:2 complexes with absorption maxima at 545 and 500 nm, respectively; while excess of Fe^{3+} forms a 1:1 complex with absorption maximal at 586 nm. The optimal formation of the complex having the maximal absorption at 545 nm has been shown to be in 0.084 *M* perchloric acid. Molot *et al.* (*11*) also used this complex formation for the estimation of Fe^{3+}. They buffered their solutions to a pH of 2.6 using chloride–acetate buffer.

The formation of a complex between titanium, xylenol orange, and hydrogen peroxide has been reported by Makoto Otomo (*9*), who has used this complex for the estimation of small amounts of titanium in the presence of a large excess of hydrogen peroxide. Tammes and Nordschow (*12*) used the triple complex formation for glucose determinations by measuring the peroxide formed through oxidation. The wave length for absorption measurements used in the estimation (*9*) was 532 nm, but the wavelength of the absorption maximum of the complex was shown to have a slight dependence on the hydrogen peroxide concentration. The absorption peak shifted from 520 to 535 nm when the concentration of H_2O_2 in the solution was increased from about 5×10^{-5} to 2×10^{-2} *M*. The stability of the complex also was shown to depend on the hydrogen peroxide concentration. Cations such as bismuth(III), iron(III), gallium(III), tin(IV), thallium(III), and zirconium(IV); and other species such as the fluoride ion, the oxalate ion, NTA, and EDTA were shown to interfere with the complex formation.

In the present work, the formation of the two complexes and their absorbance characteristics have been examined in detail for optimal application to determine micromolar concentration of H_2O_2 in irradiated solutions. The methods for H_2O_2 determination are: (I) the oxidation of

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ferrous ions by H_2O_2 and complexing of the ferric ions so formed with xylenol orange; and (II) the formation of triple complex, titanium–xylenol orange–H_2O_2.

PART I. DETERMINATION OF H_2O_2—USING FERROUS SULFATE–XYLENOL ORANGE REAGENT

Experimental Methods

A tetrasodium salt of xylenol orange, was dissolved in distilled water to give about 10^{-3} *M* concentration.

Sulfuric acid solution was prepared by diluting AnalaR grade material in distilled water. Stock solutions of ferric ammonium sulfate and ferrous ammonium sulfate were prepared by dissolving AnalaR materials in 0.1 *N* sulfuric acid.

A 30% solution of hydrogen peroxide was diluted with distilled water. The diluted hydrogen peroxide was titrated against standardized potassium permanganate solution.

In the complex formation studies, calculated volumes of xylenol orange, ferric ammonium sulfate and sulfuric acid were added to a 10-ml volumetric flask and the volume was made up with distilled water. For H_2O_2 estimations, ferrous solution was added at the end.

All the experiments were done at room temperature which was about 25°C. A Beckman DB spectrophotometer was used for all the measurements.

Method

Prepare a reagent solution containing xylenol orange, sodium chloride, and ferrous ammonium sulfate in sulfuric acid. Add this reagent to a 10-ml volumetric flask containing H_2O_2 solution and make up the volume with distilled water. The concentration of ferrous ions in the final solution should be more than required for the equivalent oxidation of H_2O_2. The concentration of xylenol orange should be about five times of the concentration of ferric ions expected to be produced by ferrous oxidation and the sulfuric acid concentration should be 0.05 *N*. If an organic compound is present in the H_2O_2 solution the minimum amount of sodium chloride necessary to eliminate its effect should be present.

Measure the absorbance of the solution at 540 nm against reagent blank. Calculate the concentration of H_2O_2 using the extinction coefficient of $2.68 \times 10^4\ M^{-1}\ cm^{-1}$.

Results

Figure 1 shows that the complex between ferric ions and xylenol orange has a maximal absorption at 540 nm. The complex formation de-

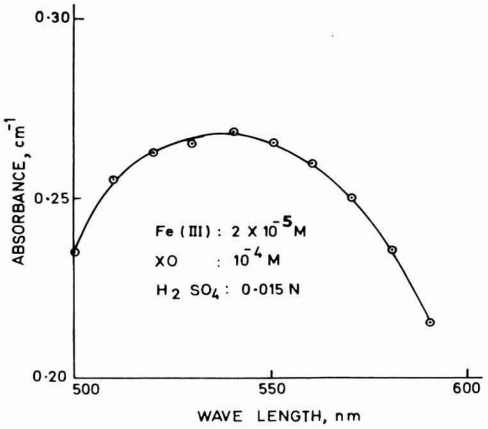

FIG.1. Absorption spectrum of Fe(III)–XO complex against XO; blank: 10^{-4} *M* XO in 0.015 *N* H_2SO_4.

pends on the sulfuric acid concentration and it is optimal in 0.05 *N* sulfuric acid (Fig. 2). Under these conditions, ferrous ions do not form any complex with xylenol orange (Fig. 3). When the concentration of ferric ions in the solution is kept constant, the absorbance at 540 nm

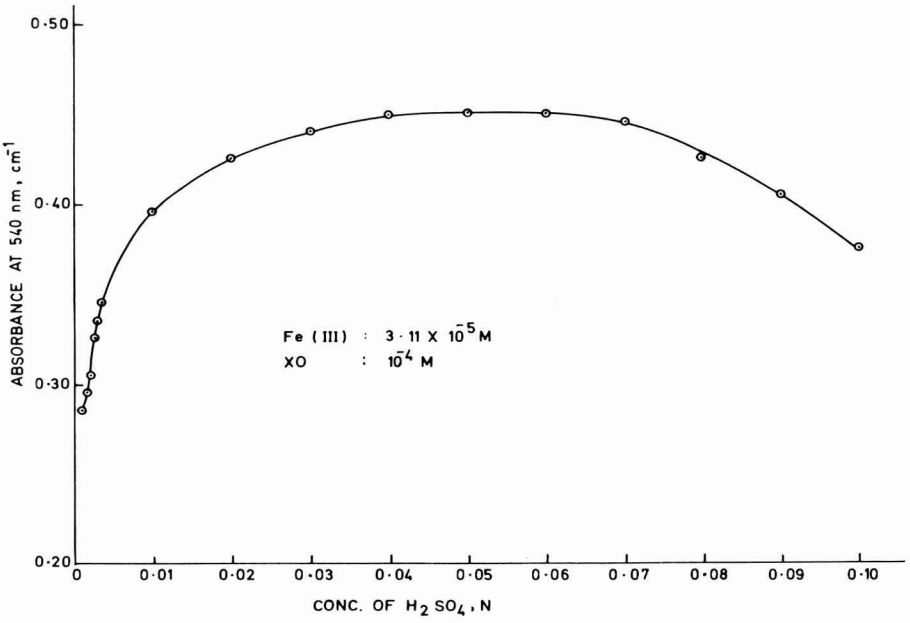

FIG. 2. Effect of sulfuric acid concentration on Fe(III)–XO complex formation; blank: 10^{-4} *M* XO in different concentrations of H_2SO_4.

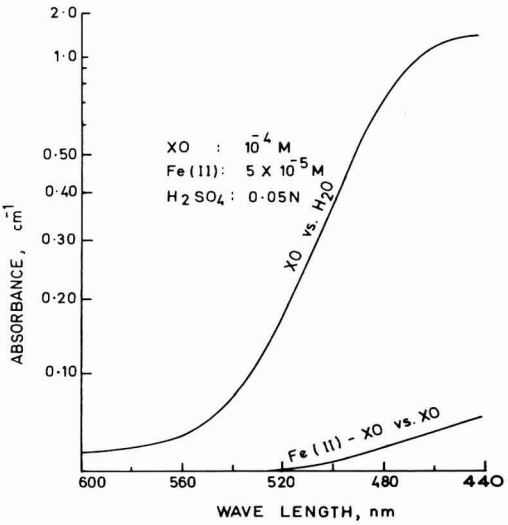

FIG. 3. Complexing behavior of Fe(II) and XO.

increases with the increase in xylenol orange concentration (Fig. 4). When the concentration of xylenol orange is about three times higher than that of ferric ions, the absorbance becomes independent of xylenol orange concentration.

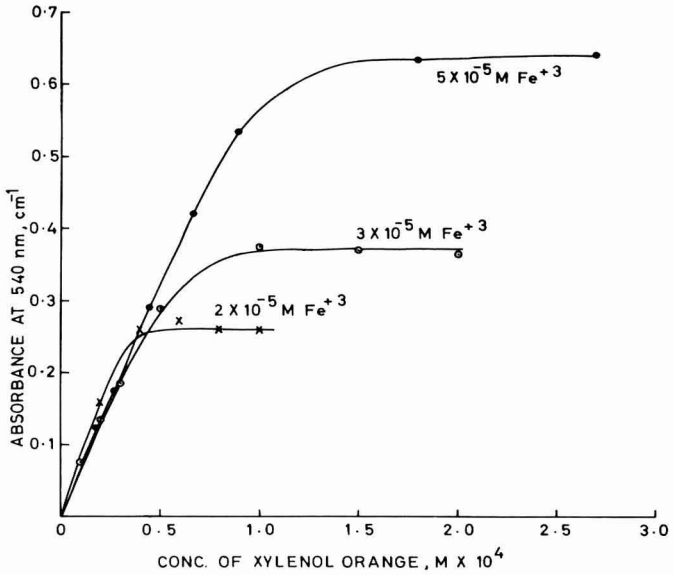

FIG. 4. Effect of XO concentration on the Fe(III)–XO complex formation; blank: different concentrations of XO in 0.05 *N* H_2SO_4.

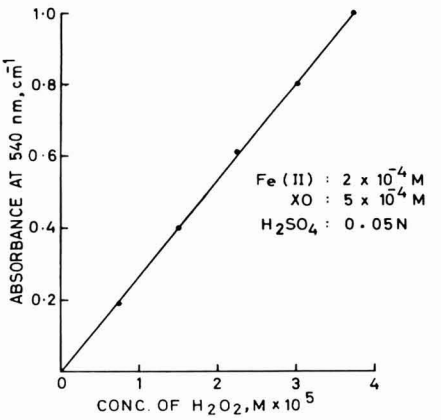

FIG. 5. Absorbance of Fe(III)–XO complex against hydrogen peroxide concentration; blank: 2×10^{-4} *M* Fe(II) and 5×10^{-4} *M* XO in 0.05 N H_2SO_4.

Figure 5 shows that in a solution containing ferrous ions and xylenol orange in 0.05 *N* sulfuric acid, the absorbance at 540 nm increases linearly with the increase in hydrogen peroxide concentration. The extinction coefficient for H_2O_2 was found to be 2.68×10^4 $M^{-1}cm^{-1}$ which was double the value obtained for the ferric ions.

Discussion

It is well known (*8*) that hydrogen peroxide oxidizes ferrous ions by the following mechanism:

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH + OH^-. \quad (1)$$

During radiolysis studies on xylenol orange, it was found (*6*) that hydroxyl radicals react about forty times faster with xylenol orange than with ferrous ions. Since xylenol orange is present in much higher concentration in the solution, most of the OH radicals produced in reaction (1) will react with it. The observed equivalent oxidation of ferrous ions by H_2O_2 shows that the product formed from the reaction of OH radicals with xylenol orange also oxidizes the ferrous ions according to the reactions (2) and (3).

$$XO + OH = XO \cdot OH, \quad (2)$$

$$Fe^{2+} + XO \cdot OH = Fe^{3+} + (XO \cdot OH^-). \quad (3)$$

Many organic compounds are known to compete with ferrous ions for the reaction with hydroxyl radicals. The organic radicals so formed may either increase or decrease the ferrous oxidation. However, the ef-

fect of organic compounds can be eliminated by adding chloride ions to the solution (Table 1). The amount of chloride required depends upon the relative concentrations of organic compound and ferrous ions in the solution and also on their relative rate constants with hydroxyl radicals.

Earlier it was observed (*7*) that the product formed in reaction (3) does not form a complex with ferric ions. So there must be a sufficient concentration of xylenol orange in the solution to react both according to reaction (3) and for the formation of the complex. Ferrous ions should also be present in a slightly higher concentration than required for the equivalent oxidation of H_2O_2. It was found that for 2×10^{-4} *M* ferrous ions and 5×10^{-4} *M* xylenol orange in 0.05 *N* sulfuric acid, the plot of absorbance at 540 nm against H_2O_2 concentration remained linear even up to 5×10^{-5} *M* concentration of H_2O_2.

The fluoride ions which have been reported (*2, 3*) to increase the absorbance of the ferric–xylenol orange complex do not change the absorbance under the present conditions.

The presence of inorganic ions does not interfere with the H_2O_2 estimation provided they do not undergo oxidation–reduction reactions with H_2O_2 and there must be sufficient xylenol orange in the solution to complex all the inorganic ions. Titanium and organic chelating agents interfere in the estimation (*9*).

This method of hydrogen peroxide estimation is more sensitive than the commonly used iodide method (*1*). The position of the absorption peak is in the visible region and this might be of some advantage in certain cases. The ferrous oxidation in air is not so fast as that of iodide where the reagents have to be prepared just before use.

TABLE 1

CHLORIDE IONS INHIBITION OF THE EFFECT OF ORGANIC COMPOUNDS ON HYDROGEN PEROXIDE ESTIMATION

Ferrous ion conc, 2×10^{-4} *M*; xylenol orange conc, 2×10^{-4} *M*; sulfuric acid conc, 0.05 *N*.

System	H_2O_2 conc, $M \times 10^5$		
	Added	Estimated	Difference
Benzene, 10^{-4} *M*	0.63	0.87	+0.24
+ NaCl, 0.10 *M*	0.63	0.63	0.00
Hydroquinone, 10^{-4} *M*	2.09	1.98	−0.11
+ NaCl, 0.10 *M*	2.09	2.09	0.00
Coumarin, 10^{-4} *M*	1.44	1.69	+0.25
+ NaCl, 0.10 *M*	1.44	1.49	+0.05

PART II. DETERMINATION OF H_2O_2—USING THE TRIPLE COMPLEX Ti–XO–H_2O_2

Experimental Methods

A known amount of TiO_2 was dissolved in concentrated sulfuric acid and diluted to give 2 mg/ml of titanium. The acidity of the solution was determined. The solution was further diluted to required concentrations.

The preparation of xylenol orange and H_2O_2 reagents has been described in Part I. The calculated amounts of these reagents to give desired concentrations were mixed in 25-ml volumetric flasks. The absorption of the solution was measured against the solution without H_2O_2 as blank.

All the experiments were done at room temperature which was about 25°C. A Beckman DB spectrophotometer was used for all the measurements.

Method

To the hydrogen peroxide solution in a volumetric flask, add sufficient volumes of titanium and xylenol orange reagents so that the concentrations are at least five times greater than that of hydrogen peroxide. Make up the volume with dilute sulfuric acid to give final acidity of the solution equal to 0.03 *N*. Measure the absorbance at 520 nm against the solution without hydrogen peroxide as blank. Use a suitable cell length to give sufficient absorbance. Calculate the concentration of H_2O_2 using the extinction coefficient value of 7400 $M^{-1}cm^{-1}$.

Another method is to refer the observed absorbance to a calibration curve for varying H_2O_2 concentrations and experimental concentrations of titanium and xylenol orange is 0.03 *N* sulfuric acid.

Results and Discussion

Absorptiometric measurements at low concentrations of H_2O_2 in the complex between titanium, xylenol orange, and hydrogen peroxide showed two absorption maxima at 520 and 562 nm depending upon the relative concentrations of titanium and hydrogen peroxide (Fig. 6). The experimental conditions for Fig. 6 are given in Table 2. When the concentrations of titanium and hydrogen peroxide were of the same order, the maximal absorption observed was at 562 nm with a hump at 520 nm. When the ratio of titanium to hydrogen peroxide concentration was either very high or very low, only one absorption band was observed near 520 nm, the actual position of the peak depending on the relative concentrations of titanium and hydrogen peroxide. The absorption of the complex depended upon the acidity of the solution and the maxi-

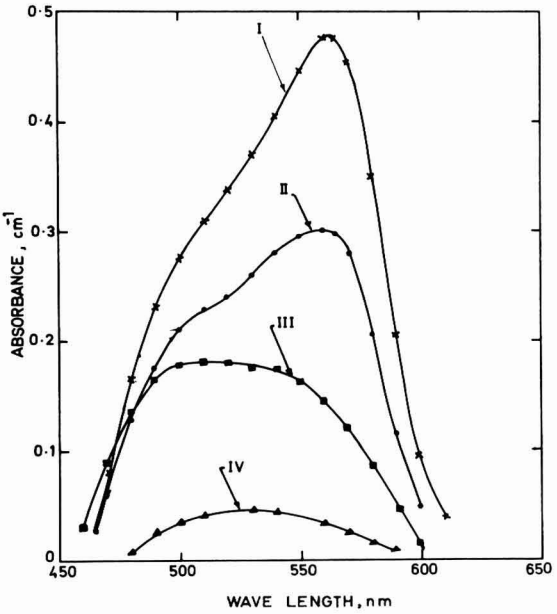

FIG. 6. Absorption spectrum of hydrogen peroxide complex with titanium and xylenol orange. (see Table 2 for details of curves).

mum complex formations at 520 and 562 nm were observed at 0.03 and 0.01 *N* sulfuric acid concentrations, respectively (Fig. 7). The point in 0.01 *N* sulfuric acid at 562 nm corresponds to a pH of 2.2.

Table 3 shows the relative intensities of the absorbance at 562 and 520 nm at different ratios of titanium and hydrogen peroxide concentrations. The results show that the absorbance at 562 nm is maximum when the concentrations of titanium and hydrogen peroxide in the solution are of the same order. The variation in absorbance at 520 nm with

TABLE 2

EXPERIMENTAL CONDITIONS FOR FIGURE 6

	Conc ($M \times 10^4$)			
Sample no.	Ti	Xylenol orange	H_2O_2	H_2SO_4 (N)
I	0.42	0.82	1.17	0.03
II	0.84	0.82	0.35	0.03
III	0.17	0.82	1.75	0.03
IV	0.84	0.82	0.06	0.03

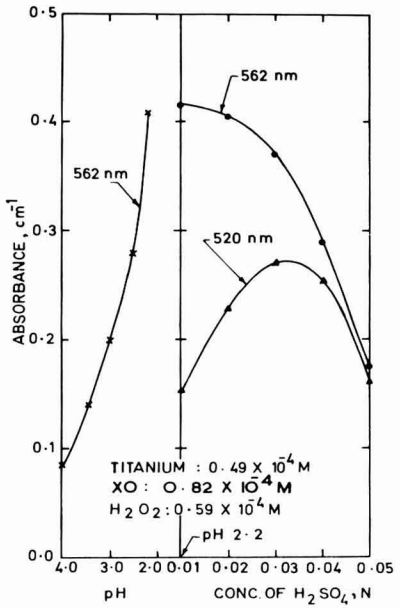

FIG. 7. Effect of acidity on absorbance.

the increase in concentration of titanium is shown in Fig. 8. There is no significant variation in the absorbance when the concentration of titanium is more than twice that of hydrogen peroxide. It seems, therefore, that the measurements at 562 nm might be better if titanium and hydrogen peroxide concentration in the solution are kept in the same range. This is possible only when the concentration of hydrogen peroxide is known approximately. In the case of quite unknown concentrations of hydrogen peroxide, it is always better to make the measure-

TABLE 3

RELATIVE INTENSITIES OF THE TITANIUM, XYLENOL ORANGE, AND HYDROGEN PEROXIDE COMPLEX AT 562 AND 520 nm

Xylenol orange conc, 0.82×10^{-4} *M*; sulfuric acid conc, 0.03 *N*.

Conc ($M \times 10^4$)		Ti conc/H_2O_2 conc	Absorbance (cm^{-1})		(Absorbance at 562 nm)/(absorbance at 520 nm)
Ti	H_2O_2		520 nm	562 nm	
0.17	1.75	0.10	0.180	0.140	0.77
0.42	1.17	0.36	0.335	0.480	1.42
0.49	0.59	0.83	0.270	0.370	1.37
0.84	0.35	2.40	0.240	0.300	1.25
0.84	0.06	14.00	0.045	0.032	0.73

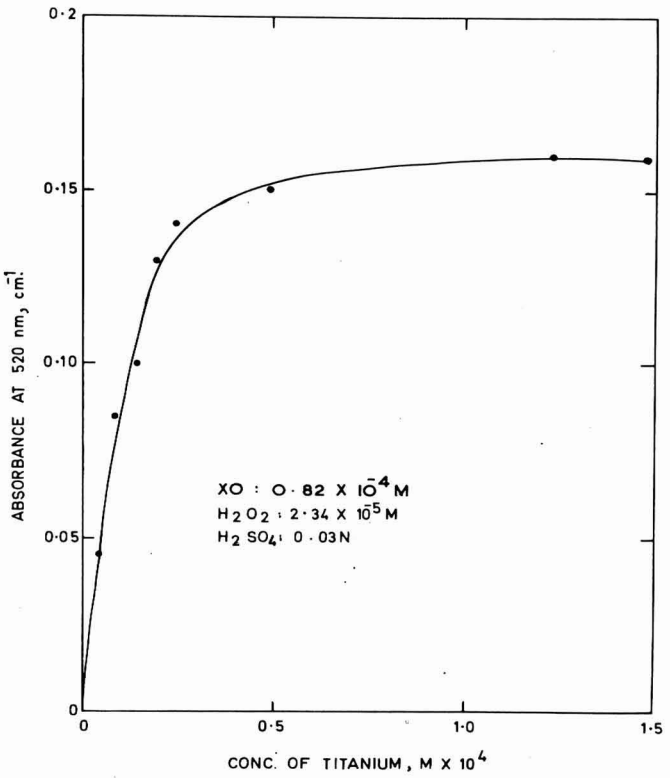

FIG. 8. Effect of titanium concentration on absorbance.

ments at 520 nm, using high concentrations of titanium. This avoids the difficulty of obtaining separate calibration curves for different ranges of hydrogen peroxide.

Figure 9 shows the increase in the absorbance at 520 nm with the increase in xylenol orange concentration.

The absorbance at 520 nm of a solution containing 1.3×10^{-5} *M* H_2O_2, 10^{-4} *M* xylenol orange, and 0.84×10^{-4} *M* titanium in 0.03 *N* sulfuric acid was found to be quite stable for over 5 hours. The instability of the complex observed by the earlier workers (*9*) is probably due to the oxidation of xylenol orange at high concentrations of H_2O_2 since the studies here have shown that at high concentrations of H_2O_2, xylenol orange solutions get decolorized slowly. However, low concentrations of H_2O_2 which are encountered in irradiated solutions, do not react with the xylenol orange to change its color. In aqueous solutions containing 10^{-4} *M* xylenol orange and up to 10^{-4} *M* H_2O_2, no change in the concentration of xylenol orange was observed even after 1 week.

A calibration curve was obtained using 0.84×10^{-4} *M* titanium (4

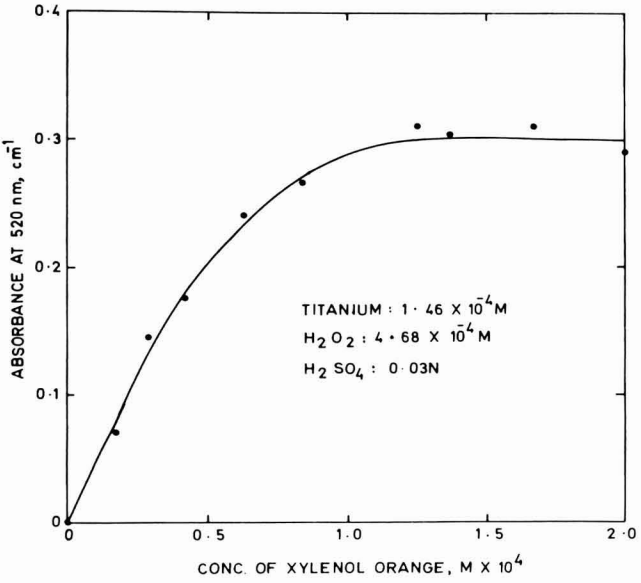

FIG. 9. Effect of xylenol orange concentration on absorbance.

μg/ml), 0.82×10^{-4} *M* xylenol orange and zero to 4×10^{-5} *M* H_2O_2 at 0.03 *N* sulfuric acid concentration. A solution containing 0.84×10^{-4} *M* titanium and 0.82×10^{-4} *M* xylenol orange at 0.03 *N* sulfuric acid was used as blank. The plot of absorbance at 520 nm against hydrogen peroxide concentration is almost linear (Fig. 10).

The extinction coefficient of the triple complex which is 7400 M^{-1} cm^{-1}, is about 10 times higher than that of the titanium hydrogen per-

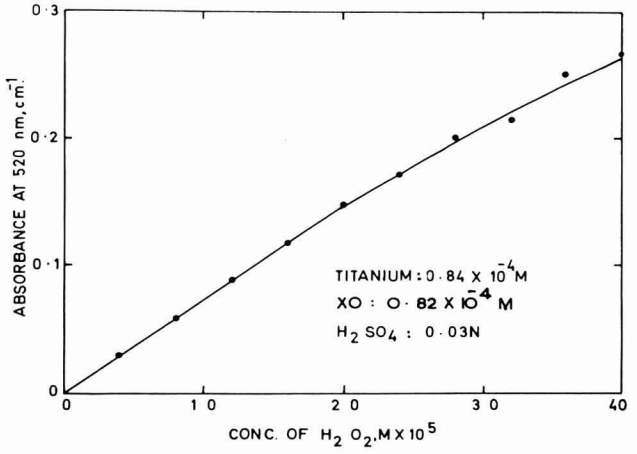

FIG. 10. Effect of hydrogen peroxide concentration on absorbance.

oxide complex alone (*5*), the value for which has been reported to be 720 M^{-1} cm^{-1} (*4*). The position of the absorption peak being in the visible region, might be of some advantage in certain cases. Another advantage of this method is that it would be possible to differentiate between organic peroxides and hydrogen peroxide. It has been observed that titanium does not form complexes with organic peroxides (*4*).

SUMMARY

The paper gives detailed development of the methods using ferric–xylenol orange and titanium–xylenol orange–hydrogen peroxide complexes for the determination of H_2O_2formed in irradiated solutions. The conditions are established to obtain linear relationships for absorbance increase with increase in hydrogen peroxide in concentration levels of interest. The results are discussed.

ACKNOWLEDGMENT

The author is grateful to G. Subrahmanian for his keen interest in and encouragement of this work. Thanks are due to Dr. A. K. Ganguly for his valuable guidance.

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MICROCHEMICAL JOURNAL 18, 375–376 (1973)

Microdetermination of Tartaric and Malic Acids Present Together

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INTRODUCTION

The history regarding Ag(III) and Cu(III) has been described elsewhere (*1*, *2*). Ag(III) and Cu(III) solutions were prepared in the form of ditellurato-argentate and ditelluratocuprate, respectively. Tartaric and malic acids required 10 and 12 equivalents of oxidant for their complete oxidation to CO_2 and H_2O stage.

In a solution containing tartaric and malic acids, Ag(III) oxidizes tartaric acid to CO_2 and H_2O stage as follows:

$$C_4H_6O_6 + 2H_2O \rightarrow 4CO_2 + 10H^+ + 10\ e^-,$$

while malic acid remains uneffected.

Whereas Cu(III) solution oxidizes both tartaric and malic acids to CO_2 and H_2O. The following reaction occurs:

$$C_4H_6O_6 + C_4H_6O_5 + 5H_2O \rightarrow 8CO_2 + 22H^+ + 22\ e^-$$

These phenomina led to a method to determine tartaric and malic acids present together.

EXPERIMENTAL METHODS

Materials

All the chemicals used were of reagent grade. Malic acid (B.D.H.) was purified by crystallization from acetone–carbon tetrachloride mixture; and its solution in water was prepared by weight, and standardized against standard sodium hydroxide solution.

Ag(III) solution was prepared and standardized as described (*1*).

Cu(III) solution was prepared and standardized as described (*2*).

Procedure for Determination of Tartaric and Malic Acids

Five ml of the mixture solution was kept with an excess of Ag(III) at 80° for 3 hours. The remaining Ag(III) in the solution was estimated

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TABLE 1

TITRIMETRIC DETERMINATION OF TARTARIC ACID

Mixture solution	1.50×10^{-2} *M* Ag(III) (ml)	Tartaric acid in mix. (mg)	
		Found	Present
1	1.33	0.300	0.300
2	2.01	0.451	0.450
3	2.67	0.602	0.600
4	4.00	0.902	0.900
5	5.32	1.200	1.200

as described (*1*). Same volume of the mixture solution was boiled with an excess of Cu(III) solution. The whole reaction mixture was cooled, and Cu(III) remaining in it was estimated (*2*).

RESULTS AND DISCUSSION

Table 1 shows that tartaric acid required 10 equivalents of the oxidant for its complete oxidation. Whereas Table 2 shows that 12 equiva-

TABLE 2

TITRIMETRIC DETERMINATION OF MALIC ACID

Mixture	3.00×10^{-2} *M* Cu(III) (ml)	Total tartaric and malic acids present (mg)	Malic acid in mix. (mg)	
			Found	Present
1	0.76	0.590	0.290	0.290
2	1.20	1.031	0.580	0.580
3	1.58	1.472	0.870	0.870
4	2.41	2.065	1.163	1.160
5	3.17	2.654	1.454	1.450

lents of oxidant are required for complete oxidation of malic acid. Thus a method for determination of mixture of tartaric and malic acids has been described. The quantity of acids present has been calculated (mg). Experiment has been repeated several times and a deviation with $\pm$ 0.9% was obtained.

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Extraction of Radiozinc, Radioiron, and Radiomanganese from Alcoholic and Acetonic Acidic Solutions

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INTRODUCTION

The extraction and separation of metal ions from acetonic and alcoholic acidic solutions was first reported in 1967 (*1*), and the work on this line has been extended thereafter (*2–4, 12*). The presence of acetone or a water-miscible alcohol in the aqueous (polar) phase was usually found to have a big effect (either enhacing or depressing) on extraction of the ions of many metals. Such an effect is certainly valuable in analytical separations, since it adds one to the factors affecting extraction and hence increases the range of choice of extraction conditions. Although the increase of acidity or salting out agent's concentration may also have a big influence on extraction and separation, the application of acetone and alcohols may be more convenient and/or suitable for many reasons. Thus the application of highly acidic solutions is generally unfavorable and the application of neutral salting out agents is sometimes inconvenient, since it is difficult to eliminate them from the aqueous phase. Acetone and alcohols, on the other hand can easily be distilled off. Alternatively, extraction data in mixed media are essential for future combined ion exchange, extraction separation procedures in such media.

The present paper reports the extraction of radiozinc, radioiron, and raiomanganese with a xylene solution of tridodecylamine (TDA) and tributyl phosphate (TBP) in the absence and presence of acetone and water-miscible alcohols.

EXPERIMENTAL METHODS

Apparatus

The purity of radioactive isotopes was confirmed using a Nuclear Chicago Single channel γ-ray spectrometer (*5*). The radioactivity of the

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organic and aqueous solutions was directly measured by counting aliquots from both phases using an EKCO scintillation counting assembly.

Reagents

Tributylphosphate (TBP), BDH and tridodecylamine (TDA) Rhone Poulenc, were used without purification. An indirect acid equivalent determination (*6*), showed that TDA was more than 99.5% pure. Xylene, acetone, and alcohols with the same specification as previously given (*6*), and AnalaR, BDH acids were applied in the present study.

Radioactive Isotopes

The raioactive isotope ^{65}Zn prepared by pile irradiation (UAR, Research Reactor I) of pure zinc metal and dissolution of the latter in hydrochloric acid. Zinc carrier was similarly prepared by dissolution of nonirradiated zinc metal. The isotopes ^{59}Fe and ^{54}Mn(divalent) were prepared as described before(*8*).

Extraction Procedure

Extraction experiments for the determination of the partition ratio (*E*) were carried out exactly as described before (*2*). Test investigations on separations were also performed as before (*8*). Kinetic experiments showed that the time of shaking (30 minutes) was quite enough for reaching extraction equilibrium. Experiments were performed only in duplicate due to the high reproducibility of the results.

RESULTS AND DISCUSSION

The Extraction of Radiozinc

The effect of methanol, ethanol, and acetone on the extraction of radiozinc by 0.06 *M* TDA and 50% TBP was investigated in a previous report at the microgram level (*2*). The aqueous phase was 1.5 *M* HCl. The effect of water-miscible alcohols and acetone on the extraction of zinc has been studied in the present work from solutions of hydrochloric and sulfuric acid of various molarities. Extraction has been investigated in the absence and presence of an inactive isotopic zinc carrier. The application of such carrier is a case which is frequently met with in analytical chemistry.

Figures 1–3 illustrate the results obtained on the effect of acetone and water-miscible alcohols on the extraction of radiozinc from 1.2, 2.4, and 5.55 *M* HCl, respectively, in the absence of an inactive zinc carrier. The organic phase is 0.06 *M* TDA in xylene. Water-miscible additives are seen to have a depressing effect on the extraction of tracer

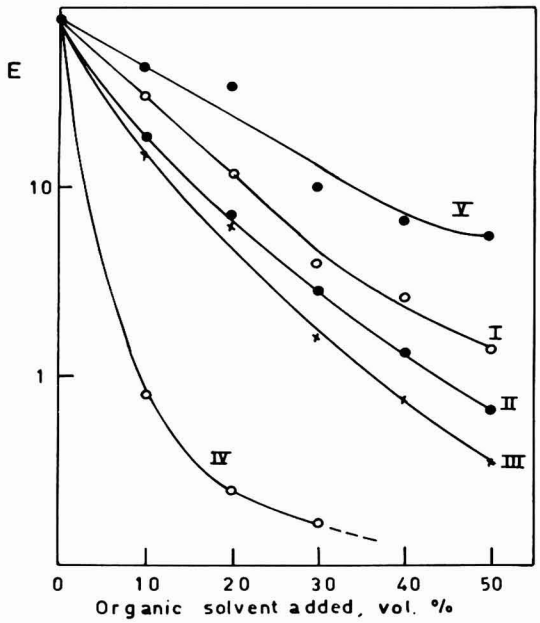

FIG. 1. Extraction of radiozinc by TDA from 1.2 *M* HCl in presence of: (I) methanol; (II) ethanol; (III) isopropanol; (IV) isobutanol; (V) acetone.

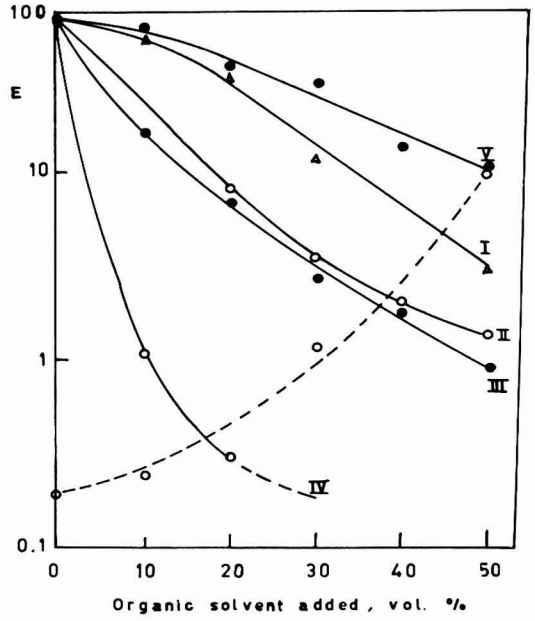

FIG. 2. Extraction of radiozinc by TDA from 2.4 *M* HCl in presence of: (I) methanol; (II) ethanol; (III) isopropanol; (IV) isobutanol; (V) acetone; (—) effect of acetone on *E* of radiocobalt.

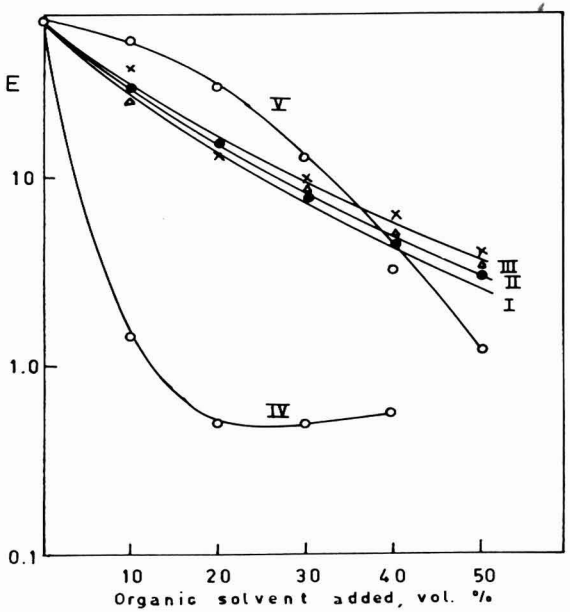

FIG. 3. Extraction of radiozinc by TDA from 5.55 *M* HCl in presence of: (I) methanol; (II) ethanol; (III) isopropanol; (IV) isobutanol; (V) acetone.

radiozinc. At 1.2 *M* HCl such an effect increases in the order acetone < methanol < ethanol < isopropanol < isobutanol. In other words the effect increases with increasing the chain length (number of carbon atoms) and with the decrease of the dielectric constant of the alcohol added. From the analytical point of view the addition of alcohols is so effective that conditions can be adjusted to render the highly extractable zinc nonextractable; viz., by the addition of ~20% isobutanol. The latter alcohol, however is much more miscible in the organic phase. Its effect on extraction cannot be related, however, to the increase of hydrochloric acid concentration in the equilibrium aqueous phase, as a result of the passage of the alcohol to the organic phase, and the consequent decrease in the volume of the aqueous phase. In support of this view, is the effect of hydrochloric acid concentration on the extraction of radiozinc from pure aqueous solutions by 0.06 *M* TDA (Fig. 4). Extraction clearly decreases with increase of the acid concentration in the aqueous phase, but to a much lower extent than in case of the parallel increase of acidity with the addition of isobutanol (see also Table 1). The change in the equilibrium acid molarity is much less in case of the other alcohols (*6*). The effect of acetone and alcohols on radiozinc extraction by TDA is rather different from various hydrochloric acid solutions. Thus from 1.2 and 2.4 *M* HCl the position of the partition curves in case of acetone, methanol, and isobutanol is the same, while

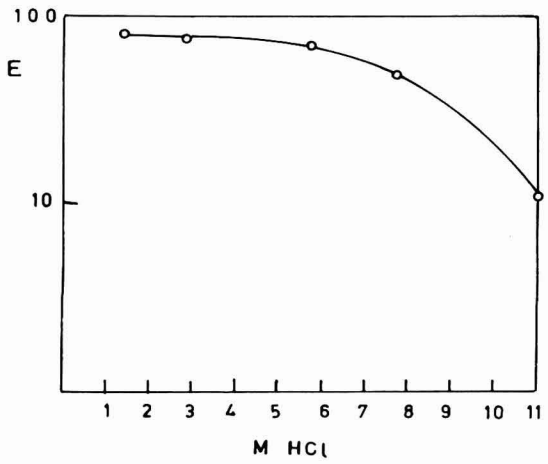

FIG. 4. Effect of Hydrochloric acid concentration on E of radiozinc for extraction by 0.06 M TDA.

it is reversed in case of ethanol and isopropanol. At still higher acidities (5.55 M HCl), the effect of acetone is minimum, that of isobutanol is maximum as usual, while for the other alcohols the effect decreases in the order methanol > ethanol anl isopropanol. Although the difference in case of the latter three alcohols is very small, the mentioned order is contrary to expectation.

TABLE 1

EXTRACTION OF RADIOZINC IN ABSENCE AND PRESENCE OF ISOBUTANOL

Original HCl molarity	Additive (%)	$[HCl]_a$[a]	$[HCl]_{org}$[a]	E	
~1.2	0	0.920	0.294	80[b]	
	20	1.07	0.255	0.35	(80)[c]
	30	1.22	0.242	0.17	
	50	1.71	0.239	0.1	
~2.4	0	2.19	0.292	75	
	10	2.18	0.285	1.01	
	20	2.43	0.261	0.30	(75)
	30	2.75	0.280	0.2	
	50	3.44	0.447	0.1	

[a] Data taken from Ref. (6).

[b] Data taken from Fig. 1, Curve IV.

[c] Corresponding data at the same equilibrium acidity in absence of isobutanol (taken from Fig. 4).

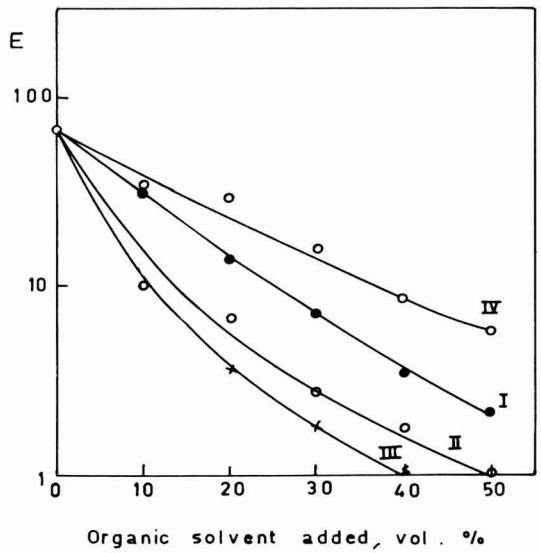

FIG. 5. Extraction of 0.01 *M* zinc by 0.06 *M* TDA from 2.4 *M* HCl in presence of: (I) methanol; (II) ethanol; (III) isopropanol; (IV) acetone.

In Fig. 5, is shown the effect of acetone, methanol, ethanol, and isopropanol on the extraction of radiozinc from 2.4 *M* HCl by 0.06 *M* TDA in presence of an inactive zinc carrier (the solution was 0.01 *M* in zinc). These results are rather similar to those obtained in the absence of a carrier, although the solvent concentration in the organic phase is not very high. The effect of the various alcohols obeys, however, the general relation with the chain length and dielectric constant.

The effect of acetone and alcohols on zinc extraction with 0.3 *M* TDA from sulfuric acid solutions in the absence and presence of a zinc carrier is illustrated in Fig. 6–9. Plots of *E* versus the volume percentage of acetone, methanol, ethanol, and isopropanol in the aqueous phase at 1.5, 3, and 4.5 *M* H_2SO_4, respectively, are given. Contrary to extraction from hydrochloric acid solution, organic additives in this case lead to an increase in the value of *E*, whereby the effect usually (at 3 and 4.5 *M* H_2SO_4) increases in the order methanol < ethanol < isopropanol < acetone. It is astonishing, however, that the order of the alcohol effect is reversed in case of extraction from 1.5 *M* H_2SO_4 (Fig. 6). As is the case for chloride extraction, the addition of zinc isotopic carrier does not change the order of the various alcohols and acetone with respect to their effect on sulfate extraction (Fig. 9). That the *E* values are generally higher than in case of the absence of a carrier (compared with the data of Fig. 7), is evidently due to the fact that the

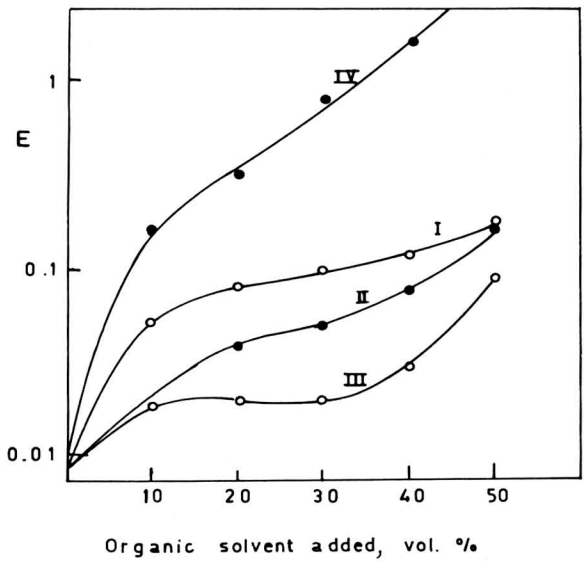

FIG. 6. Extraction of radiozinc by TDA from 1.5 *M* H_2SO_4 in presence of: (I) methanol; (II) ethanol; (III) isopropanol; (IV) acetone.

zinc carrier was dissolved in hydrochloric acid (6 *M*) and the extraction of zinc from the latter acid is known to be much higher than from sulfuric acid (see the data above). In other words, sulfate exraction is very sensitive to the presence of slight hydrochloric acid concentrations.

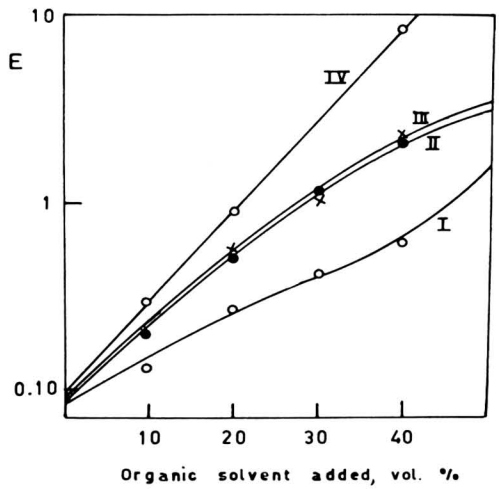

FIG. 7. Extraction of radiozinc by TDA from 3 *M* H_2SO_4 in (I) methanol; (II) ethanol; (III) isopropanol; (IV) acetone.

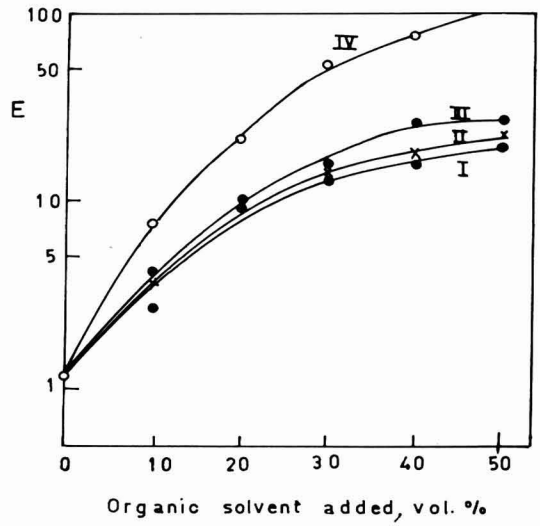

FIG. 8. Extraction of radiozinc by TDA from 4.5 *M* H_2SO_4 in presence of: (I) methanol; (II) ethanol; (III) isopropanol; (IV) acetone.

Extraction of Radioiron

The *E* values previously reported (*2*) on the effect of methanol and ethanol an iron extraction with TDA, were found to be incorrect. The

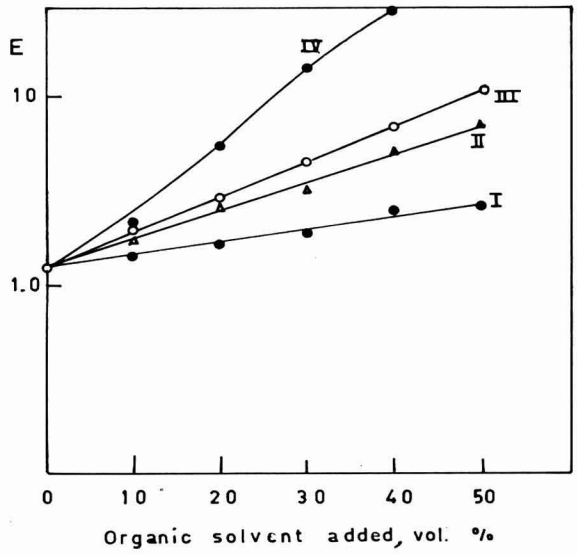

FIG. 9. Extraction of 0.01 *M* zinc by TDA from 3 *M* H_2SO_4 in presence of: (I) methanol; (II) ethanol; (III) isopropanol; (IV) acetone.

actual E values are much higher. This difference is due to the fact that the previous work was performed on irradiated iron samples, a long time after irradiation. Thus natural iron when activated in the pile induces ^{59}Fe (by n,γ reaction) and ^{54}Mn (by n,p reaction), whereby the amount of ^{59}Fe is much larger than that of ^{54}Mn. Samples of freshly irradiated iron target show, therefore, the photopeaks of ^{59}Fe. With time, however, the amount of ^{59}Fe ($t_{½}$ = 45 days) decreases and ultimately ^{54}Mn ($t_{½}$ = 278 days) predominates. Work with ^{59}Fe prepared by pile irradiation of iron targets, as a tracer should therefore be carried out after separation of ^{54}Mn. This is particularly essential when work is performed a long time after irradiation or when very high or very low extraction coefficients are expected.

In the present work, data on iron extraction were obtained applying ^{59}Fe isotope separated from ^{54}Mn isotope in a solution of pile-irradiated iron metal. Separation was carried out using one of the procedures previously recommended (*8*). The effect of hydrochloric acid concentration on the extraction of radioiron with 0.06 M TDA and 50% TBP is illustrated by an E vs acid molarity plot in a semilog scale (Fig. 10). It is evident that, in both cases, extraction sharply increases with increasing acid molarity in the aqueous solution.

Figures 11 and 12 show the effect of acetone and alcohols on the extraction of radioiron with TDA and TBP, respectively. The effect of water-miscible additives is generally considerable. According to the data of Figs. 10–12 the values of E are much higher than the corresponding

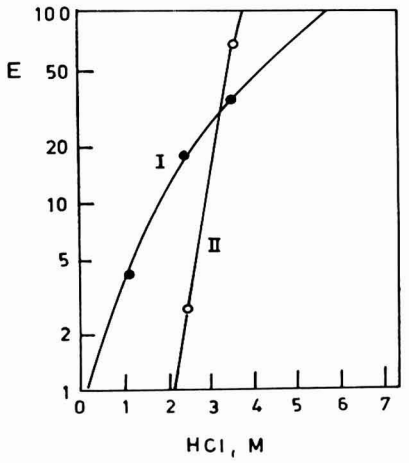

FIG. 10. Effect of hydrochloric acid concentration on the extraction of radioiron by: (I) 0.06 M TDA; (II) 50% TBP.

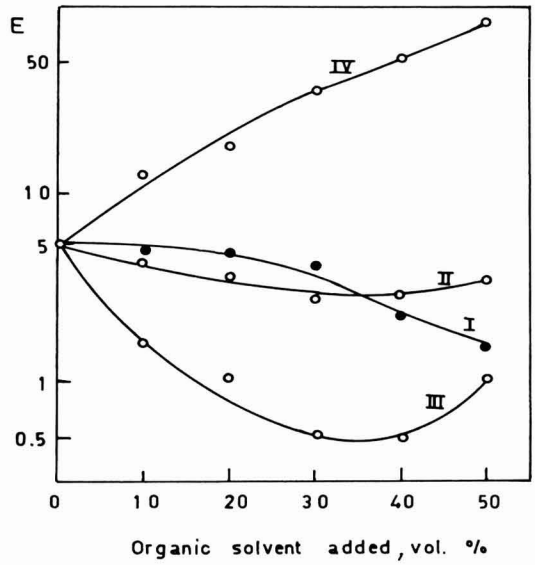

FIG. 11. Extraction of radioiron by 0.06 *M* TDA from 1.4 *M* MCl in presence of: (I) methanol; (II) ethanol; (III) isopropanol; (IV) acetone.

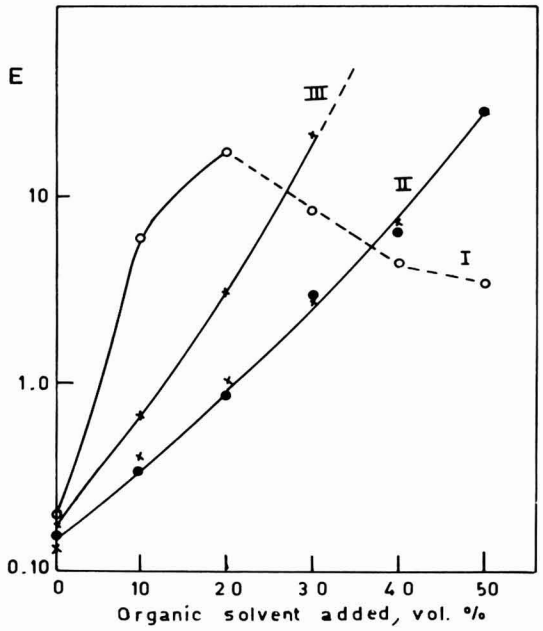

FIG. 12. Extraction of radioiron by 50% TBP from 1.4 *M* HCl in presence of: (I) methanol; (II) ethanol or isopropanol; (III) acetone.

E values previously determined, for the reason mentioned above. In case of TDA extraction, marked enhancing effect for acetone and a depressing effect for isopropanol on iron extraction is observed, while methanol and ethanol have a less pronounced effect. In case of TBP extraction (from 1.4 *M* HCl) the *E* value of iron increases with increasing the methanol concentration in the polar phase, becomes maximum at about 20% methanol and then it decreases with further increase of the alcohol concentration. The latter extraction drop may be due to the reduction of trivalent iron to the less extractable divalent state. The increase of acetone, ethanol, or isopropanol concentration, on the other hand, brings about a continuous rise of iron extraction with TBP, which can be, as usual, explained by the dehydration effect of additives.

The effect of acetone and water-miscible alcohols on the extraction of radioiron with 0.3 *M* TDA from sulfuric acid solutions was investigated at 3 various acid molarities in the polar phase. The *E* values vs acid molarity are illustrated in semilog plots in Figs. 13–15. The extraction of radioiron generally increases with increasing the acetone or alcohol concentration in the polar phase. However, the influence of additives varies with acidity as expected. Thus, while having no effect on iron extraction from 3 *M* H_2SO_4, methanol and ethanol bring about a considerable extraction increase at 4.5–6 *M* H_2SO_4. The effect of acetone is particularly high at 4.5 *M* H_2SO_4; *E* increases from less that 0.1 from pure aqueous solutions to above 10 from 50% acetone.

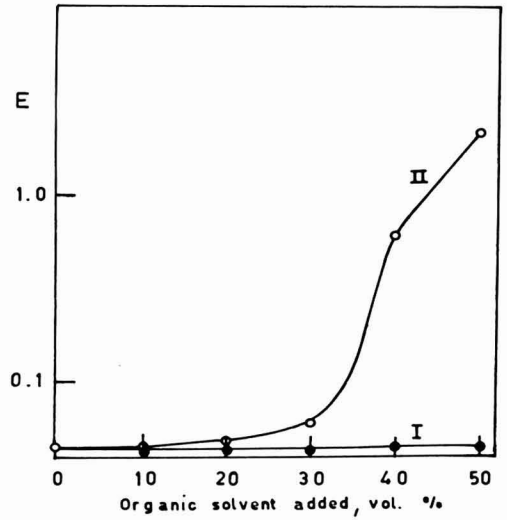

FIG. 13. Extraction of radioiron by 0.3 *M* TDA from 3 *M* H_2SO_4 in presence of: (I) methanol or ethanol; (II) acetone.

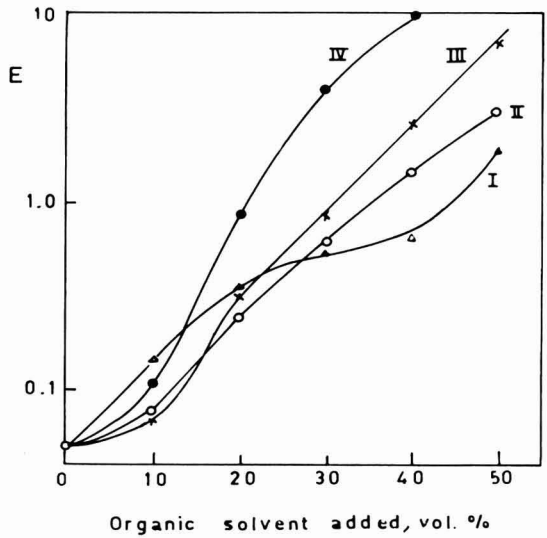

FIG. 14. Extraction of radioiron by 0.3 *M* TDA from 4.5 *M* H_2SO_4 in presence of: (I) methanol; (II) ethanol; (III) isopropanol; (IV) acetone.

Extraction of Radiomanganese

The effect of hydrochloric acid concentration on the extraction of radiomanganese by TDA and TBP is illustrated in Fig. 16. The maximum *E* value (at about 10 *M* HCl) is about 1 for 0.3 *M* TDA and less than 0.1 for 50% TBP. Figures 17 and 18 show the effect of water-miscible alcohols on the extraction of radiomanganese by TDA and

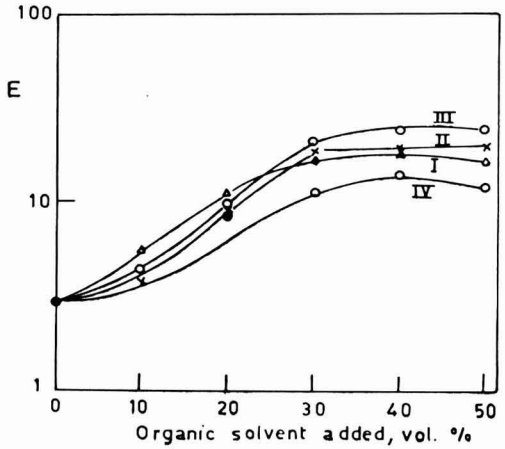

FIG. 15. Extraction of radioiron by 0.3 *M* TDA from 6 *M* H_2SO_4 in presence of: (I) methanol; (II) ethanol; (III) isopropanol; (IV) acetone.

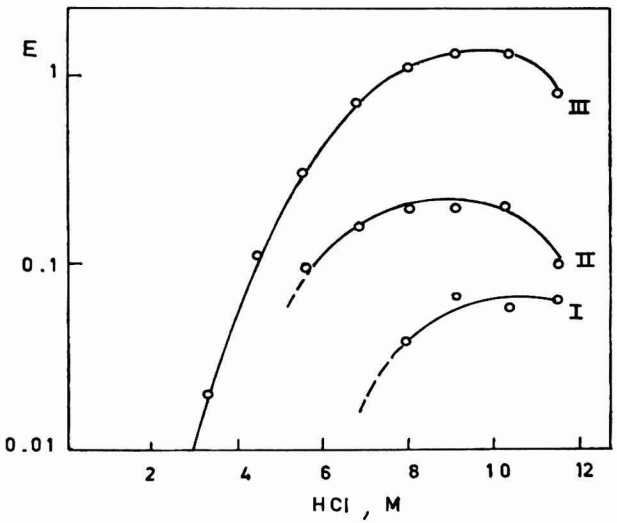

FIG. 16. Effect of Hydrochloric acid concentration on E of radiomanganese by: (I) 50% TBP; (II) 0.06 M TDA; (III) 0.3 M TDA.

TBP, respectively, from ~5.6 M HCl. Additives clearly bring about a considerable extraction rise; for extraction by 0.3 M TDA from 5.6 M HCl in 50% ethanol, the value of E is about 2, which is greater than the maximum E value for extraction from pure aqueous hydrochloric acid solutions (see Fig. 16).

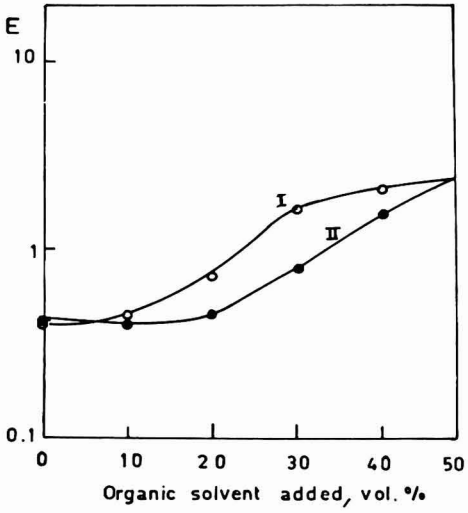

FIG. 17. Extraction of radiomanganese by 0.3 M TDA from 5.6 M HCl in presence of: (I) ethanol; (II) isopropanol.

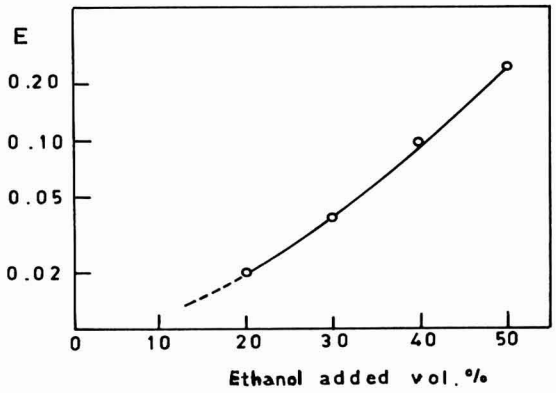

FIG. 18. Extraction of radiomanganese by 50% TBP from 5.6 *M* HCl in presence of ethanol.

The effect of TDA concentration on the extraction of radiomanganese from hydrochloric acid solutions was investigated in the absence and presence of 50 vol % ethanol. The log E vs $[TDA]_o$ relations are illustrated in Fig. 19. These relations are almost straight lines changing

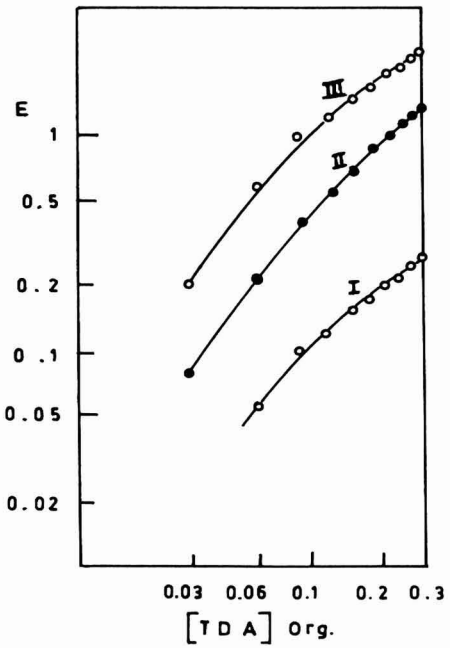

FIG. 19. Effect of TDA concentration on E of radiomanganese for extraction from: (I) pure aqueous 5.6 *M* HCl; (II) pure aqueous 8.3 *M* HCl; (III) 5.6 *M* HCl in 50% ethanol.

their slopes from about 1.4 at 0.03–0.1 *M* TDA to about 0.9 at higher amine molarities. The above slopes propose mixed solvate formation in the organic phase and at the same time reminds one of amine polymerization at higher concentrations in the diluent. It is interesting, however, to notice that the relations are almost parallel in the absence and presence of ethanol. It might therefore be proposed that the mechanism of extraction with amines which is usually adopted by most scientists remains valid in the presence of acetone and water-miscible alcohols in the polar phase:

$$x\mathrm{R_3\,N\,HX} + \mathrm{M\,X}_n \rightleftharpoons \mathrm{M}\,X_{n+x} \bullet \mathrm{R_3\,NH}.$$

This was, in fact, expected, since the role of acetone and alcohols is mainly related to their dehydration effect and to the increase of acid extraction into the organic phase.

There was no extraction at all of radiomanganese with 0.3 *M* TDA from 1–6 *M* H_2SO_4 or from mixtures of sulfuric acid and acetone or water-miscible alcohols up to 6 *M* H_2SO_4 and 50 vol % of the organic additive in the polar phase. Radioiron may thus be extracted and separated from radiomanganese by TDA from sulfuric acid solutions. The data given in Figs. 13–15 show that the best conditions for separation is about 40% acetone in 4.5 *M* H_2SO_4 or 20–30% ethanol in 6 *M* H_2SO_4; such separation is necessary in the preparation of the radioactive isotopes ^{59}Fe and ^{54}Mn, usually applied for distribution investigations in soil, plants, and animal nutrition, and also in many industrial studies. As has already been mentioned, these two isotopes are induced as a result of pile irradiation of iron and many procedures have been reported for their separation (*8–11*). In the present study, separation of ^{59}Fe from ^{54}Mn was tested on sulfuric acid solutions of recoiled concentrates of certain irradiated iron targets including some organic-iron compounds. These concentrates contained all the induced ^{54}Mn activity together with 10–15% of the total induced ^{59}Fe activity (*8*). Recovery was almost complete as tested by the standard addition technique (*7*).

Radiomanganese may also be separated from radiozinc in sulfuric acid solutions by extraction of radiozinc by TDA in presence of a water-miscible alcohol or acetone (see Figs. 7–9).

SUMMARY

The extraction of radiozinc, radioiron, and radiomanganese has been systematically studied by tridodecylamine and tributylphosphate from hydrochloric and sulfuric acid solutions in presence of water-miscible alcohols and acetone. In some cases these organic additives lead to an extraction increase, in some other cases they lead to an extraction drop, and in only a few cases, they have a negligible effect. This behavior was explained by the dehydration effect of additives

and by the competition between the acid and the metal ion for the available molecules of the extracting agent.

ACKNOWLEDGMENT

The author thanks Mr. R. Shabana and Miss Wafaa Sanad, Chemists at the Analytical Division, U.A.R., A.E.E. for helping with the experimental work.

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MICROCHEMICAL JOURNAL **18**, 393–397 (1973)

Microdetermination of Naturally Occurring Nodososide from *Cassia nodosa*, Using Chlorauric Acid as Oxidizing Agent in Alkaline Medium

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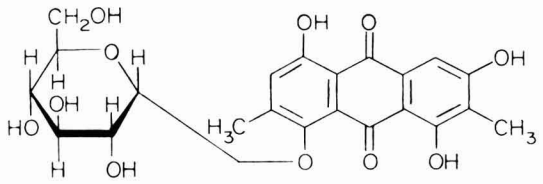
Received June 18, 1970

After elucidating the structure of nodososide, a naturally occurring product, by chemical and spectral studies it was felt necessary to estimate it. The work has, thus, been proposed to find out a quantitative method for estimating compounds isolated from natural sources.

Nodososide (*1*) is 1,3,5-trihydroxy-2,7-dimethyl-anthraquinone-8-*O*-α-D-glucopyranoside isolated from the flowers of *Cassia nodosa*. Its molecular weight is 462 and structurally it can be represented as



Present work deals with the determination of nodososide, isolated from the flowers of *Cassia nodosa*, quantitatively in micro amounts by oxidizing with chlorauric acid ($HAuCl_4$ gold chloride) in the presence of large excess of alkali. Known excess of chlorauric acid and alkali solutions were added to a known volume of nodososide to effect oxidation by heating the reaction mixture on a hot plate. After cooling at room temperature, remaining gold(III) was titrated back (*2*) by first acidifying and adding a known excess of potassium ferrocyanide solution. Remaining ferrocyanide solution was titrated against standard ceric sulfate solution using *N*-phenylanthranilic acid as indicator. The reaction between nodososide and chlorauric acid solution in presence of alkali is

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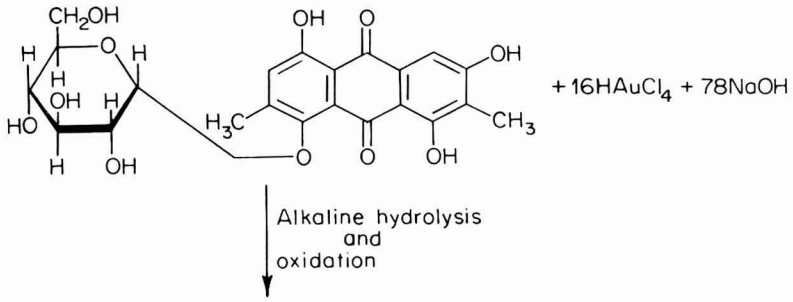
completed at 48 equivalence. Probably the following reaction takes place:



$$16Au + 64NaCl + 6CO_2 + 2CH_3 \cdot COONa + 12HCOONa + 49H_2O$$

EXPERIMENTAL METHODS

Reagents Used

Nodososide (isolated from the flowers of *Cassia nodosa,* Indian grade); chlorauric acid (Apex, Indian grade); ferrous ammonium sulfate, potassium ferrocyanide, and sulfuric acid (AnalaR, B.D.H. grade); sodium hydroxide (E Merck, grade); *N*-phenylanthranilic acid (L.R., B.D.H. grade) and ceric sulfate (Technical, B.D.H. grade).

Apparatus Used

Micropipettes and microburettes used had least count = 0.01 ml.

Nodososide solution was prepared by dissolving an accurately weighed amount of 0.001 *N* sodium hydroxide solution.

Chlorauric acid was dissolved in distilled water and standardized (*2*).

Standard ferrous ammonium sulfate solution was prepared by dissolving an exactly weighed amount in 0.01 N H_2SO_4.

The 0.0028 *N* ceric sulfate solution was prepared with 4 N H_2SO_4 and standardized by titrating against standard ferrous ammonium sulfate (in 0.01 *N* H_2SO_4) solution using *N*-phenylanthranilic acid solution as indicator.

Potassium ferrocyanide solution was prepared by dissolving in distilled water and was standardized by titrating against standard ceric sulfate (in 4 *N* H_2SO_4) solution using the above-mentioned indicator solution.

N-Phenylanthranilic acid solution was prepared by dissolving 0.1 g of it and 0.2 g of Na_2CO_3 in 100 ml of distilled water.

Procedure

To a beaker, containing known volume of standard nodososide solution, excess of known standard chlorauric acid and sodium hydroxide solutions were added with a further addition of 30 ml of distilled water —which formed a solution mixture. The solution mixture was heated on a hot plate at full heat for 150 minutes (keeping in mind that the reaction mixture may not evaporate). In case, the volume of the reaction mixture reduced 15 ml (much before 150 minutes) then, again 20 to 25 ml distilled water is added. After cooling at room temperature the precipitated metallic gold, corresponding to nodososide oxidized, was filtered and thoroughly washed with distilled water. Rejecting the precipitate, the filtrate and the washings were collected, concentrated, acidified with 20 ml of 10 *N* H_2SO_4 solution and treated with a known excess of standard potassium ferrocyanide solution. Remaining potassium ferrocyanide solution was titrated against standard ceric sulfate (in 4 *N* H_2SO_4) solution using *N*-phenylanthranilic acid solution as indicator. At the end point a reddish brown color sharply appeared.

RESULTS AND DISCUSSION

Results are given in Table 1. The range in which nodososide has been estimated varies from 9.37×10^{-5} to 23.26×10^{-5} mg/liter.

The oxidation of 1,3,5-trihydroxy-2,7-dimethylanthraquinone-8-*O*-α-D-glucopyranoside, i.e., nodososide with chlorauric acid in presence of a large excess of sodium hydroxide required 24 oxygen atoms for the rupture of the whole molecute resulting in the formation of sodium formate and acetate as main products.

The confirmation of sodium acetate and sodium formate was subjected to specific tests. The reaction mixture was acidified with 2 *N* H_2SO_4, extracted with ether solvent (Alembic), washed, and the ethereal extract was shaken with a saturated sodium bicarbonate solution. Sodium bicarbonate extract was acidified and extracted with ether. The ether extract was washed until free from sulfate ions and then concentrated. The concentrate gave positive test for formic acid; and its identity was further confirmed by paper chromatography. The identity of acetic acid was also confirmed chromatographically.

Since the reaction between nodososide and chlorauric acid in the presence of sodium hydroxide is completed at 48 equivalence, calculations were made by dividing the observed values by 48. The maximum error observed was 1.4%. The reaction proceeds with the alkaline hydrolysis; but erroneous results are obtained at lower concentrations of alkali. The method is accurate, reproducible and simple.

TABLE 1

MICRODETERMINATION OF NODOSOSIDE

Nodososide 0.001 *M* (ml)	NaOH 0.02 *N* (ml)	$HAuCl_4$ 0.0121 *M* (ml)	$K_4Fe(CN)_6$ 0.030 *M* (ml)	$Ce(SO_4)_2$ 0.0028 *N* (ml)		Amount of nodososide ($\times 10^5$ mg/liter)		
					Consumed	Taken	Found	Error (%)
—	—	—	1	10.90	—	—	—	—
—	—	2	1	2.20	8.70	—	—	—
0.2	80	2	1	5.70	3.50	9.24	9.37	1.4
0.3	80	2	1	7.48	5.28	13.86	13.99	0.9
0.4	80	2	1	9.08	6.88	18.48	18.44	0.2
0.5	80	2	1	10.88	8.68	23.10	23.26	0.6

SUMMARY

Nodososide, isolated from the flowers of *Cassia nodosa,* has been quantitatively determined by oxidizing with chlorauric acid in large excess of alkali. The oxidation reaction between nodososide and chlorauric acid is preceded by alkaline hydrolysis and is completed at 48 equivalence, resulting in the formation of sodium formate and acetate as main products. Maximum error observed was 1.4%. The method is accurate and gives reproducible results.

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MICROCHEMICAL JOURNAL 18, 398–400 (1973)

Titrimetric Microdetermination of Chromotrope 2R: Ceric Sulfate as Oxidizing Agent

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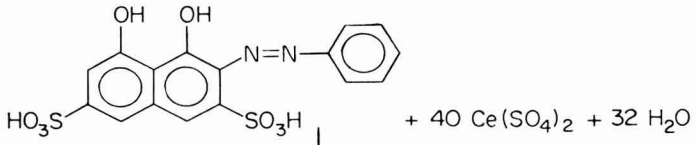
Received June 25, 1970

Chromotrope 2R is known to have formed a large number of chelates with different metal ions but, perhaps, no attention has been paid to its determination. Up-to-date literature concerning its determination is almost nil. In view of this fact it was thought necessary to estimate it quantitatively.

The present work deals with the quantitative determination of Chromotrope 2R in micro amounts by oxidizing with an excess of ceric sulfate in acidic medium. The oxidation was effected by direct heating of the reaction mixture; and 40 equivalence were required for the rupture of the molecule, producing formic acid. Probably the following reaction takes place:



$$20\ Ce_2(SO_4)_3 + 22\ H_2SO_4 + N_2 + 16\ HCOOH$$

Isolation and identification of the oxidation product of Chromotrope 2R are given in the Discussion.

EXPERIMENTAL METHODS

Reagents Used

Chromotrope 2R and *N*-phenylanthranilic acid (B.D.H. grade); sulfuric acid, ferrous ammonium sulfate, sodium carbonate and sodium bicarbonate (AnalaR, B.D.H. grade); ceric sulfate (Technical, B.D.H. grade); and solvent ether (Alembic grade).

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Apparatus Used

Micropipettes and microburettes used had least count = 0.01 ml.

Standard Chromotrope 2R solution was prepared by dissolving an exactly weighed amount in distilled water.

Ferrous ammonium sulfate solution was prepared by dissolving an exact amount in 0.1 *N* sulfuric acid solution.

0.0032 *N* ceric sulfate (in 4 *N* H_2SO_4) solution was standardized by titrating against standard ferrous ammonium sulfate solution using *N*-phenylanthranilic acid as indicator.

0.1 g of *N*-phenylanthranilic acid and 0.2 g of sodium carbonate were dissolved together in 100 ml of distilled water.

Procedure

Known volumes of standard Chromotrope 2R solution were placed in different beakers by a micropipette and to each a known excess of standard ceric sulfate (in 4 *N* H_2SO_4) solution was added along with 20–25 ml of distilled water. The reaction mixture was boiled directly on the flame for 4 minutes, cooled at room temperature, and the remaining ceric sulfate solution was titrated against standard ferrous ammonium sulfate solution in 0.1 *N* H_2SO_4 using *N*-phenylanthranilic acid as indicator. At the end point the reddish brown color vanished sharply.

RESULTS AND DISCUSSION

Results are given in Table 1. Chromotrope 2R was quantitatively determined in the range of 10.6×10^{-2} to 42.72×10^{-2} mg.

The oxidation of Chromotrope 2R with ceric sulfate in acidic medium required 20 oxygen atoms. The reaction resulted in the rupture of the molecule with the formation of formic acid as main oxidation product.

TABLE 1

Chromotrope 2R 0.0005 *M* (ml)	$Ce(SO_4)_2$ 0.0032 *N* (ml)	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, 0.005 *N* (ml)		Amount of Chromotrope 2R ($\times 10^{-2}$ mg)		Error (%)
			Consumed	Taken	Found	
—	20	12.88	—	—	—	—
0.50	20	10.88	2.00	10.60	10.60	0.04
0.75	20	9.86	3.02	15.90	16.00	0.6
1.25	20	7.84	5.04	26.50	26.71	0.8
1.50	20	6.82	6.06	31.80	32.12	1.0
2.00	20	4.82	8.06	42.40	42.72	0.7

The reaction mixture was repeatedly extracted with solvent ether (Alembic) and the etherial extract was shaken thoroughly with a saturated solution of sodium bicarbonate. The aqueous sodium bicarbonate extract was acidified with 4 N H_2SO_4 and repeatedly extracted with ether. The extract was washed with distilled water until free from sulfate ions, dehydrated, concentrated at low temperature, and examined by paper chromatography. Only one spot corresponding to the mobility of formic acid could be detected. The acid was further identified by co-chromatography with an authentic sample and performing specific tests from the concentrate.

The organic layer, left after the extraction with sodium bicarbonate solution, was washed until free from sulfate ions, dehydrated, and concentrated. No organic compound could be detected in the concentrate.

As the oxidation of Chromotrope 2R with acidic ceric sulfate requires 40 equivalence, the found values were calculated by dividing the experimental values by 40. Maximum error observed in these experiments is 1.0%. It has been observed that large variation in the time for boiling produces inaccurate results. This method is simple, accurate, and reproducible.

SUMMARY

Chromotrope 2R has been quantitatively determined in micro amounts by oxidizing with ceric sulfate in highly acidic medium. The reaction is completed at 40 equivalence; and the rupture of the molecule results in the formation of formic acid as the main oxidation product. Maximum error observed is 1.0%. The method is simple, accurate, and reproducible.

ACKNOWLEDGMENT

The author is grateful to the Council of Scientific and Industrial Research (Government of India), New Delhi for providing financial assistance.

MICROCHEMICAL JOURNAL 18, 401–404 (1973)

Direct Titrimetric Microdetermination of Tropeolin OO

I. Oxidation of Tropeolin OO with Ceric Sulfate

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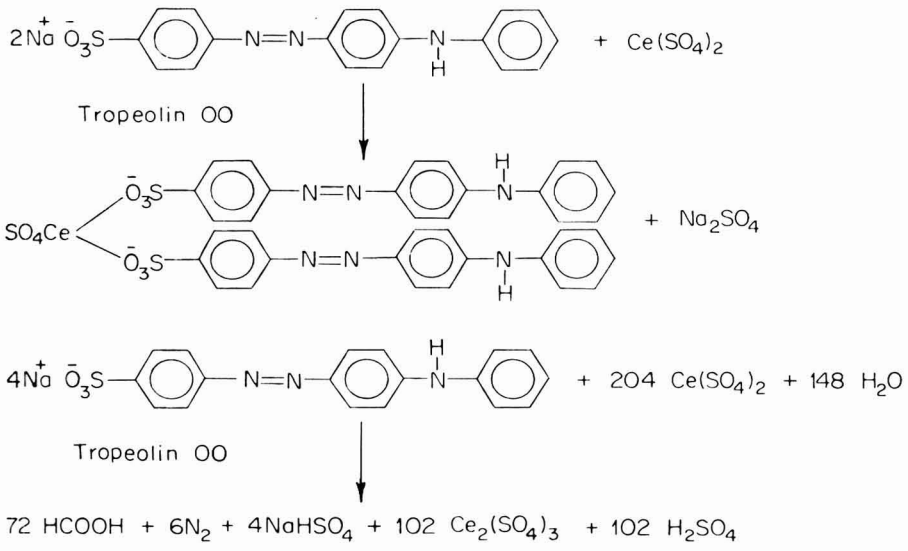
Received June 25, 1970

Tropeolin OO is very well known to have formed a number of chelates with different metal ions but, perhaps, no attention has been paid to its determination. Literature concerning its determination is not available. In view of this fact, it was thought necessary to develop methods for its determination.

The present work deals with two quantitative methods for the determination of tropeolin OO in micro amounts with ceric sulfate in presence of a large excess of acid. In one method tropeolin OO has been determined by directly titrating against standard ceric sulfate solution. In another method it has been determined by oxidizing with an excess of ceric sulfate solution and then titrating the remaining excess of ceric sulfate solution against ferrous ammonium sulfate. In the first method the reaction takes place in the ratio of 1:2; whereas the oxidation of tropeolin OO is completed at 51 equivalents. Probably the following reactions take place in the two methods mentioned:



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It is discussed later why in the first equation salt formation has been shown and not the linkage through —NH— group. The identification of formic acid formed during oxidation is also mentioned in the discussion.

EXPERIMENTAL METHODS

Reagents Used

Tropeolin OO, *N*-phenylanthranilic acid (B.D.H. grade); sodium carbonate, sodium bicarbonate, ferrous ammonium sulfate, and sulfuric acid (AnalaR, B.D.H. grade); ether (Alembic); and ceric sulfate (Technical, B.D.H. grade).

Apparatus Used

Micropipettes and burettes used had least count = 0.01 ml. Hot plate.

Standard tropeolin OO solution was prepared by dissolving an accurately weighed amount in distilled water.

0.005 *N* ferrous ammonium sulfate solution was prepared by dissolving an exact amount in 0.1 *N* H_2SO_4 solution.

0.0031 *N* ceric sulfate (in 4 *N* H_2SO_4) solution was standardized by titrating against standard ferrous ammonium sulfate (in 0.1 *N* H_2SO_4) solution using *N*-phenylanthranilic acid solution as indicator.

0.1 g of *N*-phenylanthranilic acid and 0.2 g of Na_2CO_3 were dissolved together in 100 ml of distilled water, which served as indicator.

Procedure

I. Direct titration with ceric sulfate. A known volume of tropeolin OO solution was placed in a beaker and 10 ml of distilled water were added. The solution in the beaker was titrated, by running through microburette, against ceric sulfate (in 4 *N* H_2SO_4) solution using *N*-phenylanthranilic acid solution as indicator. The colors changed from red-pink violet, violet-green and at the end point to reddish brown sharply. In case *N*-phenylanthranilic acid solution is not used then the end point shows a green color from violet but this color does not give a correct end point until the above-mentioned indicator is added to show a sharp color change with a slight excess of ceric sulfate.

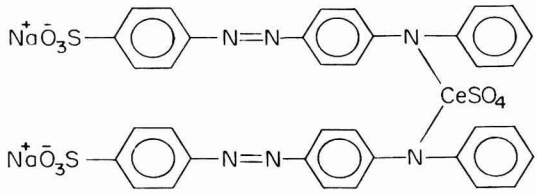
II. Oxidation of tropeolin OO. Known volumes of standard tropeolin OO solutions were placed, through micropipette, in different beakers containing 20 ml of 0.0031 *N* ceric sulfate (in 4 *N* H_2SO_4) solution and 20 ml of distilled water, which formed a reaction mixture. The reaction mixture was put on a hot plate at full heat (keeping in mind that the reaction mixture may not evaporate) for 120 minutes. In case the reaction mixture was reduced to 5 ml (much before 120 minutes), then 20 ml of distilled water were added. After cooling at

room temperature, the remaining ceric sulfate was titrated against standard ferrous ammonium sulfate (in 0.1 *N* H_2SO_4) solution using *N*-phenylanthranilic acid solution as indicator. At the end point the reddish brown color sharply vanished.

RESULTS AND DISCUSSION

Results are given in Tables 1 and 2. Tropeolin OO was estimated by the direct and indirect methods in the ranges of 7.56×10^{-2} to 94.28×10^{-2} mg; and 7.58×10^{-2} to 18.80×10^{-2} mg, respectively.

Table 1 shows that tropeolin OO has been directly titrated against ceric sulfate solution in the ratio of 1:2 and hence the observed experimental values have been divided by 2. According to the equation, it appears that the reaction between tropeolin OO and ceric sulfate results in the formation of a salt. Salt formation is the only possibility because in case of linking through –NH– the ratio would definitely remain 1:2 with the following structure:



but it is not so since diphenylamine is not titratable directly in the ratio of 1:2. Hence the possibility of linking through –NH– is ruled out. Maximum error in the case of direct titration is 0.8%.

Results in Table 2 show that the reaction between tropeolin OO and ceric sulfate required 25.5 oxygen atoms. The oxidation resulted in the formation of formic acid as main product.

TABLE 1

DIRECT DETERMINATION OF TROPEOLIN OO

Tropeolin OO, 0.001 *M* (ml)	$Ce(SO_4)_2$, 0.0031 *N* (ml)	Amount of tropeolin OO ($\times 10^{-2}$ mg)		
		Taken	Found	Error (%)
0.2	0.13	7.50	7.56	0.8
0.5	0.32	18.75	18.62	0.6
1.0	0.65	37.50	17.83	0.8
1.5	0.97	56.25	56.45	0.3
2.0	1.30	75.00	75.66	0.8
2.5	1.62	93.75	94.28	0.5

TABLE 2

DETERMINATION OF TROPEOLIN OO

Tropeolin OO, 0.001 *M* (ml)	$Ce(SO_4)_2$, 0.0031 *N* (ml)	$FeSO_4 \cdot (NH_4)_2SO_4$, 0.005 *N* (ml)		Amount of tropeolin OO ($\times 10^{-2}$ mg)		Error (%)
			Consumed	Taken	Found	
—	20	12.40	—	—	—	—
0.2	20	10.36	2.04	7.50	7.58	1.0
0.3	20	9.34	3.06	11.25	11.28	0.3
0.4	20	8.26	4.14	15.00	15.22	1.3
0.5	20	7.26	5.14	18.75	18.80	0.2

The reaction mixture was repeatedly extracted with ether and washed. The ether extract was shaken with a staturated solution of sodium carbonate. Sodium bicarbonate extract was acidified and extracted with ether. Ether extract was washed until free from sulfate ions, dehydrated, and concentrated at low temperature. The concentrate gave positive tests for formic acid; its identity was confirmed by paper chromatography.

Since the reaction between tropeolin OO and ceric sulfate is completed at 51 equivalents; hence calculations have been done by dividing with 5% the observed experimental values. Maximum error in this case was 1.3%.

Both these methods are simple, accurate, reproducible, and give concordant results.

SUMMARY

Two quantitative methods for the determination of tropeoline OO in micro amounts are described. One of the methods is by direct titration with ceric sulfate resulting in the formation of a salt in the ratio of 1:2; in another method oxidation is effected at 51 equivalents. The reason for salt formation in the first method and the identification of formic acid is discussed. Maximum error for the first and second methods is 0.8 and 1.3%, respectively. The two methods are simple, accurate, and reproducible.

MICROCHEMICAL JOURNAL 18, 405–411 (1973)

Synergism in the Solvent Extraction of Samarium by Thenoyltrifluoroacetone and Triphenyl or Trioctyl Phosphine Oxide Mixture

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Synergistic enhancement in solvent extraction of trivalent actinides and lanthanides using phosphine oxide derivatives as neutral donor and thenoyltrifluoroacetone (TTA = HA) as the chelating extractant have been generally reported. The main members of the phosphine oxides currently used are tributyl and trioctyl phosphine oxides (4–6). Using triphenyl phosphine oxide (TPPO) together with thenoyltrifluoracetone is rather limited to the work carried out by Healy for the synergistic extraction of americium and promethium *(5)*. In the present work, a systematic investigation on the extraction of samarium with TPPO and TTA mixture was carried out. From the distribution data obtained, the formula of the extracted complex is deduced and its formation constant is determined graphically. For comparison, the trioctyl phosphine oxide (TOPO)–TTA system was briefly investigated.

EXPERIMENTAL METHODS

Samarium tracer. Tht radioactive samarium (145 + 153) was prepared by irradiating spectroscopic pure sample of Sm_2O_3 (Johnson-Matthy grade) with thermal neutron flux of 10^{13} n cm^{-1} sec^{-1} in the UARR-1 reactor for 1 week. After irradiation, the sample was dissolved in nitric acid followed by evaporation to dryness. The formed samarium nitrate was then dissolved in 10^{-3} *M* nitric acid and the solution was passed through a chromatographic column (0.5 × 10 cm) containing DBDECP + TTA mixture on hydrophobic Celite *(1)*. After the elution of trace europium-155, that might be formed through the β-decay of the short lived samarium-155 (23 min), samarium was then eluted with 1 *M* HNO_3 solution. The eluted samarium, free of europium, was then evaporated to dryness and transferred to the perchlorate form by the addition of a stoichiometric amount of $HClO_4$

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with gentle evaporation to dryness. The radio samarium was finally dissolved in the desired $HClO_4$–$NaClO_4$ buffer.

Solvents and materials. Triphenyl and trioctyl phosphine oxides (obtained from Eastman-Kodak, U.S.A.) were used without any purification. Thenoyltrifluoroacetone is of practical grade reagent (Fluka A. G.) and was purified by recrystallization from benzene. All other chemicals and reagents were of analytical grade (B.D.H.).

Extraction procedure. Primary experiments for test of synergism was carried out by mixing 5 ml of benzene solution containing a different molar ratio of the two extractants (TTA and TPPO) with an equal volume of the aqueous phase. The other set of experiments was done by transferring (in stoppered test tubes) 5 ml of extractant mixture (TTA with TPPO or TOPO) containing variable concentrations of one extractant and constant concentration of the other to an equal volume of the aqueous phase. In all cases, the aqueous phase has a constant ionic strength of 0.1, adjusted at a known pH value, and traced with samarium radioactivity (10^{-5} *M* Sm). The test tubes were shaken with a mechanical shaker until equilibrium (30 min) followed by centrifugation to enhance phase separation. An equal volume of both phases was used for γ-radiometric assay using a well-type NaI(Tl) crystal connected to a Philips-type scaler. The distribution coefficient, D_{Sm}, was evaluated from the counting ratio of the organic to the aqueous phase.

RESULTS AND DISCUSSION

Preliminary experiments, carried out to measure the distribution of Sm between 0.05 *M* TTA or TPPO in benzene and aqueous phase of pH 2 and ionic strength of 0.1, gave a distribution value less than 10^{-3} in both cases. When a mixture of the two solvents was used as extractant, an increase in the extraction of the element was achieved. This is shown in Fig. 1 for TPPO and TTA mixture having total molar concentration of 0.05 and different molar ratio of both extractants. In this case, an increase in the extraction by a factor more than 10^4 is observed, at the organic composition of 0.03 *M* TTA and 0.02 *M* TPPO, when using aqueous solution of pH 2 and ionic strength of 0.1.

To determine the solvation number for the two extractants used, the variables [TTA] and [TPPO] in the system were examined while keeping the pH value and one of the extractants constant at a time. Subsequently, a log–log relation of the variation in D_{Sm} with TTA concentration (at constant pH and TPPO concentration) gave straight lines of slopes ranging from 2.3 to 2.8, Fig. 2. The value of the slope could be considered as the expected value of 3 and a trisolvate may be suggested for TTA in the extracted complex. Increase in the deviation from slope

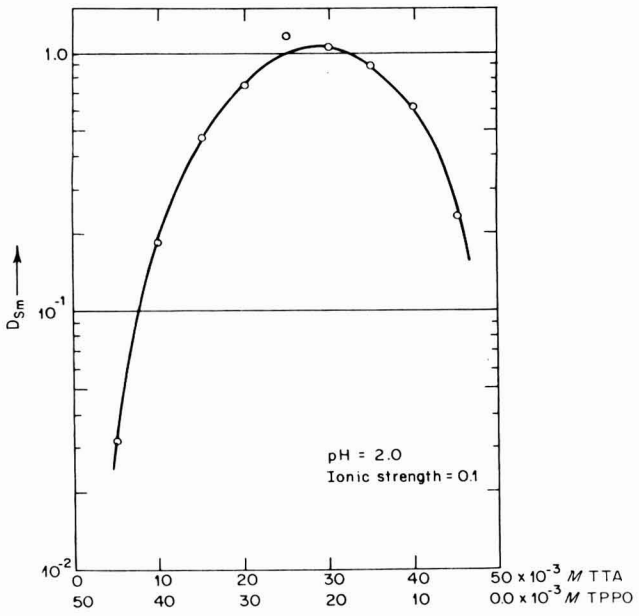

FIG. 1. Test of synergism.

3 observed with the increase in the pH value, could be attributed to the possible formation of metal chelate soluble in the aqueous phase *(9, 10)*. On the other hand, measurements of the extraction of samarium in the organic phase containing constant TTA concentration and variable TPPO concentration, gave straight lines of slopes change from 1.7 to 2.1, Fig. 3, indicating the contribution of two TPPO molecules in the extracted metal adduct. As a result of these informations, the main species extracted could be satisfactorily formulated as $SmA_3 \cdot 2TPPO$.

In order to evaluate the formation constant for the synergistic reaction in the organic phase, it was generally assumed that interaction between HA and the neutral donor (B) is negligible, polymerization in the organic phase or hydrolysis in the aqueous phase are excluded and no samarium perchlorate or hydroxy complexes are extracted into the organic phase. Accordingly, in absence of the neutral donor B (TPPO or TOPO), the extraction could be given simply by

$$Sm^{3+} + 3HA_{org} \rightleftharpoons SmA_{3org} + 3H^+ , \tag{1}$$

for which

$$K_{3,0} = \frac{[SmA_3]_{org}\,[H^+]^3}{[Sm^{3+}]\,[HA]_{org}^3} . \tag{2}$$

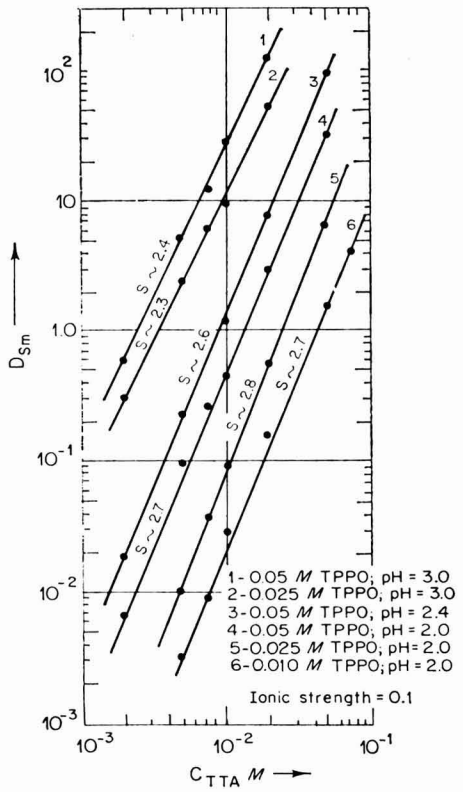

FIG. 2. Variation of D_{Sm} versus C_{TTA} at constant concentrations of TPPO.

When a neutral donor is added and on the assumption that only one extracted mixed complex is predominating at a time, the extraction could be represented by Eq. (3).

$$Sm^{3+} + 3HA_{org} + nB_{org} \rightleftharpoons SmA_3 \cdot nB_{org} + 3H^+ , \tag{3}$$

for which

$$K_{3,n} = \frac{[SmA_3 \cdot nB]_{org} [H^+]^3}{[Sm^{3+}] [HA]^3_{org} [B]^n_{org}} . \tag{4}$$

On the other hand, the distribution coefficient D is given by the expression

$$D = \frac{[SmA_3]_{org} + [SmA_3 \cdot nB]_{org}}{[Sm^{3+}]} . \tag{5}$$

From Eqs. (2) and (4), Eq. (5) can be written in the form,

$$D = K_{3,0} \frac{[HA]^3_{org}}{[H^+]^3} + K_{3,n} \frac{[HA]^3_{org} [B]^n_{org}}{[H^+]^3} , \tag{6}$$

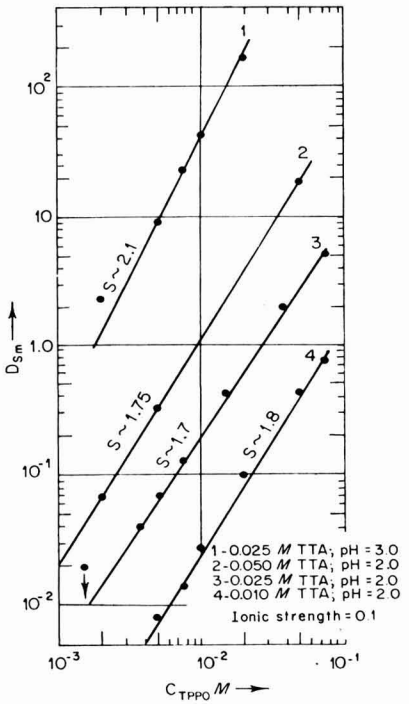

FIG. 3. Variation of D_{Sm} versus C_{TPPO} at constant concentrations of TTA.

by arrangements and taking the log of both sides, Eq. (6) takes the following form,

$$\log \left\{ \frac{D[H^+]^3}{K_{3,0}\,[HA]^3_{org}} - 1 \right\} = \log \frac{K_{3,n}}{K_{3,0}} + n \log [B]\,, \qquad (7)$$

where n is the solvation number of the neutral donor.

Since the formation constant of the synergistic reaction β equals to $K_{3,n}/K_{3,0}$ as given by Irving (7), a plot of log $\{(D[H^+]^3/K_{3,0}\,[HA]^3_{org}) - 1\}$ against log [B] will give a straight line having slope of n and intercept with the Y axis at zero B concentration to give the value of log β.

From the experimental data obtained, together with the values previously reported for $K_{3,0}$ *(11)*, the mentioned relation (Eq. 7) is given in Fig. 4. From Fig. 4, the β and $K_{3,n}$ values were evaluated and are shown in Table 1. In general, it is clear that TOPO forms stronger adducts than TPPO which could be related to the known powerful electron donor proparties of the former extractant. On the other hand, the straight lines obtained in Fig. 4 show a slope of 2 for both TPPO and TOPO. For TPPO, the value of the slope obtained confirms the

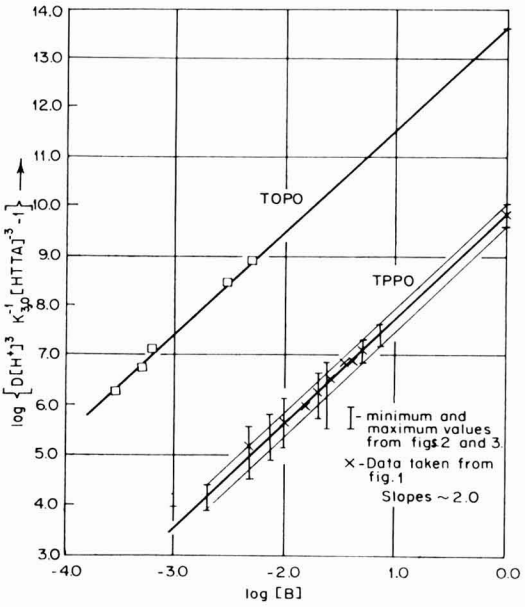

FIG. 4. Graphical evaluation of β value.

solvation number of 2 previously deduced from Fig. 3. In regard to TOPO, it is also clear from Fig. 4 that 1 mole of samarium chelate is reacting with 2 moles of TOPO to form the extracted complex having the formula $Sm_3A \cdot 2TOPO$.

In spite of the fact that the formula of the extracted complex is established fairly well, yet its structure by no means established with certainty. Table 1, shows that the formation constant is dependent on the system used as well as the metal cation itself. This would suggest that the neutral donor is most probably bonded directly to the metal.

TABLE 1

EQUILIBRIUM CONSTANT($K_{3,0}$) OF METAL CHELATE MA_3, MIXED EQUILIBRIUM CONSTANT($K_{3,2}$) OF $MA_3 \cdot 2B$ AND SYNERGISTIC EQUILIBRIUM CONSTANT $\beta = K_{3,2}\ K_{3,0}^{-1}$

		$K_{3,2}$		β (estimated)	
Element	$K_{3,0}$ [a]	TOPO	TPPO	TOPO	TPPO
Pm^{3+}	2.7×10^{-8}	2.7×10^{2} [b]	6.0 [b]	9.8×10^{9}	2.2×10^{8}
Am^{3+}	8.9×10^{-9}	3.2×10^{2} [b]	7.0 [b]	3.6×10^{12}	8.5×10^{8}
Sm^{3+} [c]	2.1×10^{-8}	8.0×10^{5}	3.9×10^{2}	3.9×10^{13}	8.2×10^{10}

[a] See Ref. (*11*).
[b] See Ref. (*5*).
[c] Evaluated from the present work.

Batzer *et al. (2)* and Irving and Edgington *(8)* further assumed that the neutral donor replaces a water molecule from the coordination sphere of the cation. In this case, either the coordination number of the metal increases beyond its usual number *(5, 8)*, or the chelate rings may be opened and one or more TTA molecules become monodentate *(3)*. The authors feel that the latter assumption is most probable; however, further infrared and NMR investigation of the formed complex are required to confirm this proposal.

SUMMARY

Synergistic extraction of samarium with TTA(HA) and TPPO or TOPO (B) mixtures were investigated. The extracted complex was proved to have the general formula $SmA_3 \cdot 2B$. A graphical determination for the formation constants of these complexes gave the values 3.9×10^{13} and 8.2×10^{10} for $SmA_3 \cdot 2TOPO$ and $SmA_3 \cdot 2TPPO$ in benzene, respectively.

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MICROCHEMICAL JOURNAL 18, 412–421 (1973)

Spectrophotometry of Iron Chelates with 2-Hydroxy-5-methylpropiophenone Oxime

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A few *o*-hydroxyoximes, viz., salicylaldoxime *(1)*, salicylamidoxime *(2)*, o-hydroxyacetophenone oxime *(3)*, resacetophenone oxime (4–6), 2,4-dihydroxypropiophenone oxime *(7, 8)* have been employed for spectrophotometric determination of iron. The reagent, 2-hydroxy-5-methylpropiophenone oxime (HMP) has already been used for spectrophotometric determination of nickel *(9)* and palladium *(10)*. In the present work, studies concerning chelation of this reagent with ferric ions have been carried out. It has been found that two complexes are formed in the system, one of which can be extracted into nonpolar organic solvents. The nature of the complexes formed under different conditions and their suitability for spectrophotometric determination of ferric iron have been worked out. The study has revealed that the reagent can be used for determination of micro amounts of iron, though it is not very selective.

EXPERIMENTAL METHOD

Reagents

Ferric solution. Ferric perchlorate solution was prepared by dissolving freshly precipitated ferric hydroxide in minimum amount of perchloric acid. The solution was diluted to a known volume with double distilled water and iron content was determined gravimetrically as Fe_2O_3.

HMP solution. 4.0×10^{-2} *M* solution was prepared by dissolving 2-hydroxy-5-methylpropiophenone oxime in ethanol.

A Unicam spectrophotometer, SP 600, was employed for the measurement of optical density. The pH measurements were made on a Metrohm pH meter, type E-350.

Iron(III) forms two soluble complexes with the ligand, HMP, the formation of which is pH dependent. A blue colored complex is formed at lower pH values; whereas at higher pH values another complex, which is brown-red in color, is obtained. The pH values were adjusted with dilute solutions of perchloric acid or sodium hydroxide.

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A. Studies on the Blue Iron(III) Chelate

The blue complex was formed at lower pH values on adding ligand solution to that of iron(III). A high concentration of ethanol is necessary to prevent the precipitation of the reagent. It has been found that no significant change in absorbance takes place by varying ethanol concentrations from 60 to 80% (v/v). However, 75% ethanol concentration was maintained in all the studies. The blue chelate could not be extracted into water-immiscible organic solvents.

The optical density of the complex was found to remain constant only for about 20 minutes. After a lapse of more than 20 minutes, the color faded gradually. The fading of color may be due to the reduction of Fe(III) by the ligand at lower pH values as shown by the fact that ferrous iron does not give a blue color with the reagent. All measurements were, therefore, carried out within this time period.

Absorption spectra and effect of pH. The absorption spectrum of the chelate formed between ferric iron and the reagent at pH 2.0 is shown in Fig. 1. The λ_{max} of the complex lies at 580 nm. Since ferric perchlorate gives color reaction with ethanol, corresponding metal blanks were also prepared and their absorbances were subtracted from those of the ferric chelate. The ligand, however, does not absorb in the visible region.

The blue chelate starts forming at pH 1.9 and thereafter, the absorbance increases up to pH 2.05. The optical density of the complex remains constant over a narrow range of pH (2.05 to 2.15). Above pH

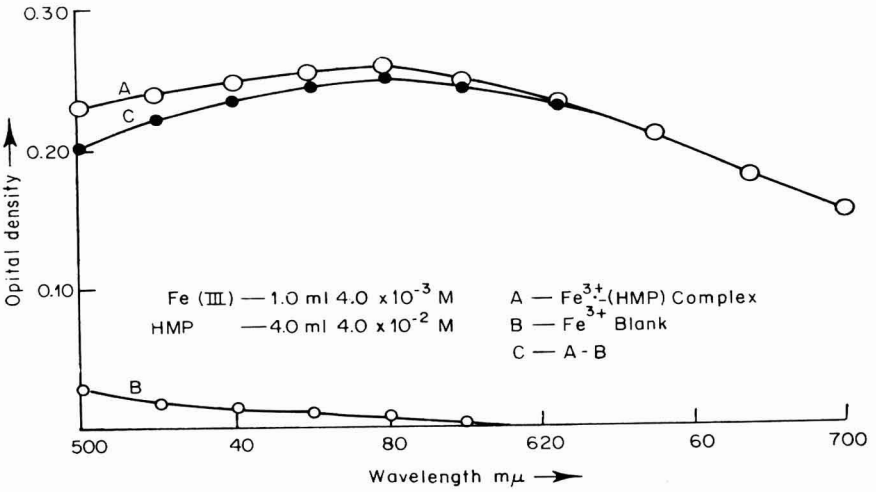


FIG. 1. Absorption spectra of iron–HMP complex (blue) and iron blank.

2.15, a sharp increase in the absorbance of the complex was observed and beyond pH 2.65 formation of another complex, which is brown-red in color, appears. However, a constant pH of 2.10 was maintained in all the studies in the case of blue chelate.

Effect of ligand concentration. The color of the complex goes on increasing with increase in ligand concentration. This shows that the iron chelate is very week and its formation is not complete even when a large excess (about 80 times) of the ligand has been added.

Beer's law and sensitivity of the reaction. The system obeys Beer's law up to 28 ppm of ferric iron at 580 nm. The sensitivity of the color reaction was found to be 0.092 μg of Fe/cm^2 for log $I_0/I = 0.001$ at 580 nm and the molar absorptivity of the complex is 622.5, as calculated from Beer's law curve.

Composition of the complex. The blue complex formed by ferric ion with the oxime is unstable and decomposes gradually. The color intensity of the complex increases continuously with increase in reagent concentration. Since the Job's, mole ratio and slope ratio methods cannot be used to ascertain the composition of the chelate in such systems, logarithmic *(11)* and Asmus *(12)* methods were employed for the purpose.

The logarithmic method of Bent and French *(11)* has been modified as follows:

The reaction of a metal ion M^{n+} with an organic reagent HR, giving a chelate MR_n, can be represented as

$$M^{n+} + n(HR) \rightleftharpoons MR_n + nH^+$$

The equilibrium constant of the above equation is given by

$$K = \frac{[MR_n]\,[H^+]^n}{[M^{n+}]\,[HR]^n}.$$

The above equation can be expressed as:

$$\log \frac{[MR_n]}{[M^{n+}]} = n \log [HR] - n \log [H^+] + \log K,$$

where $[MR_n]$ and $[M^{n+}]$ are the concentrations of complex formed and free metal ion, [HR] is the concentration of the ligand and K is the equilibrium constant. If a curve is plotted between log $[MR_n]/[M^{n+}]$ and log [HR], at constant hydrogen ion concentration, a straight line is obtained with slope equal to n which corresponds to the number of ligand molecules bound per metal ion.

Similarly the equation for Asmus method *(12)* can be represented as:

$$1/[HR]^n = K\left[\frac{C\epsilon}{A} - 1\right] \cdot \frac{1}{[H^+]^n}$$

where A denotes the absorbance of the complex formed, C is the total metal ion concentration and ϵ the molar extinction coefficient. If the total metal ion concentration C and $[H^+]$ ion concentration are kept constant and a curve is plotted between $1/A$ and $1/[HR]^n$, giving different integral values to n, $(n=1, 2, 3, \ldots)$, a straight line will be obtained only when n corresponds to the actual number of ligand molecules bound to the metal ion, which gives the molar composition of the complex.

A set of solutions containing varying amounts of the reagent in ascending order and the same amount of ferric iron were prepared at a fixed pH of 2.10 and in 75% ethanolic medium, in a total volume of 10.0 ml. The concentration of the complex in terms of optical density was determined by plotting reciprocal of the reagent concentration (1/[HR]) against the observed optical density. Since the optical density of the complex increases with increasing concentration of ligand, the curve was extrapolated to zero value of 1/[HR], i.e., where $[HR]=\infty$. The value of optical density at this point corresponds to complete complexation of the metal ions.

The required values of log $[MR_n]/[M^{n+}]$ and log [HR] for logarithmic method were calculated and a curve is plotted (Fig. 2). A straight line of slope equal to 0.97 is obtained which reveals the composition of the complex as 1:1 (Fe^{3+}:oxime). For Asmus method, the values for

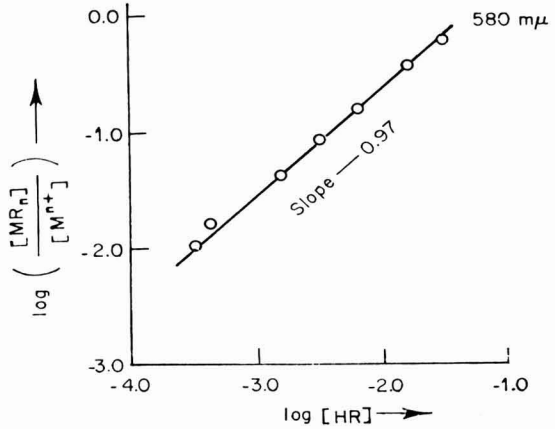


FIG. 2. Composition of iron–HMP complex (blue) by logarithmic method.

reciprocal of optical density, $1/A$, and $1/[HR]^n$ giving different integral values to n, i.e., 1, 2, 3, . . . were calculated and a curve (Fig. 3) is plotted. A straight line could only be obtained when n is taken to be equal to 1, which confirms the composition of the complex.

B. Studies on the Brown-red Iron(III) Chelate

A brown-red ferric chelate is formed at pH values higher than 2.65. The chelate is extractable in chloroform and other nonpolar solvents. The extracted chelate does not exhibit maximum absorption in the visible region, but the optical density remains practically constant in the range of 480 to 510 nm (Fig. 4). Subsequent studies were carried out at 500 and 600 nm in 20% enthanolic medium, in a total volume of 20 ml. It was observed that when ethanol concentration in the aqueous phase is increased above 25% the soluble brown-red complex does not completely pass into the chloroform layer in one extraction. At lower

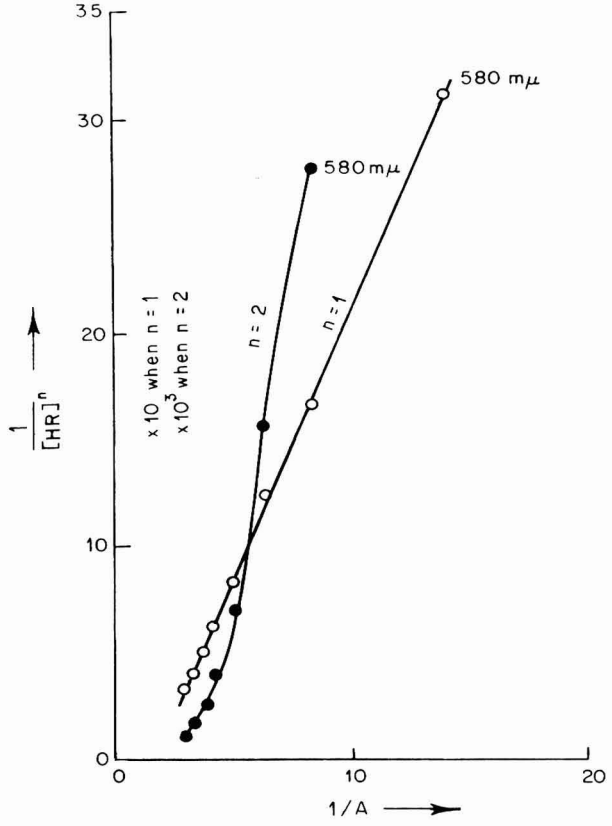


FIG. 3. Composition of iron–HMP complex (blue) by Asmus method.

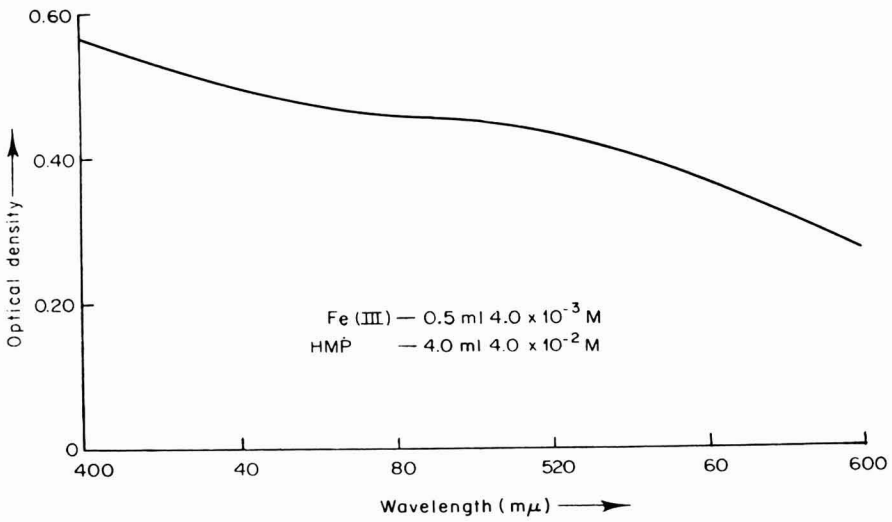


FIG. 4. Absorption spectrum of iron–HMP complex (brown-red).

concentrations chloroform layer in one extraction. At lower concentrations of ethanol, the extraction is complete and a part of the reagent which slowly gets precipitated from this medium, also passes into chloroform along with the complex. In view of this 20% (v/v) concentration of ethanol was maintained. The brown-red chelate was immediately extracted in 10.0 ml of freshly distilled chloroform. It has been found that absorbance of the extracted species remains constant for more than 24 hours; whereas if the chelate is allowed to remain in aqueous solution, the optical density starts decreasing after about 10 minutes.

Effect of pH and concentration of the reagent. The extraction of the brown-red complex into water-immiscible organic solvents, such as chloroform, has been found to be dependent on the pH of the aqueous phase. The pH of the aqueous phase was initially adjusted to desired values and was finally noted when equlibrium was attained between chloroform layer and the aqueous solution. The optical density of the extracted chelate was found to be maximum and constant from pH 8.5 to 9.5, showing complete extraction of the complex. Above this pH, the absorbance decreases. The effect of reagent concentration was studied at pH 8.5; and the study revealed that a minimum of 60-fold molar excess of the reagent is needed for maximum color development.

Adherence to Beer's law and sensitivity of the reaction. A linear relationship between concentration of iron and optical density has been

found to hold good up to 44.68 ppm of iron. The sensitivity of the reaction has been found to be 0.024 μg of Fe/cm^2 for log $I_o/I = 0.001$ at 500 nm. The molar extinction coefficient, as calculated from Beer's law plot, is equal to 2250 at 500 nm.

Recommended Procedure for Determination of Iron(III). To a solution containing ferric ion up to 45 ppm, and excess of the reagent solution in ethanol is added. The pH of the resulting solution is adjusted to any value between 8.5 and 9.5. The volume of the aqueous phase is maintained at 20 ml keeping the ethanol concentration at 20%. The ferric chelate is quickly extracted by shaking with 10 ml of chloroform. The organic layer is separated after equilibration. The separated organic layer is centrifuged to remove water droplets and absorbance is recorded at 500 nm against chloroform blank as the reagent does not absorb in the visible region.

Interferences

The effect of diverse ions was studied by preparing solutions containing 11.17 ppm of ferric iron and different foreign ions. The iron content was determined as outlined above. The tolerance limits of foreign ions were considered as the amounts which may be present without causing an error of more than $\pm 3\%$. Cd^{2+}, Mn^{2+} and Pb^{2+} (100 ppm); Zn^{2+} (80 ppm); UO_2^{2+} (50 ppm); $C_2O_4^{2-}$, Cl^- (180 ppm); Br^-, $S_2O_3^{2-}$ (200 ppm); I^- (320 ppm) and IO_3^- (45 ppm) did not interfere when present in amounts given in parentheses.

A number of other ions, e.g., PO_4^{3-}, F^-, $B_4O_7^{2-}$, EDTA, Mn^{2+} Cr^{3+}, Mo^{6+}, W^{6+}, and Al^{3+}, etc., were found to interfere.

Stoichiometry of the Complex

The usual methods could not be used for determining the composition of the weak chelate. Therefore, the logarithmic method of Bent and French *(11)* and Asmus *(12)* method were applied for the purpose. A set of solutions was prepared containing a fixed amount of ferric iron and increasing amounts of the reagent. The optical density of the extracted complex was measured at 500 and 600 nm. The values of log $[MR_n]_o/[M^{n+}]$, log $[HR]_o$, $1/A$, and $1/[HR]_o^n$ (suffix "o" denotes the organic phase) were calculated for logarithmic and Asmus methods as in the case of blue ferric chelate. In Fig. 5, the slope of the line is 3, which means that the composition of the extracted chelate is 1:3 (Fe^{3+}: oxime). Figure 6 shows that a straight line is obtained when n is equal to 3. Consequently, the metal:ligand ratio in the chelate is 1:3, which confirms the results obtained by the Bent and French method.

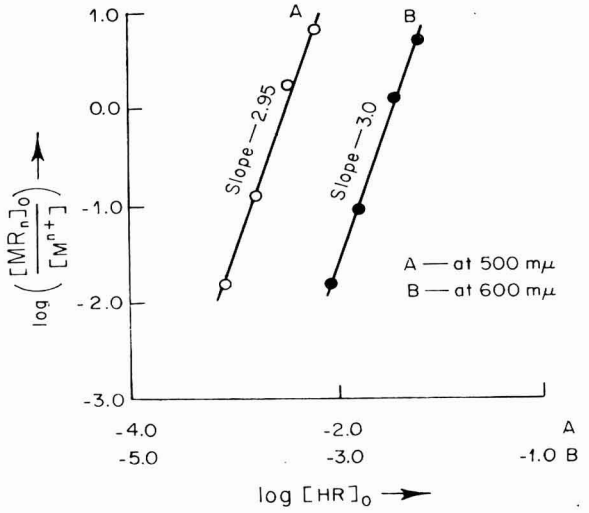


FIG. 5. Composition of iron–HMP complex (brown-red) by logarithmic method.

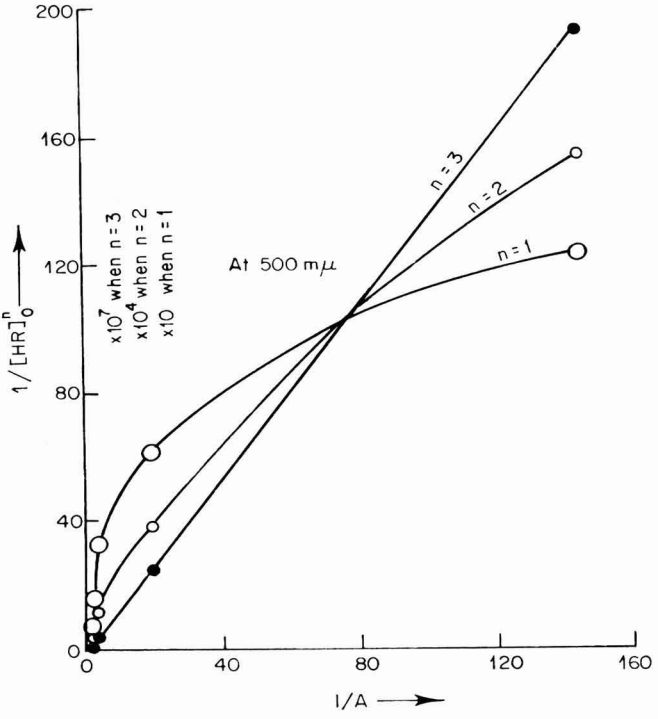
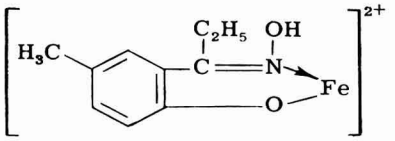


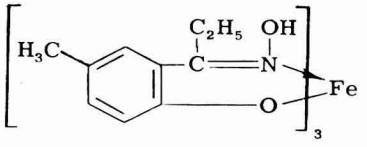
FIG. 6. Composition of iron–HMP complex (brown-red) by Asmus method.

Structure of the Complexes

The molar composition of the blue complex of iron(III) with HMP has been found to be 1:1. The chelate is not extracted in nonpolar organic solvents like carbon tetrachloride, chloroform, etc. This shows that the complex is ionic in character. On the basis of these facts, the following tentative structure is proposed for the complex:



As the pH of the system is raised, another complex, which is brown-red in color starts forming which shows constant absorbance in the pH range 8.5–9.5. This complex can be extracted into usual nonpolar organic solvents and its molar composition has been found to be 1:3 (metal:oxime). Keeping these observations in view, the following tentative structures is assigned to the complex:



SUMMARY

2-Hydroxy-5-methylpropiophenone oxime (HMP) forms two complexes with ferric iron, the formation of which is pH dependent. Blue colored complex is formed at lower pH values. This complex cannot be extracted into water-immiscible organic solvents. Another complex, brown-red in color, is formed at higher pH values which is extracted into organic solvents. The molar composition of two complexes has been ascertained by using logarithmic and Asmus methods. In the case of blue chelate, the composition is 1:1 (Fe^{3+}: oxime) and the composition of brown-red extracted complex is 1 : 3. The two complexes adhere to Beer's law over a fairly wide range of iron concentration and the sensitivity in terms of Sandell's definition has been calculated. Effect of some foreign ions has been investigated and tentative structures have been assigned to the two complexes.

ACKNOWLEDGMENT

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MICROCHEMICAL JOURNAL **18,** 422–427 (1973)

Microdetermination of Arsenic(III) and Osmium(VIII) Through Osmium–Thiourea Reaction

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Procedures (*1–3*) have been described for the determination of osmium through its complexation with thiourea. In these procedures, the earlier authors suggested a high concentration of thiourea for the rapid complexation of osmium. According to them thiourea first reduce Os^{8+} to Os^{3+}, then the latter gives a red complex by complexing with thiourea which is present in excess. They stated that unless the thiourea is present in large excess the full intensity of the color is attained only after a couple of hours. We have observed that the slowness of color formation is due to the inability of thiourea to be oxidized rapidly by osmium(VIII); but not due to the complex formation of osmium(III) with thiourea. Therefore according to us, the following two reactions are responsible for the color formation of osmium(VIII) with thiourea:

$$2\ OsO_4 + 10\ NH_2CS\text{–}NH_2 + 6\ H^+ \text{-----} \rightarrow 2\ Os^{3+}$$

$$+\ 5\ \begin{array}{l} H_2N \\ \diagdown \\ \quad C\text{—}S\text{—}S\text{—}C \\ \diagup \quad\quad \diagdown \\ HN \quad\quad NH \end{array} \begin{array}{l} \\ \diagup \\ \\ \diagdown \\ NH_2 \end{array} + 8\ H_2O\ \text{(slow)}, \quad (1)$$

$$Os^{3+} + 6\ NH_2CSNH_2 \text{-----} \rightarrow [Os(NH_2CSNH_2)_6]^{3+}\ \text{(rapid)} \quad (2)$$

The final reaction is the addition of these two reactions,

$$2\ OsO_4 + 22\ NH_2CSNH_2 + 6\ H^+ \text{-----} \rightarrow 2\ [Os(NH_2CSNH)_6]^{3+} + 5(NH_2CSNH)_2 + 8\ H_2O.$$

Because of the slowness of reaction (1), the earlier authors recommended a large excess of thiourea and keeping of 30 minute on stand for getting the full intensity of the color. Since the reaction (1) is slow, we tried some catalysts to make it rapid. In this study, arsenic(III) and

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antimony(III) were found to be very effective. In the presence of either of these two, the reaction proceeds very fast and in fact a direct titration between osmium and thiourea can be performed. The mechanism for the catalysis of arsenic(III) on osmium–thiourea reaction is assumed as follows:

$$Os^{8+} + 2\,As^{3+} \longrightarrow Os^{4+} + 2\,As^{5+}\ \text{(fast)}, \qquad (3)$$

$$2\,Os^{4+} + 2\,NH_2CSNH_2 \longrightarrow 2\,Os^{3+} + (NH_2CSNH)_2 + 2\,H^+\ \text{(fast)}, \qquad (4)$$

$$Os^{3+} + 6\,NH_2CSNH_2 \longrightarrow [Os(NH_2CSNH_2)_6]^{3+}\ \text{(fast)}. \qquad (5)$$

Arsenic(III) can rapidly reduce osmium(VIII) to osmium(IV) as can be seen by performing a simple experiment. If we add arsenic(III) to osmium(VIII) in acid solutions, immediately a black colloidal precipitate of osmium(IV) appears, and hence that reaction is said to be fast. When once osmium(VIII) is reduced to osmium(IV), it is obvious that osmium(IV) will, in turn, further reduce to osmium(III) by reacting with thiourea rapidly since one electron is involved in this redox process. (In redox reactions, if one electron transfer is involved, that reaction is said to be fast.) From Eqs. (3), (4), and (5), it is evident that $[As^{3+}] \propto [Os^{4+}] \propto [Os^{3+}] \propto [Os \cdot \text{Thio complex}]$. So if we measure the intensity of color, the arsenic(III) concentration can be determined easily provided the secondary reaction, namely, the direct reduction of osmium(VIII) by thiourea should be negligible, which can be made possible, we have found from preliminary experiments, by controlling the acid concentrations and that of thiourea. For controlling the concentration of thiourea, the exact amount of thiourea required for the reduction of osmium(IV) to osmium(III) and for complexation, i.e., total 7 moles according to Eqs. (4) and (5), is to be added which can be made either by direct photometric titration of thiourea with osmium(VIII) in 4 *N* sulfuric acid contain 0.1 ml of 0.1 *N* arsenic(III) using blue or green filter; or by determining the individual concentrations of osmium(VIII) and thiourea by standard methods and adjusting their amounts such that for every 1 mole of osmium 7 moles of thiourea are present. If these two solutions, osmium(VIII) and thiourea, are mixed in the ratio 1:7 instead of the latter being added in excess, we found that the final product attained to 100% only after 2 hours in the absence of arsenic(III), but in its presence, the reaction is very rapid and can be completed within 1 minute. Further, we also observed that the rate is also influenced by the sulfuric acid concentration to some extent as shown in Table 1. The values given in Table 1 show that the

TABLE 1

RATE OF FORMATION OF COMPLEX (Os:thiourea, 1:7)

	Time taken for developing full intensity of color (min)	
Conc of sulfuric acid (*M*)	In absence of As(III)	In presence of As(III)
0.5	120	50
1.0	60	10
2.0	50	3
2.0	40	Immediate
3.0	60	8
4.0	100	20

secondary reaction of osmium(VIII)–thiourea can be controlled by adjusting the thiourea concentration. So if we mix osmium and thioure in ratio 1:7, osmium(III) should be formed through osmium(VIII)–arsenic(III) reaction followed by osmium(IV)–thiourea reaction. These findings are utilized for the determination of osmium and arsenic. Though the osmium thiourea complex had been suggested by earlier authors (*1–3*) for the colorimetric determination of osmium, we are proposing now another method for rapid determination of osmium without waiting for 30 minutes for attainment of full color intensity; and further, in these procedures, 1 ml of 1% thiourea is sufficient.

Procedure for the Determination of Osmium

Take an aliquot of osmium tetroxide containing from 5 to 750 μg of osmium in a 50-ml flask. Add 10 ml of 1:1 sulfuric acid and 1 ml of 1% thiourea followed by 1 drop of 0.1 *N* arsenic(III). Mix well and dilute the contents to the mark with water. Measure the intensity of the solution at 480 nm in the case of Uvispek-Hilger spectrophotometry or use blue or green filter in Klett-Summerson photoelectric colorimeter against water as a blank. The accuracy of the method is ± 0.5%.

Procedure for the Determination of Arsenic(III)

In the preceding paragraphs it has been already stated that the concentration of arsenic(III) is proportional to the intensity of the color (optical density of the complex). So if optical density of the complex is measured it indicates the amount of arsenic present, if the secondary reaction of direct reduction of osmium by thiourea is negligible. Although the secondary reaction is comparatively negligible under the present experimental conditions (ca. Table 1), we have observed that better accuracy can be obtained if the time is kept constant. The values of the optical density of the complex at constant ti of 5 minutes as

TABLE 2

CALIBRATION CURVE (readings taken after 5 min)

Ten ml 1:1 sulfuric acid plus 30 ml of water plus 3 ml of 4.3×10^{-3} *M* thiourea plus *x* μg/ml of arsenic(III) plus 1.92 ml of 9.383×10 *M* osmium tetroxide diluted to 50 ml. Measured with Klett-Summerson photoelectric colorimeter using a green filter.

Conc of As(III) (μg/ml)	Photometer dial readings
0.075	30
0.15	35
0.30	44
0.45	54
0.60	64
0.75	74
0.90	84
1.05	94

given in Table 2 shows that the optical densities are proportional to arsenic(III) concentrations. Since the optical densities and arsenic(III) concentration are linear, it is possible for determining arsenic(III) in unknown solutions by measuring its absorbance at 5 minutes and read out from the graph shown in Fig. 1. (Here there is no restriction of keeping the time of 5 minutes, any time can be chosen, but keep it constant throughout analysis). A number of determinations have been carried out by this procedure and some representative results given in Table 3 show the accuracy of the results from 0 to $\pm$ 2%.

Place different volumes of arsenic(III) solution (7 μg/ml) in 50-ml volumetric flasks. Add to each flask 10 ml of 1:1 sulfuric acid and 3 ml of 4.3×10^{-3} *M* of thiourea. Shake the mixture gently. Then allow

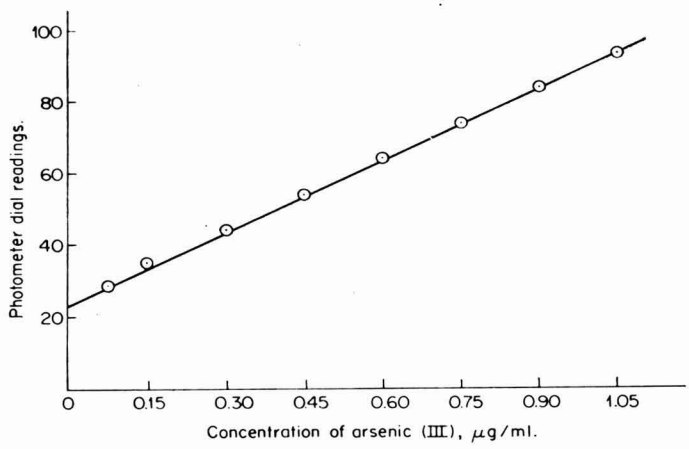

FIG. 1. Calibration curve.

TABLE 3

DETERMINATION OF ARSENIC(III) THROUGH ITS CATALYTIC REACTION ON OSMIUM–THIOUREA

Amount of arsenic(III) (ppm)	
Taken	Found
2.22	2.24
7.00	7.12
15.2	14.9
32.9	32.2
39.2	39.6
46.6	46.6

1.92 ml of 9.38×10^{-4} *M* osmium solutions to run down the sides of the flasks. (Any concentrations of osmium and thiourea can be used but their ratio should be kept at 1:7). Then dilute the contents to the mark with water, and mix well. Measure the absorbance of the color at 5 minutes by Klett-Summerson photoelectric colorimeter using a green filter. A graph of the concentrations of arsenic(III) and photometer dial readings gives a straight-line calibration curve (Fig. 1). Then proceed similarly for solutions containing arsenic(III) of unknown concentrations and read their concentrations from the calibration curve.

The catalytic reaction of arsenic further make it useful for a rapid detection of both arsenic(III) and osmium(VIII).

Procedure for the Detection of Arsenic(III)

Place 0.2 ml of 20 *N* sulfuric acid and 0.2 ml of 7×10^{-4} *M* thiourea in a narrow test tube. Mix well. Add 0.2 ml of test sample solution followed by 0.2 ml of 1×10^{-4} *M* osmium solution and dilute to nearly 1 ml. Mix well. If a red color appears immediately with 1 minute the presence of arsenic(III) is indicated. Amounts of 0.15 μg/ml can be detected by this method.

Interferences

Ni^{2+} (100 μg); Co^{2+} (25 μg); Cr^{3+} (150 μg); Mo^{6+} (1000 μg; U^{6+} (550 μg); Sn^{4+} (1000 μg; Ti^{4+} (2000 μg); 0.5 g each of: Ca^{2+}, Mg^{2+}, Al^{3}, K^{+}, Na^{4}; Se 6^{+} (600 μg); Te^{6+} (600 μg); 0.1 g each of C^{3+}, Mn^{2+}, V^{5+}; Cd^{2+} (150 μg); Pb^{2+} (50 μg); and Hg^{2+} (10 μg) do not interfere. If iron(III) and W(VI) are present, add 1 drop of phosphoric acid; thus the interference of each, up to 0.2 mg, can be avoided. Chlorides (smaller amounts), nitrates, phosphates, sulfates, and perchlorates also do not interfere.

Procedure for the Detection of Osmium(VIII)

Place 0.2 ml each of 20 *N* sulfuric acid, 1% thiourea, and 0.02 *N* arsenic(III) in a narrow test tube and dilute to nearly 1 ml. Mix well. Then add 0.2 ml of sample solution and mix. If a red color appears, it is a positive test for osmium. If sample solution contains iron(III) or tungsten(VI), add 1 or 2 drops of phosphoric acid before adding the sample solution to the reaction mixture. Besides the ions mentioned above, other platinum metal ions (each up to 10 μg) do not interfere.

SUMMARY

Osmium–thioureau reaction is slow under conditions described in earlier methods. In the present study it has been observed that arsenic(III) catalyzed the reaction. Based on this, qualitative and quantitative methods are described for the determination of both osmium and arsenic. Interference study of 30 ions showed they do not interfere.

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Applications Involving the Iodide Ion

VII. Determination of Small Amounts of Cerium(IV) and Analysis of Its Mixtures with Some Metal Ions

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INTRODUCTION

Very recently the stoichiometry of the reaction between iodide and each of a number of oxidants involving cerium(IV) (*9*) and of mercury (II) was the basis underlying the accurate determination of such oxidants by back-titrating excess iodide with mercury(II) using silver amalgam as the indicator electrode. The aim of the present work was to apply the same method to estimation of cerium with emphasis on the micro-ramge, the interfering cations, and the analysis of a variety of mixtures especially with thorium or other rate-earth cations.

Oxalate as primary standard for cerium(IV) was used under conditions of high temperature (*17, 18*), in presence of indicator (*11*), by running a blank or by using certain catalysts (*11, 17, 18*). Air oxidation or loss of carbon monoxide [(*11*), p. 51] were possible sources of error. The arsenite method involves some of the above tedious precautions [(*11*), p. 131]. The acetone–potassium iodide method (*12*) gives low results owing to partial reduction of cerium with acetone and iodoacetone. The potentiometric method using cerium(IV) as titrant for iodide (*8*) cannot be used in the micro-range. The Mohr's salt as primary standard (*6*) lost favor due to inherent contamination with manganese(II), zinc, and magnesium (*13*). Arsenate-iodimetric determination of cerium(IV) in mixture with thorium (*14*) is too complicated, time and reagent consuming. Cerium(IV) and sodium nitrite were used to determine each other amperometrically in molar nitric acid at 0.4 V without interference from 13 cations (*19*). Quinol and analogous reducing agents were used as titrants for potentiometric titeration of 0.1 down to 5×10^{-4} *M* cerium(IV) in 2 to 15% sulfuric acid (*15*).

The redox reaction between cerium(IV) and methyl orange was the basis of potentiometric method suitable also for analysis of alloys (*7*).

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EXPERIMENTAL METHOD

The water used was always twice distilled. The chemicals were all of highest purity available. These were iodide, dichromate, and cyanide of potassium; hydroxide thiosulfate, and carbonate of solium; nitrates of mercury(II), calcium, strontium, lathanum, thorium, scandium, and zinc; sulfates of cerium(IV), cerium(III), copper, cobalt, cadmium, nickel, iron(III), and ferrous ammonium sulfate; nitric, sulfuric, and glacial acetic acids; disodium ethylenediaminetetraacetate (EDTA), Eriochrome black T (EBT); pyrocatechol violet (PCV); methyl thymol blue (MTB), murexide, diphenylamine; *o*-phenanthroline–ferrous sulfate (ferroin) and starch indicators.

Solutions

The 0.084 *M* cerium(IV) stock solution was prepared from a ceric sulfate sample (Laborchemie Proanalyse) by dissolving 40 g into 1 liter making the solution 1.008 in respect to sulfuric acid, and standardized with iodide and thiosulfate using starch as indicator, and by ferrous ammonium sulfate using ferroin indicator. The 0.1 *M* iodide solution was prepared normally and standardized potentiometrically against mercuric solution using silver amalgam as indicator electrode. The 0.051 *M* mercury(II) solution was prepared and standardized potentiometrically against standard potassium iodide and volumetrically with standard EDTA in urotropine and (MTB) indicator. The 0.05 *M* EDTA solution was standardized against a standard 0.05 *M* zinc solution prepared from an oxide sample and nitric acid. The 0.1 *M* dichromate solution was prepared from recrystalized sample. The 0.05 *M* solutions of the above salts were prepared and standardized by recommended procedures. Lower concentrations whenever required were prepared by accurate dilution. 10% H_2O_2 solution was prepared normally.

The titration cell and potentiometer were described elsewhere.

Procedures

(A) To determine cerium(IV), add to a known volume of cerium(IV) (1–5 ml) into the titration vessel an excess of iodide (3.5–5.5), make the solution about 2–0.2 *N* in respect to sulfuric acid with micro- and macro-amounts, respectively; titrate excess of iodide with mercury(II) and silver amalgam electrode. Similarly determine cerium(IV) in presence of a variety of cations which do not interfere with iodide.

(B) With binary mixtures determine cerium(IV) as in (A). To determine the other cation, in an identical mixture, reduce cerium(IV) using the least amount of H_2O_2, evaporate to a small volume on a hot plate to

TABLE 1

DETERMINATION OF MILLIGRAM AMOUNTS OF CERIUM(IV) [a]

No.	Ce(IV) (mg) Taken	Found	Error (±%)	Titrant (mV/0.1 ml)
1	35.035	35.173	0.39	390
2	28.028	28.308	0.99	395
3	21.021	21.021	0.00	410
4	14.014	14.118	0.74	359
5	7.007	7.077	0.99	388
6	35.035	35.035	0.00	285
7	28.028	28.308	0.99	245
8	21.021	21.144	0.59	255
9	14.014	14.096	0.59	269
10	7.007	7.118	1.58	262
11	35.035	35.035	0.00	245
12	28.028	27.886	0.51	322
13	21.021	21.021	0.00	295
14	14.014	14.014	0.00	250
15	7.007	7.118	1.58	158
16	4.203	4.203	0.00	350
17	2.802	2.775	0.96	340
18	1.401	1.401	0.00	351
19	4.203	4.203	0.00	382
20	2.802	2.820	0.64	350
21	1.401	1.401	0.00	324

[a] Nos. 1–15: 0.1 *M* I^- × 0.053 Hg(II); nos. 16–21: 0.02 *M* I^- × 0.01 Hg(II); nos. 6–10: in presence of 60 mg of a mixture 0.05 *M* in each of Ca, Sr, La, Th, Sc, Ce(III), Cd, Cu(II), Fe(III), Ni, Co, and Mg ions; nos. 11–21: in presence of 120 mg of the above mixture.

ensure removal of last traces of H_2O_2; add excess EDTA, 8 ml of 10% hexamine, few drops of 0.5 *M* NaOH necessary to adjust the pH to the desired initial potential of the cell (+0.04–0.06 V) and finally back-titrate excess of EDTA than required to chelate both cations, with standard mercuric solution. Determine the other cation by difference.

(C) With any ternary mixture determine cerium(IV) as in (A); in another identical mixture reduce Ce(IV) as described above, add excess EDTA and continue to determine the total of the three cations as in (B).

With Ce(IV) + Th + La, precipitate thorium as benzoate (*10*); reduce Ce(IV) and continue to determine Ce(IV) + La; compute the equivalent of EDTA to each component of the mixture.

With Ce(IV) + Sc + Cu(II) or Ce (IV) + Ce(III) + Ni determine Ce(IV) alone and the total of the three components as above; in a third

TABLE 2

DETERMINATION OF MICROGRAM AMOUNTS OF CERIUM(IV) [a]

No.	Ce(IV) (μg) Taken	Found	Error (±%)	Titrant (mV/0.1 ml)
1	420.390	420.768	0.09	242
2	280.260	281.914	0.59	218
3	140.130	140.827	0.64	224
4	42.040	43.077	2.47	110
5	420.390	420.390	0.00	250
6	280.260	283.063	1.00	180
7	140.130	138.525	1.14	147
8	42.040	42.286	0.37	100

[a] Nos. 1–3 and 5–7: 0.002 *M* I^- × 0.001 Hg(II); nos. 4 and 8: 0.0002 *M* I^- × 0.0001 Hg(II); nos. 5–8: in presence of 120 mg of a mixture 0.05 *M* in each of Ca, Sr, La, Th, Sc, Ce(III), Cd, Cu(II), Co, Ni, Fe(III), and Mg ions.

indentical mixture reduce Ce(IV) and separate Ce(III) and Sc or Ce(III), respectively, as hydroxide using 1 *M* NH_4OH solution, determine Cu(II) or Ni in the filtrate by titration with EDTA using murexide indicator (*1, 2*); compute the equivalent of EDTA to each component.

With Ce(IV) + Fe(III) + Cd determine Ce(IV) alone and the total of the three components as above; in a third identical mixture reduce Ce(IV) and separate Ce(III) and Fe(III) as hydroxides using ammoniacal buffer (54 g of NH_4Cl + 350 ml of conc NH_4OH/ liter) solution, determine Cd in the filtrate by titration with EDTA using PCV as indicator (*3*). Compute the equivalent of EDTA to each component.

With the quaternary mixture Ce(IV), Ce(III), Th, and La, determine Ce(IV) and total as above; from a third identical mixture separate Th as benzoate (*10*), reduce Ce(IV) and determine the total of the three components Ce(IV), Ce(III), and La by back-titration as above, demask La with fluoride (1 ml of 0.05 *M* NH_4F for 1 ml of 0.05 *M* La) and titrate liberated EDTA in the same solution with mercury(II) and the silver amalgam electrode in urotropine buffer, pH9; compute the equivalent of EDTA to each component.

With Ce(IV) Sc, Cu(II), and Cd, determine Ce(IV), and total in two identical mixtures as above; in a third mixture reduce Ce(IV) and separate Ce(III) and Sc as hydroxides as above; to the filtrate add excess EDTA, titrate the excess of the latter with zinc solution at pH 10 using EBT; demask Cu(II) with cyanide, to the appearance of the blue color of EBT, titrate liberated EDTA with zinc solution (*4*); compute the equivalent of EDTA to each component.

TABLE 3

ANALYSIS OF BINARY MIXTURES

Ce (mg)		Error	M (mg)	
Taken	Found	(±%)	Taken	Found
7.007	7.048	0.58	65.320 Th	65.087
14.014	14.153	0.99	52.225	52.069
21.021	21.144	0.58	39.192	39.330
28.028	28.196	0.60	26.128	26.127
35.025	35.240	0.59	13.064	13.133
7.007	7.034	0.40	13.215 Sc	13.487
14.014	13.985	0.21	10.572	10.717
21.021	20.977	0.21	7.929	7.970
28.028	28.028	0.00	5.286	5.283
35.035	34.962	0.21	2.643	2.621
7.007	7.048	0.58	33.070 La	33.268
14.014	14.084	0.50	26.448	26.448
21.021	21.228	0.98	19.836	19.836
28.028	28.172	0.51	13.224	13.279
35.035	35.240	0.59	6.612	6.654
7.007	7.007	0.00	37.555 Ce(III)	37.415
14.014	14.153	0.99	30.044	30.016
21.021	20.894	0.60	22.533	22.512
28.028	28.015	0.04	15.022	15.414
35.035	35.018	0.04	7.511	7.504
7.007	7.011	0.00	9.369 Co(II)	9.282
14.014	14.143	0.92	6.246	6.246
21.021	20.894	0.61	3.123	3.106
7.007	6.992	0.22	9.159 Ni(II)	9.091
14.014	14.152	0.98	6.106	6.128
21.021	21.144	0.22	3.053	3.071
7.007	7.007	0.00	9.246 Cu(II)	9.214
14.014	14.041	0.19	6.164	6.101
21.021	20.935	0.41	3.082	3.114
7.007	6.936	1.01	18.546 Cd	18.612
14.014	13.957	0.41	12.364	12.432
21.021	21.021	0.00	6.182	6.182
7.007	6.978	0.41	1.575 Fe(III)	1.574
14.014	14.034	0.14	1.050	1.060
21.021	20.765	1.21	0.525	0.531

RESULTS AND DISCUSSION

Representative results of determining Ce(IV) in the milli- and microgram ranges either in pure solutions or in presence of a cluster of cations involving those of alkaline earths, heavy metals, and iron(III) are listed in Tables 1 and 2, respectively. The data show high accuracy in most cases and excellent potential jumps ranging from a maximum

TABLE 4

ANALYSIS OF TERNARY MIXTURES

Ce(IV) (mg)		Metal (mg)			
Taken	Found	Taken	Found	Taken	Found
7.007	6.936	22.743 Th	22.507	9.585 La	9.654
14.014	13.957	15.162	15.038	6.390	6.250
21.021	20.894	7.581	7.633	3.195	3.264
7.007	6.936	7.929 Sc	7.957	9.246 Cu	9.189
14.014	13.958	5.286	5.304	6.164	6.164
21.021	21.021	2.643	2.629	3.082	3.095
7.007	7.007	22.533 Ce(III)	22.421	9.159 Ni	9.217
14.014	14.069	15.022	14.854	6.106	6.164
21.012	20.896	7.511	7.561	3.053	3.023
7.007	6.965	1.575 Fe(III)	1.563	9.369 Co	9.399
14.014	14.014	1.050	1.061	6.246	6.366
21.021	20.896	0.525	0.530	3.123	3.094

of 410 to a minimum of 100 mV/0.1 ml of titrant with both ranges, respectively. They further show high selectivity of the present method and its reliability in determining amounts of Ce(IV) ranging from 35 mg down to 42 μg/20 ml, i.e., 2.1 ppm.

Tables (3–6) list representative results of analyzing binary, ternary, and quaternary mixtures of a variety of cations with cerium(IV). With all mixtures the data show reliability and simplicity of the procedures suggested for analysis of such mixtures. Analysis of mixtures with Th, Ce(III), Sc, and La applies also to mixtures with other rare earths.

Even though it is reported that cerium(III) catalyzes the atmospheric oxidation of iodide (*5*), yet excess of the latter is immediately consumed in forming the tetraiodo-mercurate(II) and subsequent precipitation of

TABLE 5

ANALYSIS OF QUATERNARY MIXTURES

Ce(IV) + Ce(III) + Th + La.

Ce(IV) (mg)		Ce(III) (mg)		Th (mg)		La (mg)	
Taken	Found	Taken	Found	Taken	Found	Taken	Found
7.007	7.076	22.449	22.631	22.623	22.624	9.585	9.654
14.014	13.873	14.966	14.924	15.082	14.966	6.390	6.389
21.021	21.021	7.483	7.497	7.541	7.541	3.195	3.185

TABLE 6

ANALYSIS OF QUATERNARY MIXTURES

Ce(IV) + Sc + Cu(II) + Cd.

Ce(IV) (mg)		Sc (mg)		Cu(II) (mg)		Cd (mg)	
Taken	Found	Taken	Found	Taken	Found	Taken	Found
7.007	6.934	7.829	7.912	9.246	9.279	18.546	18.546
14.014	13.873	5.286	5.329	6.164	6.164	12.364	12.309
21.021	21.021	2.643	2.652	3.082	3.083	6.182	6.126

mercuric iodide. There is no opportunity for iodide air oxidation and hence the high accuracy of the present methods.

In analyzing ternary mixtures of Ce(IV) with Th and La, use is made of the present method to determine Ce(IV) selectively, its reduction with H_2O_2 to determine total by back-titration and separation of Th, as benzoate followed by reduction of Ce(IV) to determine Th alone and total Ce and La. Such an analysis involving three potentiometric titrations all using the silver amalgam as indicator electrode, required about 1 hour. Analysis of other ternary mixtures involved two potentiometric and one volumetric titration. The analysis consumed a maximum of 1 hour.

With quaternary mixtures, the simple procedures described involved only three titrations, making use of the selectivity of the present method for Ce(IV), benzoate as precipitant for Th, EDTA as masking agent for La together with other cations, and fluoride as demasking agent for La–EDTA complex.

In the case when Cu and Cd cations were in mixture with Ce(IV) and Sc, use is made of simple separation of Ce(III) and Sc as hydroxides and of the higher stability of the Cd–EDTA than that of the Cu–EDTA to liberate EDTA from the Cu complex with cyanide and hence to determine simultaneously the two cations.

SUMMARY

A simple, rapid, and reliable method for cerium(IV) alone; in presence of a variety of cations involving rare earths and iron(III); or in binary, ternary, and quaternary mixtures is given. By its aid 10^{-3} down to 1.5×10^{-5} mole of cerium(IV) were determined with requisite accuracy and precision. The potential breaks detecting the end points ranged from a maximum of 410 to a minimum of 100 mV/0.1 ml of 0.05 or 10^{-4} *M* titrant, respectively. Analysis of 15 mixtures using the present method together with other recommended procedures was always much less tedious or time-consuming than reported methods.

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Applications, Involving the Iodide Ion

VIII. Direct and Indirect Determination of Mercury(I) and Analysis of Mixtures. Analysis of Chromium(VI)–Chromium (III) Mixtures. Determination of Hypochlorite

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INTRODUCTION

In a series of papers we have recently applied the potentiometric back titration of iodide with mercury(II) to the indirect determination of oxidants that are quantitatively reduced with iodide (*8*) or metal ions that form slightly soluble salts with iodide (*7–9*) either in pure solution or in mixtures, with or without separation of the precipitated iodide.

The aim of the present work is to apply the same method to the determination of mercury(I) and to ascertain the feasibility of determining mercury(I) by direct titration with iodide and analysis of its mixtures with some other cations, determination of hypochlorite and analysis of chromium(III)–Chromium(VI) mixtures.

Mercury(I) has been recently determined gravimetrically as phthalate dried at 130°C without interference from Ag, Hg(II), Pb, Bi, Fe^{3+}, So_4^{2-}, Cl^- and other anions that form precipitate with Hg(I). However many other species in 100-fold excess interfere (*4*). The indirect volumetric method using excess ferricyanide and iodide sufficient to form tetraiodo-mercurate(II), zinc ions to precipitate ferrocyanide and thiosulfate to titrate liberated iodine is suitable for 0.1 to 0.6 g of Hg(I) with an error of less than 0.5%. However, strong oxidizing or reducing agents, Cu(II), Ni, and Co(II), interfere but Hg(II), Pb, and Ag(I) in concentration equal to that of Hg(I) do not (*1*).

Permanganate was used as titrant for Hg(I) (0.1 to 0.2 g) in acid medium in presence of fluoride either visually or potentiometrically (platinum electrode), with less than 1% error (*5*). An indirect method involved oxidation of Hg(I), (0.016 to 0.16 g) with 10-fold excess of permanganate in alkaline medium, acidification, addition of excess ferrous and back-titration of its excess with permanganate (*6*).

Other methods cited in the literature involved back-titration of iodate

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after separating mercurous iodate from nearly neutral solution (*3*); titration of mercury(I) with 0.1 *N* thiocyanate saturated with mercuric thiocyanate in nitric acid and iron(III) indicator (*2*); oxidation of mercury(I) with cerium(IV) in hot sulfric acid followed by potentiometric back-titration of excess cerium(IV) with ferrous iron (*11*); and reduction of mercury(I) with iodide to metallic mercury followed by addition of excess iodine and back-titration of its excess with thiosulfate.

The present method has the advantage over the above-mentioned ones of being simple, rapid, and highly accurate.

The literature is plentiful in methods of determining hypochlorite, the most simple and reliable being the iodometric method. The present method is a modification involving the potentiometric back-titration of excess iodide with mercury(II).

Chromium(VI) has been recently determined in pure solutions of chromate and dichromate (*8*).

EXPERIMENTAL METHOD

The water used was always twice distilled from all-glass equipment. The chemicals were all of the requisite purity. They were, nitrates of mercury(I), mercury(II), magnesium, calcium, cadmium, zinc, nickel, copper(II), manganese(II); disodium salt of ethylenediaminetetraacetic acid (EDTA); Eriochrome black T (EBT); murexide; pyrocatechol violet (PCV); chromium(III) sulfate; chloride, iodide, cyanide, hydroxide, and dichromate of potassium; acetone; sodium thiosulfate; hexamine; starch; and acetic acid.

Solutions

The 0.05 *M* mercury(I) solution was 15 g/liter of $HgNO_3H_2O$ (May and Baker) sample (Mol wt, 280.6) made 0.05 *M* in respect to nitric acid and shaken thereafter with pure mercury metal for 12 hours. Standardization was carried out by titration with permanganate in presence of fluoride (*5*): The 0.05 *M* mercuric nitrate solution was prepared and standardized by recommended procedure. The 0.1 *M* potassium iodide was prepared by dissolving the calculated amount in water and was standardized potentiometrically against the mercury(II) solution. The above metal nitrate solutions were prepared and standardized following recommended procedures. The 0.05 *M* potassium hypochlorite was prepared by passing pure chlorine gas in 0.1 *M* potassium hydroxide. The hypochlorite was determined iodometrically. The 0.05 *N* dichromate solution was prepared from a recrystallized sample. The 0.053 *M* Cr(III) sulfate solution was prepared and standardized by recommended procedure.

TABLE 1

DIRECT MACRODETERMINATION OF MERCURY(I) [a]

No.	Hg(I) (mg) Taken	Hg(I) (mg) Found	Error (±%)	Titrant (mV/0.1 ml)
1	54.150	53.860	0.53	445
2	43.320	43.250	0.16	447
3	32.490	32.260	0.70	459
4	21.660	21.460	0.92	464
5	10.830	10.770	0.55	468
6	14.042	14.021	0.14	360
7	12.036	12.054	0.14	342
8	10.030	10.050	0.19	356
9	8.024	8.044	0.24	356
10	7.021	7.038	0.24	349
11	6.519	6.519	0.00	346
12	6.018	6.008	0.16	356
13	4.012	3.992	0.49	351
14	3.009	3.018	0.29	377
15	2.006	1.996	0.49	353
16	1.404	1.402	0.14	234
17	1.003	0.997	0.59	234
18	8.024	7.964	0.75	313
19	4.012	3.992	0.48	356
20	4.012	3.992	0.48	345
21	6.018	5.998	0.33	280
22	8.024	8.004	0.24	238
23	10.030	10.050	0.19	221

[a] Nos. 1–5: 0.054 M Hg_2^{2+} × 0.1013 M I^-; 6–15 and 18–23: 0.01 M Hg_2^{2+} × 0.01 M I^-; 16 and 17: 0.001 M Hg_2^{2+} × 0.001 M I^-; 18/23: respectively, in presence of the following (mg): 7 Ni + 6 Mg; 5 Mg + 10 Zn; 5 Mg + 9 Cd; 2 Ni + 10 Cu; 5 Mg + 6 Cu; 5 Mg + 10 Zn + 13 Cu; and 4 Mg + 18 Cd + 16 Cu.

Lower concentrations, whenever required, were prepared by accurate dilution.

Procedures

(A) Direct method: titrate mercury(I) (1–7 ml of 0.05 down to 10^{-4} M made with water up to 25 or 10 ml), with standared iodide solution (0.1 down to 10^{-4} M) using silver amalgam as the indicator electrode, with pure solutions or in presence of a variety of cations.

(B) Indirect method: to determine milligram down to submicrogram amounts of mercury(I) (0.5–3 ml of 0.01 down to 10^{-4} M) add excess

iodide (2–8 ml of 0.01 down to 10^{-4} *M*) and back-titrate with standard mercuric solution and the silver amalgam electrode.

(C) With binary mixtures, determine mercury(I) by method (A), simultaneously determine the other cation, after separating mercurous iodide by filteration (cations of Mg, Cd, or Zn with EDTA and EBT, at pH 10, of Ni, Cu(II) or Ca with EDTA and murexide at recommended pH, and of Mn(II) with EDTA and PCV, at pH 10).

(D) With binary mixtures of mercury(I) and mercury(II),

1. Determine the total by titration with iodide as in (A); in another identical mixture, determine mercury(I) with permanganate in presence of fluoride ion (*5*).

2. Determine the total as above; in another identical mixture, separate mercury(I) as chloride and determine mercury(II) with iodide and silver amalgam electrode.

(E) With ternary mixtures of mercury(I), Mg, and Zn or Cd and Cu(II), determine mercury(I) as in (A); separate precipitated HgI_2; mask Cd, Zn, or Cu(II) with cyanide; determine Mg volumetrically using EDTA and EBT, at pH10; demask Zn or Cd with acetone (25 ml); and finally titrate the liberated cation with EDTA. In case Cu(II) is present, determine it iodometrically in another identical mixture after separating mercury(I) as chloride.

(F) With quaternary mixtures of Hg(I), Mg, Cu(II), and Zn or Cd, determine Hg(I) as in (A); separate Hg_2I_2 by filtration; to the filterate and washings mask Cu(II) and Zn or Cd with cyanide; titrate Mg with EDTA and EBT, at pH10; demask with acetone (25 ml), Zn or Cd; titrate the liberated ions with EDTA and EBT; in another identical mixture separate Hg(I) as chloride (with KCl) prior to iodometric determination of Cu(II). Compute the equivalent of EDTA to each component.

(G) With Cr(VI–Cr(III) mixtures determine Cr(VI) alone by potentiometric back-titration of excess iodide with Hg(II) (*8*). In another identical mixture reduce Cr(VI) by boiling on a hot plate with 5 *M* H_2SO_4 (0.5 ml) and 5% sodium sulfite (5 ml) until excess of SO_2 is expelled (~10 minutes); add excess EDTA (4–12 ml of 0.05 *M*); boil for 15 minutes to develop the violet color of Cr(III–EDTA complex; and finally back-titrate excess EDTA with Hg(II) and silver amalgam electrode, at pH 9–10; compute the equivalent of EDTA to Cr(III) plus reduced Cr(VI).

(H) With hypochlorite, to 0.5–4 ml of the solution (0.05–0.0045 *M*) acidified with 2 ml of conc. acetic acid, add excess iodide (3–5 ml of 0.1–0.01 *M*); back-titrate excess iodide with mercury(II) and silver amalgam electrode.

TABLE 2

DIRECT MICRODETERMINATION OF MERCURY(I) [a]

No.	Hg(I) (μg) Taken	Hg(I) (μg) Found	Error (±%)	Titrant (mV/0.1 ml)
1	802.4	804.4	0.24	198
2	601.8	559.7	0.33	221
3	501.5	499.5	0.39	183
4	401.2	399.2	0.49	177
5	300.9	297.0	1.26	240
6	200.6	198.6	0.99	238
7	160.5	159.7	0.49	117
8	120.4	121.0	0.49	115
9	100.3	99.0	1.29	113
10	60.18	59.0	1.9	149
11	40.1	40.0	0.25	155
12	30.09	30.0	0.30	146

[a] Nos. 1–6: 10^{-3} *M* Hg_2^{2+} × 10^{-3} *M* I^- in final total volume of 25 ml; 7–9: 10^{-3} *M* Hg_2^{2+} × 10^{-4} *M* I^- in final total volume of 25 ml; 10–12: 10^{-4} *M* Hg_2^{2+} × 10^{-4} *M* I^- in final total volume of 10 ml.

Cell and Equipment

The titration system, pH, and potentiometer were essentially the same as those described before (*9*).

TABLE 3

INDIRECT DETERMINATION OF MERCURY(I) [a]

No.	Hg(I) (mg) Taken	Hg(I) (mg) Found	Error (±%)	Titrant (mV/0.1 ml)
1	10.030	10.050	0.19	273
2	7.021	7.081	0.85	329
3	5.015	5.035	0.39	357
4	3.009	3.029	0.66	330
5	2.006	2.016	0.45	367
6	1.003	0.993	0.99	345
7	0.602	0.600	0.33	268
8	0.401	0.398	0.74	235
9	0.201	0.202	0.49	246
10	0.050	0.050	0.00	125
11	0.040	0.040	0.00	127

[a] Nos. 1–6: 10^{-2} *M* Hg_2^{2+}, 10^{-2} *M* I^- × 5 × 10^{-3} *M* Hg^{2+}; 7–9: 10^{-3} *M* Hg_2^{2+}; 10^{-3} *M* I^- × 5 × 10^{-4} *M* Hg^{2+}; 10–11: 10^{-4} *M* Hg_2^{2+}, 10^{-4} *M* I^- × 5 × 10^{-5} *M* Hg^{2+}.

TABLE 4

ANALYSES OF BINARY MIXTURES [a]

No.	Hg(I) (mg)		Error (±%)	Metal (mg)	
	Taken	Found		Taken	Found
1	54.15	54.06	0.16	9.93 Hg(II)	9.83
2	43.32	43.17	0.35	14.89	14.83
3	32.49	32.49	0.00	19.86	19.66
4	21.66	21.70	0.19	24.82	24.67
5	8.024	7.994	0.37	8.024	8.080
6	2.006	1.996	0.49	6.018	6.036
7	2.006	1.985	0.24	6.87 Ni	6.87
8	6.018	5.994	0.39	4.58	4.59
9	10.030	9.990	0.39	2.29	2.27
10	10.030	10.090	0.59	5.535 Mg	5.525
11	3.009	2.988	0.69	5.535	5.502
12	6.018	6.027	0.45	3.321	3.307
13	2.006	2.016	0.50	1.107	1.118
14	14.042	13.979	0.44	13.77 Cd	13.66
15	10.030	10.010	0.19	4.59	4.63
16	4.012	3.992	0.50	18.36	18.29
17	10.030	10.010	0.19	16.342 Zn	16.260
18	8.024	7.964	0.75	9.805	9.828
19	2.006	1.996	0.49	3.268	3.265
20	8.024	7.964	0.75	11.975 Mn	11.975
21	2.006	1.996	0.49	9.580	9.600
22	10.030	10.090	0.59	6.442 Cu	6.454
23	7.021	7.001	0.28	9.663	9.588
24	4.012	4.022	0.24	16.105	16.135
25	10.030	10.050	0.19	10.105 Ca	10.140
26	6.018	5.997	0.30	6.063	6.063
27	5.015	4.995	0.39	4.042	4.024

[a] Nos. 1–4: Procedure (D)1; 5–6: Procedure (D)2.

RESULTS AND DISCUSSION

Tables 1, 2, and 3 list representative results of determining milli- and microgram amounts of mercury(I) by procedure (A) and by procedure (B), respectively. The data show that the present methods are extremely reliable for 55 mg/25 ml down to 30 μg/10 ml, i.e., 3 ppm of mercury(I) without interference from many metal ions which are indifferent towards iodide. Large potential breaks are obtained with such low dilutions and the time required for a single determination does not exceed 15 minutes.

The constancy of the electrode potentials at, and after the end point and the stoichiometry of the iodide–mercury(II), reaction in presence of

TABLE 5

ANALYSIS OF TERNARY MIXTURE

Hg(I) (mg)		Metal (mg)		Metal (mg)	
Taken	Found	Taken	Found	Taken	Found
10.030	9.970	2.216 Mg	2.239	16.342 Zn	16.277
4.012	3.992	4.432	4.485	9.805	9.706
2.006	1.996	5.540	5.558	3.268	3.168
10.030	10.009	2.216	2.239	22.815 Cd	22.862
4.012	3.992	4.432	4.444	9.126	9.039
10.030	10.090	4.432	4.438	6.442 Cu	6.448
6.018	6.038	3.324	3.328	9.663	9.567
10.030	10.050	4.626 Ni	4.660	6.442	6.442
6.018	5.998	2.313	2.348	9.663	9.597
4.012	3.992	6.939	6.957	3.221	3.221

Hg_2I_2 (procedure B) indicate that mercuric ions have no influence upon the mercury(I) iodide precipitate, in the sense that they cannot shift the dissociation of Hg_2I_2 toward production of its ions. This is in harmony with the fact that the solubility of HgI_2, as referred to by Kohlrausch and Rose (*10*), amounts to 4×10^{-4} g/liter at 18°C, corresponding to 8.8×10^{-7} mole/liter, and the solubility of Hg_2I_2 from the solubility product of 4.5×10^{-29} amounts to 6.7×10^{-15} mole/liter. However, the direct method is more rapid and less reagent consuming. Moreover it permits the simultaneous determination of up to two cations in mixture with mercury(I) with the additional use of masking with cyanide and demasking with acetone (Table 4 to 6).

With the same principle underlying the analysis of mixtures, we determined the four components of certain quaternary mixtures using only two identical aliquots. The time required for analysis of a ternary or a quaternary mixture does not exceed 1 hour.

TABLE 6

ANALYSIS OF QUATERNARY MIXTURES

Hg(I) (mg)		Metal (mg)		Metal (mg)		Metal (mg)	
Taken	Found	Taken	Found	Taken	Found	Taken	Found
10.030	10.010	4.432 Mg	4.473	13.073 Zn	12.996	16.105 Cu	16.043
8.024	8.004	4.432	4.424	9.805	9.686	12.885	12.835
8.024	8.004	2.216	2.226	6.530	6.530	9.663	9.645
10.030	10.050	4.432	4.473	18.36 Cd	18.29	16.105	16.154
8.024	8.004	3.324	3.339	13.77	13.66	12.884	12.896

TABLE 7

ANALYSIS OF CHROMIUM(VI)–CHROMIUM(III) MIXTURES

Cr(III) (mg)		Error	Cr(VI) (mg)		Error
Taken	Found	(±%)	Taken	Found	(±%)
2.828	2.808	0.74	2.481	2.487	0.21
6.657	6.614	0.74	2.481	2.482	0.02
8.485	8.563	0.91	2.481	2.482	0.02
14.142	14.142	0.00	2.481	2.478	0.15
19.799	20.013	1.0	2.481	2.478	0.15
6.915	6.863	0.7	1.757	1.757	0.00
6.915	6.993	1.0	3.515	3.515	0.00
6.915	6.835	1.1	5.272	5.249	0.4
6.915	6.780	1.7	7.030	6.933	0.8

Combination of the potentiometric back-titration of excess iodide with mercury(II) [for chromium(VI)] and of excess EDTA with the same titrant [for chromium(III) equivalent to chromium(VI) plus chromium(III) in mixture with it] using the silver amalgam electrode, provided the basis of analysis of the mixtures (Table 7) with requisite accuracy and precision.

The results of determining hypochlorite by procedure (H) (Table 8) show high accuracy in most cases. The potential breaks indicating the end points ranged from 125 to 214 mV/0.1 ml of 0.01 to 0.05 *M* titrant. Such relatively lower jumps are attributed to the presence of chloride ions which imprison free mercuric ions added just beyond the end point in the stable tetrachloromercurate(II) ion (log $K = 16.22$).

TABLE 8

DETERMINATION OF HYPOCHLORITE

	ClO^- (mg)		Error	Titrant
No.	Taken	Found	(±%)	(mV/0.1 ml)
1	1.296	1.288	−0.61	214
2	2.593	2.579	−0.57	186
3	6.019	5.968	−0.97	183
4	7.781	7.899	1.48	153
5	9.538	9.661	1.29	148
6	5.451	5.477	0.56	154
7	0.660	0.660	0.00	138
8	0.440	0.440	0.00	144
9	0.330	0.332	0.6	125
10	0.220	0.221	0.45	169
11	0.110	0.110	0.00	189

SUMMARY

Mercury(I), down to 3 ppm, has been accurately determined by direct titration with iodide or by back-titrating excess of iodide with mercury (II) using silver amalgam as the indicator electrode. The direct method and additional volumetric ones were applied to the rapid analysis of various mixtures involving mercury(I) with fair accuracy and precision. Analysis of Cr(VI)–Cr(III) mixtures involved potentiometric back-titration of excess iodide and of excess EDTA separately with mercury(II). Back-titration of excess iodide was successfully applied to the determination of hypochlorite.

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Book Reviews

Aerosols and Atmospheric Chemistry. Edited by G. M. HIDY. Academic Press, New York, 1972. 348 pp. $14.50.

This book is a report of the Kendall Award symposium honoring Professor Milton Kerker at the ACS Meeting in Los Angeles in 1971. Sixty-five contributors combine to prepare 31 chapters on various phases of the chemistry and physics of aerosols.

The text is divided into three main parts. In the first part, the experimental methods for preparing aerosols are presented. These include aerosols produced by metal oxide particles in the hydrogen–oxygen flame, aerosols produced by X-rays and photolysis, and aerosols produced in the flow reactor. The optical and dynamical properties of aerosols are developed first by Milton Kerker and then expanded by several other investigators. The mechanism of aerosol formation and the nature of an aerosol are explored in detail. An interesting advance is the development of a light-scattering device for studying individual microparticles in their natural state. Individual particles (100–5000 mn in size) are introduced into a chamber where they are suspended by a combination of pneumatic and electrostatic controls and their properties studied with the aid of a laser beam.

The second part of the text is devoted to the application of the principles of the first part to the atmosphere. The formation of the synthetic and smog aerosols is compared as to formation and growth. The chemistry of their formation is also developed in detail.

The third part of the book is devoted to the Pasadena smog aerosol experiment of 1969. This was a collaborative research effort by investigators from the Universities of Minnesota and Washington, of the California Institute of Technology, the California State Department of Public Health, and the California Statewide Air Pollution Research Center. Data were obtained during a 4-week experiment from August 19 to September 19, 1969.

Various parameters were explored such as source of formation, size distribution, chemical composition, and the physical properties of the smog particles. Equipment such as the electron microscope for studying individual particles, the Whitby aerosol analyzer, the Minnesota aerosol-analyzing system, nuclei counters, computers, and a host of other sophisticated instruments were applied to the problem. The results of this extensive study are documented in the text. In general it seems that the photochemical generation of nuclei from the exhaust materials of combustion followed by hydration and aggregation of the particles is a major cause of smog.

The text is a classic in its field and would necessarily be a source book for those engaged in research in the field. To the microanalyst it is also of great value in that it demonstrates several ways of attacking the analysis of particles in the nanometer size range.

The book is well written and profusely illustrated. The literature in the field is also extensively reviewed by the various authors.

SAMUEL NATELSON, *Department of Biochemistry, Michael Reese Hospital and Medical Center, 29th Street and Ellis Avenue, Chicago, Illinois 60616*

Chemistry of Marine Natural Products. By PAUL J. SCHEUER, Academic Press, New York, 1973. xi + 201 pp. $14.00.

Organic compounds derived from marine life provide the subject matter for this interesting and entertaining book. Rather than the usual cataloging of compounds that one would expect from the title, the author has chosen to organize his material along structural chemical lines. Thus, the five chapters cover isoprenoid, steroid, benzenoid, nitrogenous, and nonaromatic compounds.

Each chapter is amply illustrated with structural diagrams and is followed by a substantial bibliography. There is both a subject and author index. The author has provided sufficient historical information to give perspective in this field of investigation which is taking a giant step forward with the advent of the new techniques for handling small amounts of material and the current interest in the ecological aspects of the sea.

Biological and miscellaneous data add further dimensions to this book. An example of the miscellany is the observation reported that a number of marine sesquiterpenes are optical antipodes of the corresponding terrestrial material.

Anyone interested in marine biology or a chemist contemplating a new program of investigation would do well to take a look at this little book.

BILL ELPERN, *9 Surrey Way, White Plains, New York 10607*

Photomicrography. By DOUGLAS LAWSON. Academic Press, London, 1972. xii + 494 pp. $17.50.

If you had any questions regarding photomicrography I assure you the answer could be found in this book. The author has performed this remarkable feat of covering the subject matter in a novel approach. The book does not have chapters; they have been replaced by nearly 80 subject headings. This arrangement is designed for easy reference and minimizes repetition. The net result of subject headings is a form of mini-chapters, with references at the end of each section.

The text is designed as a guide for those individuals who wish to use photomicrography and to produce better pictures. The author uses a straightforward method of explanation, supported with numerous illustrations and line diagrams. The excellent illustrations used are primarily biological, but there are photomicrographs which also illustrate metallurgical and chemical applications. The readership audience for a text of this sort can thus be extensive, with emphasis on the use by biologists.

I believe there is no other text available that has this range of information. The author's style is informative, but not to the extent that it is pedantic. His enthusiasm for the subject is contagious, and it will help the reader learn more of photomicrography. I think the book has filled a void. It will be an invaluable guide and source of reference in all libraries. For the serious student of photomicrography, it provides an enormous source of information on the subject, organized, and effectively presented.

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Analytical Profiles of Drug Substances. Edited by KLAUS FLOREY. Vol. 2. Academic Press, New York, 1973. xi + 575 pp. $18.50.

The second volume of "Analytical Profiles of Drug Substances" presents in-depth information about important drug substances. The profiles include physical and chemical properties of drug substances as well as synthesis, methods of analysis, pathways of

physical and biological degradation and metabolism, solubility, pH and pK values, spectra and spectrophotometric constants, and stability data.

Drug compounds mentioned in Vol. 2 are: Ampicillin, Chlorprothixene, Chloral Hydrate, Clidinium Bromide, Dexamethasone, Dioctyl Sodium Sulfosuccinate, Fluorouracil, Fluphenazine Enanthate, Fluphenazine Hydrochloride, Isocarboxizid, Isopropamide, Levallorphan Tartrate, Methyprylon, Phenelzine Sulfate, Primidone, Propiomazine Hydrochloride, Sulfamethoxazole, Sulfisoxazole, Triclobisonium Chloride, Triflupromazine Hydrochloride, and Trimethobenzamide Hydrochloride.

Although the drug substances described in this book are defined as to identity, purity, strength, and quality in the official compendia (United States Pharmacopeia and National Formulary), these profiles provide supplemental information that contributes to the better understanding of drug characteristics. The information presented in this volume is a collection of data scattered throughout the literature and files of pharmaceutical laboratories. The profiles are sufficiently thorough and provide an authoritative source of information concerning the properties of drug substances as well as up-to-date references.

This book provides a valuable and convenient reference and should be welcomed by research pharmaceutical chemists and research pharmacists.

DAVID F. TOMKINS, *Hoffmann-La Roche Inc., Nutley, N. J. 07110*

Ring Forming Polymerizations, by R. J. COTTER AND M. MATZNER. Volume 13-B, 2. Academic Press, New York, 1972. $39.50.

This book is part of a series whose object, as stated in the preface of the book, is to serve as a comprehensive review and compilation of ring-forming polymerization reactions that proceed with heterocyclic ring formation. The topics covered in this volume are rings containing four carbon atoms, intra-intermolecular polymerizations leading to heterocyclic rings, alpha, beta-unsaturated aldehyde polymerizations, and some miscellaneous polymerizations.

The stated goal of serving as a compendium of reactions is met. There is extensive literature coverage and tables indicating properties and synthetic methods up to 1970 with a few references in 1971. The authors are uncritical in that the large majority of the book is made up of reporting of results from the literature with almost no evaluation of the results. A novice in the field should not pick this book as a means of gaining an introduction to the subject because there is so little discussion or evaluation of data.

The book is recommended as a good reference guide to the literature. However, the high price ($39.50) will probably lead to purchase primarily by libraries.

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Quality Control in the Pharmaceutical Industry

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VOLUME 1

This multi-volume treatise represents a convenient, practical and comprehensive guide to nearly every aspect of the quality control of pharmaceutical products. It encompasses the spectrum of relevant scientific disciplines — including biochemistry, analytical chemistry, physiology, and microbiology — as well as administrative matters such as the function of government agencies. The authors discuss each topic in sufficient detail to be of immediate practical value to pharmaceutical quality control managers and their technical staffs. In addition, the treatise will enable the scientist or administrator in the industry to broaden his knowledge of technical areas outside of his own speciality.

This treatise will be a necessary addition to the libraries of technical and administrative personnel in the pharmaceutical industry.

1972, 260 pp., $17.00

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