ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 31, No. 6, p. 501–608, December 1964

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 31, No. 6, December 1964

THE THERMAL DISSOCIATION OF SOME METAL CUPFERRATE CHELATES

The thermal dissociation of the cupferron complexes with Cu(II), Ni, Co(II), Zn, Cd, Mn(II), Hg(II), Mg, Ca, Ba, Sr, Al, Fe(III), Ce(III), La, and Nd was studied by differential thermal analysis (DTA) and by pyrolysis into a mass spectrometer. The DTA curves consisted mainly of endothermic peaks although some contained exothermic peaks as well. The mass spectrometer showed that cupferron decomposes slightly above room temperature, giving off N_2, NO, N_2O, NH_3 and H_2O. A mechanism for the thermal dissociation of the copper(II) cupferrate is proposed.

W. W. Wendlandt, S. Iftikhar Ali and C. H. Stembridge,
Anal. Chim. Acta, 31 (1964) 501–508.

DETERMINATION OF ARSENIC IN SEA WATER, MARINE PLANTS AND SILICATE AND CARBONATE SEDIMENTS

Cocrystallization with thionalide in a 0.05 *N* sulphuric acid medium is proposed for the recovery of microgram amounts of arsenic from sea water and from solutions prepared by the decomposition of silicates and marine plants. After destruction of the organic precipitant, arsenic is determined photometrically by means of a single-solution molybdenum blue method. The overall recovery for the whole process is 97–98%. Arsenic was determined in sea water with a coefficient of variation of 1.3% at a level of 2 μg As/l. Coefficients of variation of 2.6% and 1.7% were found for the determination of the element in marine sediments and plants at levels of 6.6 μg/g and 1.7 μg/g respectively. The U.S. Geological survey standard granite G 1 was found to contain 1.2 μg As/g.

J. E. Portmann and J. P. Riley,
Anal. Chim. Acta, 31 (1964) 509–519.

SYSTEMATIC ANALYSIS BY SOLVENT EXTRACTION METHODS

PART I. QUALITATIVE ANALYSIS

A systematic scheme of separation by solvent extraction methods is described for 19 metals.

R. A. Chalmers and D. M. Dick,
Anal. Chim. Acta, 31 (1964) 520–527.

RUTHENIUM COMPLEXES OF LIGANDS CONTAINING THE FERROIN GROUP AS FLUORESCENT PRECIPITATION INDICATORS FOR IODIMETRY

Chelates of ruthenium(II) with several methyl-substituted derivatives of 1,10-phenanthroline and 2,2′-bipyridine were studied as fluorescent–precipitation indicators for iodimetry. Accurate results were obtained under various conditions where starch will not function. The indicators are stable in solution, sensitive and reversible, and are particularly useful for titrations in colored or very dilute solutions.

B. Kratochvil and M. Clasby White,
Anal. Chim. Acta, 31 (1964) 528–533.

LIQUID–LIQUID EXTRACTION WITH LONG-CHAIN QUATERNARY AMMONIUM HALIDES

The extraction of anionic chloro-complexes of certain metal ions using various long-chain quaternary ammonium halides in toluene and chloroform is described. The investigation has concerned itself mainly with cobalt(II) and iron(III); a few extractions have also been carried out with indium(III) and gallium(III). The ion association of chloro-anionic complexes of iron, cobalt, indium and gallium in aqueous chloride media (hydrochloric acid or lithium chloride) with the quaternary ammonium ion in the organic phase is responsible for the extraction of the metal ion into the organic phase. The extraction efficiency varies with the nature of the metal ion system involved as well as with the distribution of the quaternary compound and the size, shape and nature of the organic groups substituted in the quaternary compound.

M. L. Good, S. C. Srivastava and F. F. Holland, Jr.,
Anal. Chim. Acta, 31 (1964) 534–544.

A RAPID RADIOCHEMICAL METHOD FOR ANTIMONY AND ARSENIC

PART I. FORMATION OF STIBINE AND ARSINE BY FLASH ELECTROLYSIS

The formation of stibine and arsine affords a clean, one-step, method of separating antimony and arsenic from fission products. The development of a high-current electrolytic cell for the rapid formation of these hydrides from a hydrochloric acid electrolyte, is described. A chemical yield of 45% was achieved for both antimony and arsenic in 10 sec. The effects of pH and antimony and arsenic oxidation states were also studied. In 5 *N* hydrochloric acid, the chemical yield is independent of the antimony oxidation state. For arsenic however, the yield of arsine is 7 times greater for As(III) than for As(V).

L. Tomlinson,
Anal. Chim. Acta, 31 (1964) 545–551.

DETERMINATION OF CERIUM IN FERROUS ALLOYS

A method for the determination of cerium in ferrous alloys is described. Cerium (with lead and bismuth) is separated from other elements by anion exchange in a medium consisting of 95% methanol and 5% 5 *N* nitric acid; cerium alone is then eluted with 90% methanol–10% 6 *N* hydrochloric acid and determined in the eluate by titration with EDTA to xylenol orange indicator. Application of the method to several steel samples was successful.

S. S. Ahluwalia and J. Korkisch,
Anal. Chim. Acta, 31 (1964) 552–556.

THE DETERMINATION OF ZINC IN ROCKS BY NEUTRON ACTIVATION ANALYSIS

A neutron activation method for the determination of zinc in rocks and minerals is described. The method is precise, accurate and has a sensitivity of 0.01 p.p.m. of zinc. An ion-exchange separation of zinc together with precipitation of zinc as oxinate, gives good yields. Interference from conflicting (n,p), (n,α) and ^{235}U(n,f) reactions is negligible. The zinc contents of G-1 and W-1 determined by the method were 45.7 and 82.8 p.p.m. of zinc respectively.

R. H. FILBY,

Anal. Chim. Acta, 31 (1964) 557–562.

THE DETERMINATION OF OXYGEN IN PLUTONIUM AND ITS COMPOUNDS BY EMISSION SPECTROSCOPY

(in French)

The FASSEL method is applied to the determination of oxygen in various plutonium compounds by emission spectroscopy. Technical difficulties were found in adapting the method for radioactive materials; these were partially overcome by the introduction of a special electrode carrier, but the volume of the carrier was established as too large to enable the full possibilities of the method to be exploited. A lower sensitivity limit of 250 p.p.m. was found for a 200-mg sample; the precision obtainable was of the order of 40%.

M. CHAPUT ET J. N. SAVARIT,

Anal. Chim. Acta, 31 (1964) 563–575.

SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM WITH CHROME AZUROL S

A comprehensive investigation of the spectrophotometric determination of beryllium with chrome azurol S is described. At pH 4.6, in the presence of EDTA, only chromium(III) and fluoride interfered seriously. A molar absorptivity of 4060 at 569 mμ was found for the complex, with a relative standard deviation of $\pm$ 0.4% at the 25-μg Be level. Beer's law was obeyed from 0 to 3.2 μg Be/ml. Chrome azurol S has several advantages over the widely used Berillon II.

P. PAKALNS,

Anal. Chim. Acta, 31 (1964) 576–582.

A POTENTIOMETRIC STUDY OF THE PICOLINATES OF LANTHANUM, PRASEODYMIUM AND NEODYMIUM

(in French)

A potentiometric method is used to determine the stepwise stability constants of lanthanum, praseodymium and neodymium picolinates in aqueous solution at two ionic strengths ($\mu = 0.02$ and $\mu = 0.5$; sodium perchlorate medium) at 25°. The stability and the solubility of these picolinates increase from La to Nd.

L. MOYNE AND G. THOMAS,

Anal. Chim. Acta, 31 (1964) 583–589.

METHYL-2-PYRIDYL KETOXIME AS A COLORIMETRIC REAGENT FOR RHENIUM

Reduction of the perrhenate ion by tin(II) in hydrochloric acid solution in the presence of methyl-2-pyridyl ketoxime yields a species which has an absorption peak at 490 mμ. Beer's law ($\varepsilon = 3836$) is obeyed in the range 10 to 50 p.p.m. rhenium, and as little as 0.5 p.p.m. rhenium can be detected readily. The ligand solution is stable; the color formation is complete within 30 min and stable for at least 48 h.

R. J. THOMPSON, R. H. GORE AND F. TRUSELL,
Anal. Chim. Acta, 31 (1964) 590–594.

THE RAPID SEPARATION OF RARE EARTH MIXTURES BY THIN-LAYER CHROMATOGRAPHY

(Short Communication)

T. B. PIERCE AND R. F. FLINT,
Anal. Chim. Acta, 31 (1964) 595–597.

THE DETECTION AND ESTIMATION OF THE RELATIVE AMOUNTS OF PRIMARY AND SECONDARY HYDROXYL GROUPS USING N.M.R.

(Short Communication)

A. MATHIAS,
Anal. Chim. Acta, 31 (1964) 598–601.

SCHULEK ELEMÉR

1893-1964

It is with great regret that we note the death of Professor Elemér SCHULEK on October 14th, 1964. Professor SCHULEK was Professor of Inorganic and Analytical Chemistry at the Eötvös Loránd University in Budapest, and was also a leading member of the Hungarian Academy of Sciences, as head of its research group in quantitative analytical chemistry.

His contributions to analytical chemistry were many and varied. His early investigations included many extensions of iodimetric processes and his work on the analysis of pyrazolone-type drugs and natural alkaloids, on indicators for bromate titrimetry, and on the utilization of inter-halogen compounds for analytical purposes are also particularly noteworthy. It is a tribute to the flexibility of his mind that in more recent years, he concerned himself with modern techniques of radiochemistry, spectroscopy, *etc.* He twice received the Kossuth Prize, awarded by the Hungarian Government for outstanding scientific achievements.

Analytical chemistry is the richer for his work and the poorer for his death.

P.W.W.
A.M.G.M.

THE THERMAL DISSOCIATION OF SOME METAL CUPFERRATE CHELATES

W. W. WENDLANDT, S. IFTIKHAR ALI AND C. H. STEMBRIDGE

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(Received April 16th, 1964)

The use of cupferron (ammonium salt of N-nitrosophenylhydroxylamine) as an organic precipitant for copper(II) and iron(III) ions was first proposed by BAUDISCH[1] in 1909. Since that time, much work has been done using the reagent for the determination of these 2 metal ions and other ions[2] as well.

Perhaps the least studied physical parameter of these metal cupferrates has been their thermal properties. Previous studies on this subject have consisted mainly of weight-loss determinations on the thermobalance[3,4]. Normally, the precipitated complexes are contaminated with excess cupferron or are of such low thermal stability that they cannot be weighed as metal complexes but must be ignited and weighed as metal oxides. Only the copper(II) and iron(III) complexes show any possibility of being weighed as the $Cu(Cup)_2$ and $Fe(Cup)_3$ (Cup = cupferrate ion) complexes, respectively, on the basis of their thermal stability[3]. The rare earth cupferrates also appear to possess excellent thermal stability properties although they are usually ignited to the metal oxides and weighed as such[4].

Very little is known concerning the fate of the organic ligand on ignition of the metal cupferrates in the solid state. In solution, cupferron is said to decompose to nitrosobenzene on heating[5]. Likewise, the sodium salt of *p*-nitrocupferron decomposes to *p*-nitrosonitrobenzene while the silver salt gives free silver and nitrosobenzene in boiling solutions[6]. It was thus the object of this study to investigate the thermal dissociation of several of the metal cupferrates by differential thermal analysis and mass spectrometric analysis of the pyrolysis decomposition products.

EXPERIMENTAL

Preparation of complexes

Most of the metal cupferrates were prepared according to previous procedures[2]. The rare earth cupferrates were prepared as previously described[7]. All of the precipitated complexes were washed with water and alcohol and air-dried for at least 24 h at room temperature. The complexes were analyzed for metal content by ignition of the air-dried complexes to the metal oxide at the temperatures previously recommended[3]. The metal contents of the complexes are given in Table I.

TABLE I

METAL CONTENTS OF CUPFERRON METAL CHELATES

Metal cupferrate	*Per cent Metal*	
	Theoretical	*Found*
$Cu(Cup)_2$[a]	18.81	18.7
$Ni(Cup)_2$	17.63	18.1
$Co(Cup)_2$	17.69	17.8
$Zn(Cup)_2$	19.25	19.0
$Cd(Cup)_2$	29.07	28.9
$Mn(Cup)_2$	16.69	16.5
$Hg(Cup)_2$	42.24	42.0
$Mg(Cup)_2$	8.14	8.06
$Cu(Cup)_2 \cdot 2H_2O$	11.44	11.5
$Ba(Cup)_2 \cdot 3H_2O$	29.49	29.5
$Sr(Cup)_2 \cdot 2H_2O$	22.02	22.1
$Al(Cup)_3$	6.15	6.03
$Fe(Cup)_3$	11.95	12.0
$Ce(Cup)_3$	25.40	25.3
$La(Cup)_3$	25.24	25.1
$Nd(Cup)_3$	25.97	25.4

[a] Cup = cupferrate ion, $C_6H_5N(NO)O^-$.

Differential thermal analysis apparatus

The apparatus employed has previously been described[8]. The samples were decomposed in either a vacuum, less than 1 mm Hg pressure, or in a static atmosphere of argon. In the latter case, the air was first removed from the system by evacuation to less than 1 mm Hg, then filled with argon to atmospheric pressure. Sample sizes ranged in weight from 60 to 80 mg and were pyrolyzed at a heating rate of 10°/min. Excellent agreement was found between duplicate and triplicate runs on the same sample.

Pyrolysis studies

The pyrolysis decomposition products were introduced into a Consolidated Engineering Corp. Model 21-602 mass spectrometer by means of an "L"-shaped pyrolysis tube connected directly to the sample inlet chamber of the mass spectrometer. The pyrolysis tube contained a small Nichrome wire wound furnace, 1.5 cm in diameter by 10 cm in length, into which was placed a small porcelain boat containing 1–10 mg of sample. After evacuation to less than 1-micron pressure, the furnace and sample were slowly heated to about 300°. The resulting pyrolysis products were then analyzed by mass spectrometry.

To determine the temperature at which certain pyrolysis products were evolved, the samples were heated at about 5°/min and the various m/e peaks were scanned at periodic intervals. From the intensity increase of the various peaks, the amount of decomposition product could be ascertained as a function of temperature.

The temperature of the pyrolysis furnace was detected by a Chromel–Alumel thermocouple located between the furnace windings and the glass wall of the pyrolysis tube. The voltage output from the thermocouple and the reference 0° thermocouple was recorded on a Varian Model G-10 strip-chart recorder.

RESULTS AND DISCUSSION

The differential thermal analysis (DTA) curves of the metal cupferrates, in argon, are given in Figs. 1–3.

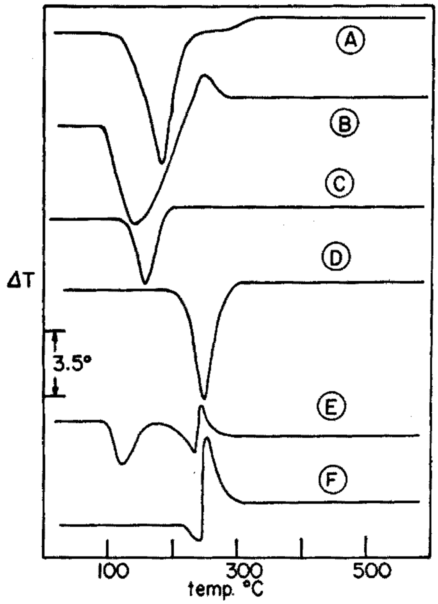


Fig. 1. DTA curves of cupferron and metal cupferrates (argon). A, cupferron; B, $Ni(Cup)_2$; C, $Co(Cup)_2$; D, $Cu(Cup)_2$; E, $Zn(Cup)_2$; F, $Mn(Cup)_2$.

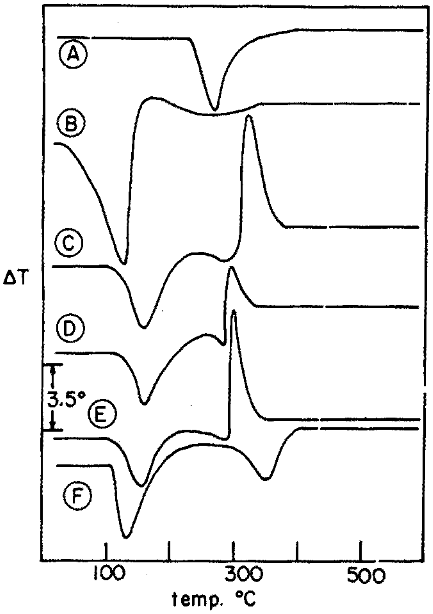


Fig. 2

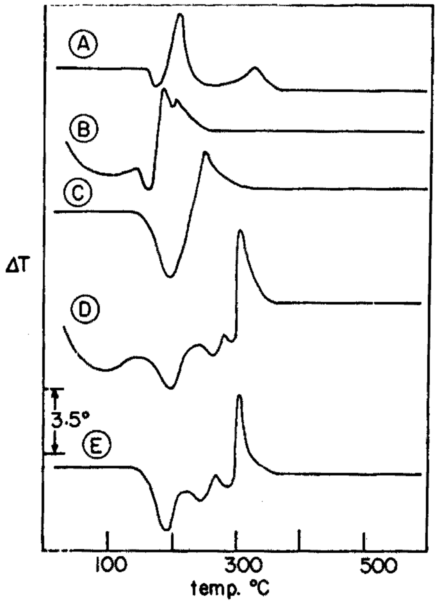


Fig. 3

In general, the DTA curves consisted mainly of endothermic peaks but a number of them also contained exothermic peaks. Since the complexes were studied in an argon atmosphere or vacuum, the origin of the exothermic peaks must be due to the exothermic decomposition of the compounds and not to air-oxidation reactions of the pyrolysis intermediates. Although it is not possible to characterize each peak as a specific decomposition or dissociation reaction, the endothermic peaks must be the result of heat-absorbing bond-breaking reactions. This initial DTA peak was then followed by other endothermic or exothermic peaks which must be due to reactions involving pyrolysis intermediates.

The DTA curve for cupferron contained but a single endothermic peak with a peak maximum temperature of 185°. Since the peak began or deviated from the base line at about 130°, there must have been considerable decomposition before the fusion temperature[5] of 163–164° was reached.

The DTA curves for the cobalt(II), copper(II), mercury(II), and cadmium(II) cupferrates consisted of a single endothermic peak at temperatures of 155°, 250°, 130°, and 260°, respectively. Based upon the temperature at which the curve deviated from the base line, the cadmium complex appeared to be the most stable.

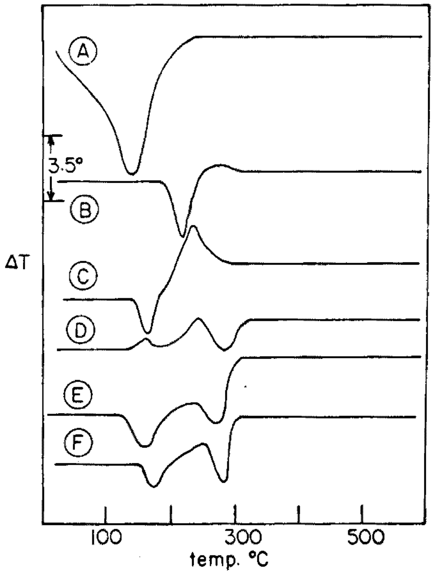


Fig. 4

For the nickel(II), manganese(II), aluminum, and iron(III) cupferrates, the DTA curves consisted of an endothermic peak followed by an exothermic peak or peaks. Generally, the reaction which was responsible for the exothermic peak started as an endothermic one and then changed to exothermic as the reaction progressed. The exact dissociation sequence cannot be determined from the DTA curve itself.

The DTA curves for the calcium, strontium, and barium cupferrates were all quite similar. In contrast, the curve for magnesium cupferrate was different because the exothermic peak was absent. The peak temperatures for the first endothermic peak were: Mg, 130°; Ca, Sr, and Ba, 155°; and for the exothermic peak, Sr and Ba, 300°; Ca, 320°. Because water of hydration occurs with these complexes, it is probable that the first endothermic peak is related to the dehydration reaction.

For the rare earth cupferrates, the DTA curves for lanthanum and neodymium were quite similar. The lanthanum cupferrate curve had endothermic peaks at 200°, 270°, and 300° with an exothermic peak at 310°. Similarly for neodymium, the peak temperatures were 195°, 250°, 295°, and 305°, respectively. Cerium(III) cupferrate exhibited a curve with a single endothermic peak at 200° followed by an exothermic peak at 250°. This anomaly might be expected because of the different oxides obtained, CeO_2, compared to La_2O_3 for the lanthanum complex.

The DTA curves of the metal complexes *in vacuo* are shown in Fig. 4. The most pronounced differences between the vacuum and argon curves were the change in peak maxima temperatures and the decrease in intensity of the endothermic and exothermic peaks. For example, the endothermic peak maximum for cupferron shifted from 185° in argon to 140° in vacuum. Normally, a phase transition should not be pressure-dependent, as was illustrated previously with sodium nitrate[8]. Thus, the curve for cupferron must involve decomposition as well as fusion, which would explain the pressure dependency.

The vacuum DTA curves for the lanthanum and neodymium cupferrates showed only 2 endothermic peaks. The peak maxima were 160° and 280° for lanthanum and 175° and 290° for neodymium. As seen previously, the argon DTA curves contained 3 endothermic peaks followed by an exothermic peak. The endothermic peak maximum for copper(II) cupferrate shifted from 250° in argon to 220° *in vacuo*.

Pyrolysis studies

The results of the pyrolysis studies are shown in Figs. 5–8.

The total mass spectra of the pyrolysis products of cupferron and the copper(II) and iron(II) cupferrates are given in Fig. 5. The spectrum for cupferron indicated

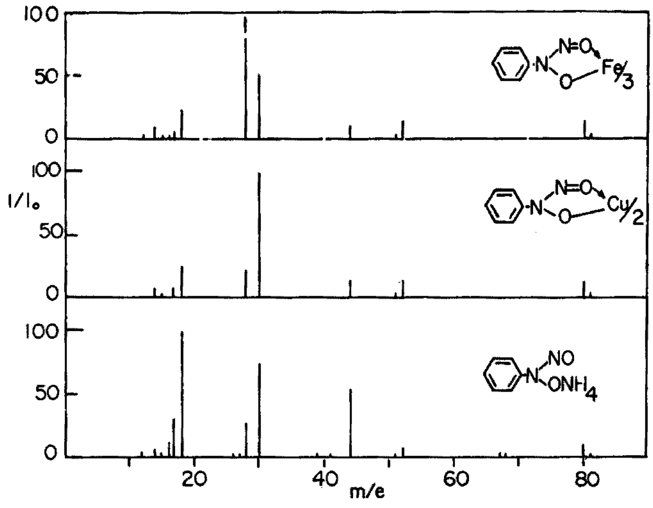


Fig. 5

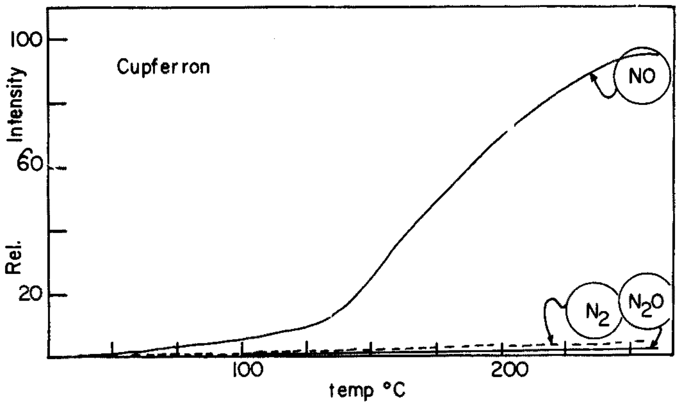


Fig. 6

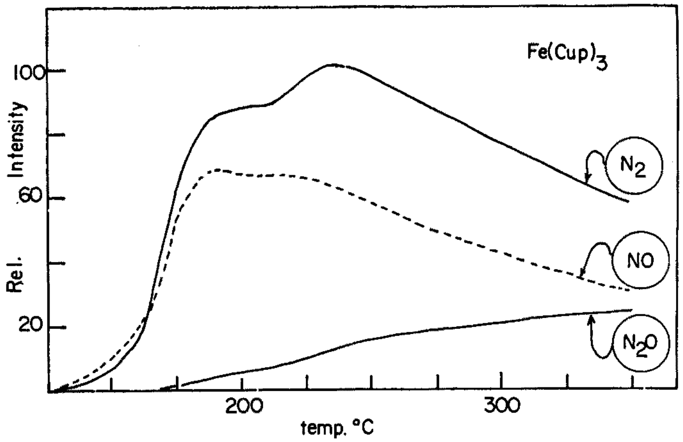


Fig. 7

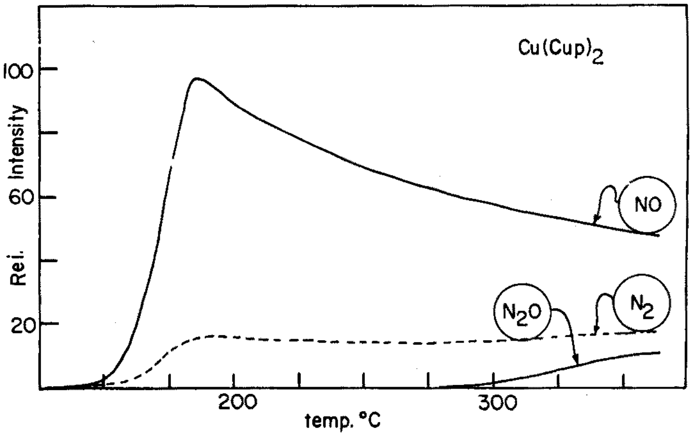
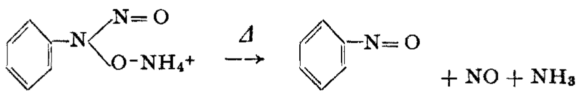


Fig. 8

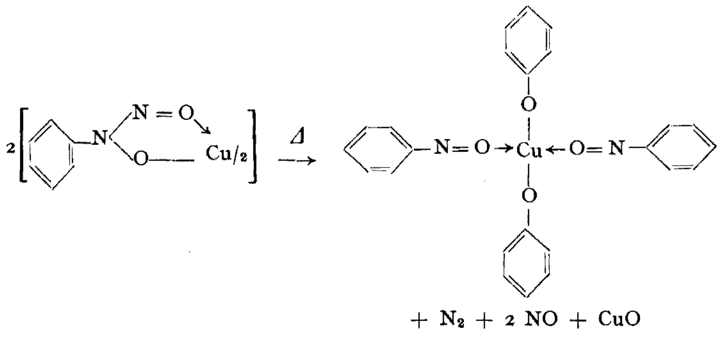
the presence of ammonia, water, nitrogen(II) oxide, nitrogen, nitrogen(I) oxide, and a hydrocarbon entity with a maximum peak intensity at m/e of 80. The 100% I/I_0 peak was positioned at a m/e of 18 for water. For the metal cupferrates, the mass spectra contained similar peaks except for the absence of ammonia. The 100% peaks were different; NO for copper(II) and N_2 for the iron(II) complex.

The curves obtained by oscillating over the 100% m/e peaks for N_2O, NO, and N_2 are given in Figs. 6–8. For cupferron, the curves indicated that NO was detectable at temperatures slightly above ambient. The compound was unstable under conditions of high vacuum with respect to the evolution of nitrogen(II) oxide. Although not shown on the curve, ammonia and water were also evolved at these low temperatures. Most of the water probably came from adsorption and not necessarily from pyrolysis since the amount evolved was dependent on how long the material was contained within the high vacuum system. Thus, the initial decomposition probably involved the reaction:



Only at temperatures greater than 100° were appreciable amounts of nitrogen and nitrogen(I) oxide detected in the pyrolysis products. These gases could result from further decomposition of the cupferron and/or from hot-tube reactions involving nitrosobenzene, nitrogen(II) oxide, and other products.

The situation was similar for the pyrolysis of the copper(II) cupferrate chelate. The decomposition gases, NO and N_2, were detectable at about 150° with the maximum intensities for the gas evolution being obtained at about 185°. Nitrogen(II) oxide was present in the largest amount followed by nitrogen and then nitrogen(I) oxide. A mechanism which could explain this behavior is as follows:



According to this mechanism, additional nitrogen(II) oxide could be evolved at still higher temperatures as well as a hydrocarbon entity and CuO. An alternative mechanism at higher temperatures could possibly involve the evolution of N_2O instead of N_2 from the organic ligand.

The mass spectra curves for the pyrolysis of iron(III) cupferrate revealed an interesting feature. The evolution of N_2 and NO began at about 125°, giving a break in the curve at 185°. Then, at temperatures near 210°, additional N_2 and NO were evolved. From the DTA curve, *in vacuo*, it is seen that the curve contained an endothermic peak at 170° followed by an exothermic peak near 245°. The endothermic reaction evolved NO and N_2 as was found with copper cupferrate, while the exothermic peak reaction evolved still more N_2 and NO as well as N_2O. The difference in the amount of nitrogen compared to NO in the pyrolysis gases may be due to the greater stability of iron(III) oxide compared to copper(II) oxide. Thus, the C–N and N–O bonds would be broken more easily than the Fe–O bonds.

The mass spectra curves for several of the other metal cupferrates revealed similar results. All involved only the gaseous products given off by the two examples presented here.

The support of this work by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-23-63 is gratefully acknowledged.

SUMMARY

The thermal dissociation of the cupferron complexes with Cu(II), Ni, Co(II), Zn, Cd, Mn(II), Hg(II), Mg, Ca, Ba, Sr, Al, Fe(III), Ce(III), La, and Nd was studied by differential thermal analysis (DTA) and by pyrolysis into a mass spectrometer. The DTA curves consisted mainly of endothermic peaks although some contained exothermic peaks as well. The mass spectrometer showed that cupferron decomposes slightly above room temperature, giving off N_2, NO, N_2O, NH_3 and H_2O. A mechanism for the thermal dissociation of the copper(II) cupferrate is proposed.

RÉSUMÉ

Les auteurs ont examiné la dissociation thermique des complexes du cupferron avec Cu, Ni, Co, Zn, Cd, Mn, Hg(II), Mg, Ca, Ba, Sr, Al, Fe(III), Ce(III), La et Nd, par analyse thermique différentielle et par pyrolyse dans un spectromètre de masse. On constate que le cupferron se décompose légèrement, au-dessus de la température ordinaire, en donnant N_2, NO, N_2O, NH_3 et H_2O. Un mécanisme de dissociation thermique du cupferrate de cuivre est proposé.

ZUSAMMENFASSUNG

Die thermische Dissoziation von Cupferron-Komplexen mit Cu(II), Ni, Co(II), Zn, Cd, Mn(II), Hg(II), Mg, Ca, Ba, Sr, Al, Fe(III), Ce, La, und Nd wurde mittels der Differentialthermoanalyse (DTA) und durch Pyrolyse in einem Massenspektrometer untersucht. Die DTA-Kurven besitzen neben einigen exothermen Maxima hauptsächlich endotherme Maxima. Die massenspektrometrischen Untersuchungen zeigten, dass Cupferron sich oberhalb der Raumtemperatur leicht zersetzt unter Abgabe von N_2, NO, N_2O, NH_3 und H_2O. Es wird ein Mechanismus für die thermische Dissoziation des Kupfer-Komplexes vorgeschlagen.

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DETERMINATION OF ARSENIC IN SEA WATER, MARINE PLANTS AND SILICATE AND CARBONATE SEDIMENTS

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(Received May 9th, 1964)

In the course of an investigation of the marine chemistry of arsenic, procedures were required for the determination of low concentrations of the element in sea water, sediments and marine plants. Much of the earlier work on the abundance of arsenic in sea water[1-4] is unreliable owing to the poor analytical techniques used and to the difficulty of obtaining reagents sufficiently free from this ubiquitous element. As a consequence, the results reported were frequently more than an order of magnitude greater than the value at present accepted (*ca.* 2-4 μg As/l). RAKESTRAW AND LUTZ[5] applied the GUTZEIT method directly to evaporated samples of North Atlantic water and Atlantic coastal waters and found 6-28 μg As/l. Later work by GORGY *et al.*[6], in which arsenic was separated from the partially evaporated sample by evolution as arsine and determined photometrically as arsenomolybdenum blue, led to rather higher results (15-35 μg As/l). The quantitative evolution of such small amounts of arsenic, as arsine, from evaporated sea water samples presents great difficulties; furthermore, the comparatively large amounts of the element contained in the zinc and acid used may give rise to reagent blanks considerably in excess of the amount of the element present in the sample. ISHIBASHI *et al.*[7-9] attempted to reduce these sources of error by concentrating the arsenic by coprecipitation with ferric hydroxide before determination by the GUTZEIT method. Their procedure, however, still suffers from the poor accuracy inherent in the GUTZEIT method. SUGAWARA[10] avoided the errors in this method of determination by separating the coprecipitated arsenic from iron and interfering elements by extraction of its ethyl xanthate with carbon tetrachloride; after back-extraction arsenic was determined photometrically as arsenomolybdenum blue. SMALES AND PATE[11,12] found 1.6-5 μg As/l in the waters of the English Channel by radioactivation analysis. This procedure, although very sensitive, and free from errors arising from arsenic present in reagents used after the activation, is unsuitable for routine use unless access to an atomic pile is readily available.

Arsenic may occur in aqueous solution in two ionic forms, *i.e.* As^{3+} or As^{5+}. There has been considerable controversy concerning its state in sea water. GORGY *et al.*[6] consider that only 8-16% is present as arsenate, and that 53-60% occurs as arsenite, the remainder being organic complexes or particulate compounds of the element. ATKINS AND WILSON[13] also support the view that the arsenic is mainly in the tripositive state in sea water. Thermodynamic considerations, however, indicate that the element exists mainly as arsenate and this is confirmed by the observations of ARMSTRONG AND HARVEY[14] that arsenite is oxidised in sea water.

JAMES AND RICHARDS[15] developed a radioactivation procedure for the determination of arsenic in silicates which possesses great sensitivity, and which surmounts the difficulties involved in the decomposition of silicates without loss of this rather volatile element. In a polarographic method for the determination of arsenic in silicates, KALININ[16] opens up the samples by digestion and evaporation with a mixture of hydrofluoric, nitric, and sulphuric acids. STROCK[16], however, reported that serious losses of arsenic occur during such digestion processes. We have confirmed, using tracer techniques with ^{74}As, that very considerable losses (up to 45%) may occur when evaporations with mixtures of hydrofluoric and sulphuric acids are carried out until dense white fumes of sulphur trioxide are evolved. Even if the digestion and evaporation processes are carried out on the water bath with a mixture of hydrofluoric and nitric acids followed by a further evaporation with nitric acid, significant amounts of arsenic (up to 30%) are lost.

ONISHI AND SANDELL[17] used a sodium hydroxide fusion for opening up silicate rocks for the determination of arsenic; after leaching the melt with water, arsenic was evolved from the filtrate as arsine, absorbed and determined photometrically as molybdenum blue. A recovery of 95% for the whole process was claimed, but as noted above, it is difficult to obtain reproducible recoveries by means of the evolution method. The efficiency of the sodium hydroxide fusion process for the decomposition of silicate samples without loss of arsenic was checked by means of radioactive tracer techniques. It was found that with a deep sea clay (containing *ca.* 7 p.p.m. of As) using the conditions described in the EXPERIMENTAL section (see below), less than 0.5% of the arsenic was lost by volatilization, and less than 1% of it was retained by the residue remaining after leaching the fused mass with water. It was thus evident that sodium hydroxide fusion provided a very satisfactory means of opening up silicates.

The determination of arsenic in bio-materials is complicated by the need to guard against loss by volatilization during the preliminary destruction of the organic matter. This is particularly the case with marine plants which may retain appreciable amounts of chloride even after careful washing. Dry ashing at 450° leads to loss of most of the arsenic present[18,19], and this loss is only partially prevented by ashing with magnesium nitrate as described by EVANS AND BANDEMER[20]. Oxidation carried out in a sealed oxygen bomb is more satisfactory[21]. Considerable losses are also experienced in many wet oxidation procedures, for example, that using a mixture of nitric, sulphuric and perchloric acids, unless a reflux condenser is used; when the acid digest must be evaporated before the determination is performed, much arsenic may be volatilized. Tracer experiments on the wet ashing of the seaweed *Fucus serratus* showed that very high losses of arsenic occurred if the samples were digested with a mixture of nitric, sulphuric and perchloric acids and then evaporated until white fumes began to be evolved, in order to remove the nitrate ion. Large losses also occurred if mixtures of nitric and sulphuric acids were used, and it appeared that arsenic began to volatilize in appreciable amounts even before sulphur trioxide fumes appeared. Prolonged digestion with nitric acid was found to be entirely satisfactory for the wet ashing of samples, and no loss of arsenic was detected when the digest was evaporated to dryness on a moderately warm hot-plate (surface temperature *ca.* 180°) even if several milligrams of chloride were originally present.

For the separation of traces of arsenic, after the opening up of silicates or digestion of bio-materials, most workers have used either the arsine evolution method, or distillation of its halides. These methods, as well as being time-consuming, have the disadvantage that it is difficult to recover the element quantitatively.

Arsenic (As^{5+}) can be coprecipitated from sea water at pH 7 using ferric hydroxide, with an efficiency of 99% at a concentration of 2 μg As/l (PORTMANN, unpublished work). This concentration procedure would, however, be unsuitable for the separation of arsenic from the digests of silicates or bio-materials owing to the difficulty of separating the arsenic from >20,000 times its own weight of iron, and from the many other elements which are also coprecipitated by this unspecific reagent.

Closely allied to the technique of coprecipitation is the newer method of cocrystallization in which the solution to be analysed is treated with a solution of a water-insoluble complexing agent in an organic solvent such as acetone. The complexing agent forms an insoluble complex with the element to be separated and this is carried down by the crystallizing reagent, from which it can be recovered by the destruction of the organic compound. This method has the advantage that no inorganic matter is added during the separation. A reagent suitable for the separation of arsenic by this procedure is thioglycollic-β-aminonaphthalide (thionalide) which has been used by LAI AND WEISS[22] for the cocrystallization of silver from sea water. This reagent, which forms insoluble complexes with about 10 elements, will give[23] a definite turbidity with arsenic(III) at a dilution of 1 in 10^8. Oxidizing agents such as iron(III) oxidize the reagent, and in the presence of iron or other oxidizing agents a reducing agent must be present.

This paper describes an investigation into the use of thionalide for the cocrystallization of microgram amounts of arsenic and its application as a concentrating agent in a photometric method for the determination of the element in sea water, marine sediments and marine plants.

Investigation of the use of thionalide for the cocrystallization of arsenic

In preliminary experiments using ^{74}As as a tracer, it was shown that, as might be expected, arsenic could only be effectively cocrystallized if it was in the tri-positive state; arsenate was precipitated only to a small extent. These experiments also showed that ascorbic acid was a more satisfactory agent for carrying out the reduction than either hydroxylamine or hydrazine sulphate. Tests were then carried out to determine the optimum conditions for carrying out the reduction and cocrystallization. Samples of sea water (1 l) containing *ca.* 0.1 μC of ^{74}As with *ca.* 0.05 μg of arsenic carrier were treated with either 0.1 or 0.2 g of ascorbic acid and heated to boiling to reduce arsenate to arsenite. After cooling for 10 min a further 0.1 g of ascorbic acid was added. When the liquid had reached room temperature 10 ml of 5 *N* sulphuric acid and 7 ml of a 2% (w/v) solution of thionalide in acetone were added with vigorous stirring which was continued until the precipitate had coagulated. The solution was boiled for 30 min to remove acetone, and allowed to stand overnight at room temperature. The precipitate was filtered off on a hardened filter paper and washed with water. The filter and precipitate were wet-ashed with nitric acid and the activity of a solution of the residue was measured by means of a scintillation counter, and compared with the activity of the same volume of the original tracer solution as that added to the sea water. In this way it was found that reductions carried out with

0.1 and 0.2 g of ascorbic acid led to average recoveries of 95.4% and 97.5% respectively on duplicate runs. In all further work 0.2 g of ascorbic acid was used for the reduction of arsenate to arsenite, followed by a further 0.1 g to ensure that reducing conditions were maintained during the cocrystallization.

Effect of sulphuric acid concentration on efficiency of cocrystallization

Cocrystallizations were carried out as described above, but using sea waters which had been treated with sulphuric acid to give concentrations ranging from 0.03 to 0.40 N. Within this range, the arsenic recovery was constant at 97.3 ± 0.2%. The acidity of the sea water during the cocrystallization was maintained at 0.05 N with respect to sulphuric acid in all further work, in order to minimize contamination with the traces of arsenic always present in even the purest acid available.

Effect of acetone on recovery of arsenic

In the cocrystallization procedure described above, extremely variable results were produced if the acetone used as solvent for the cocrystallization agent was not removed by boiling. The recovery under these conditions averaged about 73%, but was sometimes as low as 50%. This reduction in efficiency is surprising since the volume of acetone added was less than 1% of the total volume of sea water used; and according to SANDELL[24] the effect is not appreciable, at least for ethanol or acetic acid, unless the solvent concentration is greater than 10–15%.

Effect of variation of the amount of thionalide used on recovery of arsenic

In order to determine whether the arsenic recovery could be increased by carrying out the cocrystallization in two stages, sea-water samples were reduced and acidified as described above, and two portions of thionalide were added, a sufficient time being allowed for the coagulation of the first precipitate before the addition of the second volume of reagent. After treatment of the precipitate in the usual way, the recovery of ^{74}As was estimated by counting. The results of duplicate experiments (Table I)

TABLE I

RECOVERY OF ARSENIC USING VARIOUS VOLUMES OF 2% THIONALIDE IN ACETONE

Volume of thionalide added (ml)		*% Recovery*	
1st precipitation	*2nd precipitation*		
3	2	94.9	95.9
4	3	96.8	98.5
5	4	97.5	97.9
6	5	99.1	97.7
5	–	94.7	95.7
7	–	97.5	97.8
9	–	97.1	97.3
10	–	97.5	97.3
11	–	97.8	97.8
12	–	98.0	–

indicated that there was no advantage in carrying out the precipitation in two stages since a reproducible recovery of 97.5 ± 1%, similar to the optimum, could be obtained by one addition of thionalide provided that at least 7 ml of 2% thionalide was used.

Mineralisation of thionalide precipitate

Owing to the volatility of arsenic, particularly in the presence of halide, there seemed a possibility that some loss of the element might occur during destruction of the precipitate if the latter retained traces of chloride. However, no loss of arsenic could be detected even in the presence of 1 mg of chloride when decomposition of the precipitate was carried out by prolonged heating with concentrated nitric acid in a loosely stoppered flask, followed by evaporation to dryness of the resultant solution on a hot plate.

Photometric determination of arsenic

A review of the literature suggested that photometric methods based on the formation of arsenomolybdenum blue offered the greatest sensitivity for the determination of arsenic. In these procedures arsenomolybdic acid, formed by the reaction of arsenate with acidified molybdate, is reduced to a blue complex, the absorption of which is measured. Stannous chloride has been used for the reduction by a number of workers[25-27], but produces colours which soon fade. If hydrazine sulphate[28-31] is employed the colour is stable, but the reduction is so slow that it is necessary to carry out the reaction at 100°. Ascorbic acid also yields a stable colour, but again the reduction is slow and requires several hours for completion. Recently, MURPHY AND RILEY[32] have described a photometric procedure for the determination of phosphate, in which a stable intense blue-violet complex was produced rapidly by treating the sample with a reagent consisting of an acidified molybdate solution containing ascorbic acid and a small amount of antimony. These workers observed that this reagent gave an analogous compound with arsenate. The optimum reagent composition for the determination of arsenic by this process was therefore investigated.

The main factor controlling the formation of heteropoly-molybdenum blues is the relative proportion of acid and molybdate present; the amount of reducing agent has only a minor influence provided that it is above a critical level. In order to investigate the optimum conditions for the determination of arsenic, 10-ml aliquots of distilled water containing 100 μg of arsenic as arsenate were treated with mixed reagents each containing varied amounts of 2% (w/v) ammonium molybdate and 4 N sulphuric acid, together with 1 ml of 0.274% (w/v) potassium antimony tartrate solution and 5 ml of 2% (w/v) ascorbic acid. The solutions were diluted to 50 ml and mixed well. After colour development was complete, the optical densities were measured at 866 mμ. The full colour intensity was rapidly attained in solutions of low acidity but only occurred after up to 6 h in solutions of high acidity. Blank determinations were carried out using 10-ml aliquots of distilled water. The results of these experiments (Table II) indicated that satisfactory sensitivity coupled with a low reagent blank could be obtained with final solutions which were 0.6 N with respect to sulphuric acid and 0.12% with respect to ammonium molybdate. Under these conditions, however, the colour development was slow and it was decided to compromise on a reagent which gave concentrations of sulphuric acid and ammonium molybdate of 0.4 N and 0.12% respectively in the final solution.

With a mixed reagent giving these concentrations, the colour was completely developed after 30 min at room temperature. The absorption at the wavelength of maximum absorption (866 mμ) remained constant for at least 6 days, although some change did occur in the colour and absorption spectrum of the complex during this time. By analogy with phosphate[32], it is likely that the coloured complex contains antimony as well as arsenic and this is borne out by the fact that the absorption maximum is at a higher wavelength that that produced in the absence of antimony (835 mμ), or when another reducing agent is used. The colour produced in the presence of antimony is *ca.* 19% less intense than that produced by a combined reagent without antimony.

TABLE II

EFFECT OF VARIATION OF AMMONIUM MOLYBDATE AND SULPHURIC ACID CONCENTRATIONS ON OPTICAL DENSITIES IN DETERMINATION OF ARSENIC

(Measured at 866 mμ in 1-cm cells unless otherwise stipulated)

ml of 4 N H_2SO_4	*ml of 2% ammonium molybdate*						
	1	*2*	*3*	*4*	*5*	*7*	*10*
2.5 Blank	0.001	—	0.020	—	—	—	—
2.5 100 μg As	0.628		0.893	—	—	—	—
5.0 Blank	0.003	0.005	0.005	0.015	0.017	0.035	—
5.0 100 μg As	0.026	0.610	0.624	0.645	0.761	1.063	—
7.5 Blank	0.000[a]	—	0.002[a]	—	0.001[a]	0.005	—
7.5 100 μg As	0.001[a]	—	0.628	—	0.613	0.613	—
10.0 Blank	0.000[a]	—	0.000[a]	—	0.002[a]	0.003[a]	0.005[a]
10.0 100 μg As	0.001[a]	—	0.000[a]	—	0.613	0.620	0.620
15.0 Blank	0.000[a]	—	0.001[a]	—	0.002	0.002[a]	0.004[a]
15.0 100 μg As	0.000[a]	—	0.002[a]	—	0.000[a]	0.083	0.571

[a] Measured in 4-cm cells corrected to 1-cm cell.

It was not found possible to find conditions for the reaction under which there would be no interference from phosphate. This is not of importance since arsenic can be separated from several thousand times its own weight of phosphate by thionalide cocrystallization. It is, however, possible to render the combined reagent insensitive to arsenate, and still maintain the sensitivity to phosphate by increasing the sulphuric acid concentration in the mixed reagent to 7.2 *N*.

Calibration curve and reproducibility

Calibration runs for μg amounts of arsenic are shown in Table III. It was found that Beer's law was obeyed up to at least 120 μg of arsenic in a 50-ml final volume (1-cm cell).

The reproducibility of the photometric procedure was tested by determining 35-μg, 20-μg and 4-μg aliquots of arsenic and diluting to final volumes of 25 ml and measuring in cells of appropriate length; coefficients of variation of 0.3, 0.2 and 0.8% respectively were found.

TABLE III

CALIBRATION OF PHOTOMETRIC PROCEDURE

A[a]			*B*[b]		
μg As	*Optical density*	*O.D. increment/μg As*	*μg As*	*Optical density*	*O.D. increment/μg As*
1.0	0.049	0.049	1.0	0.117	0.117
2.0	0.096	0.048	2.0	0.235	0.117_{5}
4.0	0.189	0.047	3.0	0.360	0.120
6.0	0.285	0.047_{5}	4.0	0.458	0.116_{5}
8.0	0.375	0.047	5.0	0.588	0.117
10.0	0.473	0.047	6.0	0.703	0.117
12.0	0.566	0.047			
14.0	0.667	0.049			
16.0	0.764	0.048			

[a] Measured in 4-cm cells at 866 mμ. Developed in 25-ml flasks.
[b] Measured in 4-cm cells at 866 mμ. Developed in 10-ml flasks.

Interferences

The possible interference in the photometric procedure of elements which cocrystallize with thionalide from acid solutions was tested by carrying out determinations in the presence of these elements, both alone and in the presence of 4 μg of arsenic (final volume of solution 10 ml). The results of these experiments are shown in Table IV, and indicate that no interference is likely in the determination of arsenic in sea water or in most sediments, silicate rocks or marine organisms. The interference found for copper is entirely caused by the absorption band of the copper(II) ion and a determination carried out on 1 mg of copper with the omission of the reagent gave an optical density of 0.054.

TABLE IV

INVESTIGATION OF CATIONS COCRYSTALLIZING WITH THIONALIDE ON PHOTOMETRIC DETERMINATION OF ARSENIC

Metal added	*Weight added (10 ml)*	*Optical density at 866 mμ*[a]	
		No added As	*With 4 μg As*
—	—	—	0.460
Antimony	10 μg	0.000	0.460
Bismuth	1 mg	0.003	0.442
Copper	1 mg	0.055	0.517
Gold	1 mg	0.005[b]	0.458[b]
Mercury	1 mg	0.003[b]	0.455[b]
Platinum	1 mg	0.018	0.460
Silver	1 mg	0.010[b]	0.488[b]
Tin	10 μg	−0.006	0.452

[a] Less reagent blank, measured in 4-cm cell.
[b] Centrifuged to remove precipitate.

EXPERIMENTAL

Apparatus

A Unicam S.P. 500 spectrophotometer was used for all spectrophotometric measurements. Measurements of ^{74}As activity in testing recoveries were made by means of a NaI (Tl) well crystal used in conjunction with an Ecko N664A scintillation counter and Ekco N530F scaler.

Reagents

Ascorbic acid solution, 5% (w/v). Prepare as required.

Thionalide solution, 2% (w/v) in acetone. Prepare as required.

Sulphuric acid, 5 N. Prepare from "Arsenic-free" acid.

Ascorbic acid solution (0.1 M), 1.76% (w/v) in distilled water. This solution should be stored at 0°, and should be rejected when it becomes oxidized.

Potassium antimonyl tartrate solution (1 mg Sb/ml), 0.274% (w/v) in distilled water.

Mixed reagent. Mix 50 ml of 5 *N* sulphuric acid, 15 ml of 4.8% (w/v) ammonium molybdate solution, 5 ml of potassium antimony tartrate solution and 30 ml of 0.1 *M* ascorbic acid. Dilute to 125 ml. This reagent should be used within 1 h of its preparation as it is unstable.

Standard arsenic solution

Prepare a stock solution of arsenic containing 100 µg As^{5+}/ml using sodium arsenate which has been assayed gravimetrically. Working solutions containing 1 µg As/ml should be prepared when required as they are said to be unstable[33].

Treatment of graduated apparatus

Fill all graduated flasks to be used in the determination of arsenic with concentrated sulphuric acid and allow to stand overnight. Rinse them thoroughly before use.

Determination of arsenic in sea water and natural waters

Place 1 l of the filtered sea water in a 2-l Erlenmeyer flask, add 4 ml of 5% ascorbic acid, cover the flask with a watch glass and heat to boiling on a hot plate in order to reduce arsenic to the tri-positive state. Remove from the hot plate and allow to cool for 10 min. Add a further 2 ml of 5% ascorbic acid and then cool to room temperature. Add, while stirring with a magnetic stirrer, 10 ml of 5 *N* sulphuric acid followed by 7 ml of thionalide solution. Stir for 5 min to coagulate the precipitate. Allow to stand for 10 min, heat to boiling on the hot-plate and boil gently for 30 min to remove all the acetone. Cool again and stir to coagulate the precipitate. Allow to stand overnight at room temperature and filter off the precipitate with gentle suction, using a 4.25 cm diameter Whatman No. 541 filter paper. Wash the precipitate and filter with distilled water.

Place the filter paper and precipitate in a 25-ml Erlenmeyer flask and add 7.5 ml of concentrated nitric acid. Close the flask with a bulb stopper and heat it gently on a hot plate until the solution is pale yellow (24–36 h). Remove the bulb stopper, rinse it with a little water and evaporate the nitric acid on a fairly cool hot plate. When a viscous yellow liquid remains, continue to heat gently while blowing in a current of carbon dioxide to remove residual nitric acid which otherwise interferes in the subsequent photometric determination. Continue to pass the gas until dense white fumes are no longer evolved. Care must be taken to avoid heating too strongly at this stage or charring may occur; if this should happen, add 1 ml of nitric acid and repeat the evaporation. Cool the residue, which should set to a pale yellow solid, add 1 ml of 1 *N* sulphuric acid and warm gently, until the solid has dissolved. Transfer the solution quantitatively to a 10-ml volumetric flask, add 2 ml of the mixed reagent and dilute to 10 ml. After not less than 30 min, measure the absorbance of the solution at 866 mμ using 4-cm cuvettes. The yellow colour of the solution may partially mask the visual blue colour of the arsenomolybdenum blue complex, but does not interfere with the spectrophotometric measurement. Determine the reagent blank for the method by carrying out the full procedure on a 1-l sample of sea water from which arsenic has been removed by coprecipitation with ferric hydroxide (equivalent to 20 mg Fe^{3+}/l). The reagent blank should not exceed 0.100 in a 4-cm cell (equivalent to *ca.* 1 μg of arsenic). Calibrate the photometric procedure by treating 2 and 5 ml of the working standard arsenic solution with 2 ml of the mixed reagent, diluting to 10 ml and measuring at 866 mμ in 4-cm cuvettes after not less than 30 min. Carry out a corresponding blank on distilled water.

Determination of arsenic in silicate rocks and sediments

Weigh *ca.* 0.25 g of the silicate rock into a silver crucible, add 1.5 g of sodium hydroxide and fuse in a muffle furnace at 750° for 10 min. After cooling, leach the fused cake with *ca.* 50 ml of water, and leave the solution to stand overnight to allow the insoluble material to settle. Filter through a hardened filter paper (Whatman No. 51) using suction, and wash the insoluble material thoroughly with distilled water. Transfer the filtrate and washings to a 1-l Erlenmeyer flask, dilute to *ca.* 500 ml and add 15 ml of 5 *N* sulphuric acid and 1 ml of ethanol. Heat for a few minutes on the hot plate to reduce any manganate formed in the fusion. Continue the analysis as described for sea water, reducing arsenic to the tri-positive state with ascorbic acid, cocrystallizing it with thionalide and determining it photometrically after destruction of the thionalide. Determine the reagent blank in the same way.

Determination of arsenic in marine plants

Weigh out *ca.* 1 g of the washed plant material into a 500-ml Erlenmeyer flask, add 15 ml of redistilled nitric acid and close the flask with a bulb stopper. Gently heat the flask on the hot plate until the sample is completely oxidized; if necessary add a further 10 ml of nitric acid. When a clear solution remains, remove the bulb stopper and gently evaporate the solution to dryness. Care must be taken to avoid overheating the residue as this tends to make it less soluble. Dissolve the residue in distilled water containing 10 ml of 5 *N* sulphuric acid, warming if necessary; dilute to *ca.* 500 ml. Cocrystallize the arsenic and determine it photometrically as described for sea water. Run a reagent blank through the whole process.

RESULTS

Accuracy and precision of methods

Sea water. The reproducibility of the method was tested by carrying out 7 replicate analyses on 1 l aliquots of filtered sea water; these showed an average arsenic concentration of $2.0 \pm 0.02_6$ μg/l, *i.e.* a coefficient of variation of 1.3%. In order to test the efficiency of recovery of arsenic from sea water, 1-l aliquots of a sample of sea water, from which arsenic had been removed by coprecipitation with ferric hydroxide were spiked with known amounts of arsenic and then analysed. The results of these experi-

TABLE V

RECOVERY OF ARSENIC FROM "ARSENIC-FREE" SEA WATER (1 l) TO WHICH INCREMENTS OF ARSENIC HAD BEEN ADDED

Arsenic present (μg)	2.0	4.0	5.0	6.0	8.0
Arsenic found (μg)	1.9	4.2	4.7	5.9	8.2

ments, which are summarized in Table V, indicate that the overall recovery in the analytical process is 99 ± 3.2%, a figure in good agreement with the percentage recovery found by tracer techniques (97.5%).

Silicates. Replicate analyses (7) were carried out on a red clay sample (from 34°11'N, 55°32'W) which had been washed free from chloride and dried at 105°. These showed the presence of 6.6 ± 0.17 μg As/g. As a check on the recovery of arsenic, 0.25 g of the same red clay sample (1.67 μg As) was spiked with known amounts of arsenic (2 and 3 μg) and then analysed; satisfactory recoveries of arsenic were obtained (3.5 and 4.6 μg, respectively). The U.S. Geological survey standard granite G 1 was found to contain 1.2 μg As/g; this sample was found by ONISHI AND SANDELL[17] to contain 1.0 μg As/g.

Marine plants. Replicate analyses (8) were carried out on an air-dried, well-washed specimen of *Fucus serratus* and showed the presence of 1.67 μg ± 0.03 As/g. Analyses carried out on the specimen after spiking with known amounts of arsenic (*ca.* 1 μg/g) showed that the recovery was satisfactory (95 ± 4%).

Storage of sea water samples

Since several days usually elapse between sampling of water and its analysis, experiments were carried out to determine whether arsenate is adsorbed by glass or polyethylene containers. Aliquots (500 ml) of filtered sea water (0.5 μ membrane filter) which had each been equilibrated with 5 μC of arsenic-74 were placed in 1-l bottles made of high density polyethylene, soda glass and Pyrex glass. The sample bottles were stored in the dark and the γ-activity of the sea water which they contained was measured at intervals over a period of 5 weeks, and corrected for loss due to radioactive decay occurring since the beginning of the experiment. Comparison of this value with the activity originally present enabled the loss of arsenic from the sea water to the walls of the bottles to be computed. It was found that losses of arsenate occurred with all the types of bottle. With soda glass bottles *ca.* 16% of the arsenate had been adsorbed by the 16th day, when equilibrium was attained. The uptake by polyethylene and Pyrex bottles was complete within 10 days and in both cases amounted to *ca.* 6%. It is thus evident that for the greatest precision, the cocrystallization of arsenic should be carried out within a few days of collection of the sample and that until the analysis is carried out, the samples should be stored, preferably frozen, in polyethylene bottles.

SUMMARY

Cocrystallization with thionalide in a 0.05 *N* sulphuric acid medium is proposed for the recovery of microgram amounts of arsenic from sea water and from solutions prepared by the decomposition of silicates and marine plants. After destruction of the organic precipitant, arsenic is determined photometrically by means of a single-solution molybdenum blue method. The overall recovery for the whole process is 97–98%. Arsenic was determined in sea water with a coefficient of variation of 1.3% at a level of 2 µg As/l. Coefficients of variation of 2.6% and 1.7% were found for the determination of the element in marine sediments and plants at levels of 6.6 µg/g and 1.7 µg/g respectively. The U. S. Geological survey standard granite G 1 was found to contain 1.2 µg As/g.

RÉSUMÉ

Les auteurs proposent une méthode par cocristallisation avec la thionalide, pour recueillir l'arsenic (en quantités de l'ordre du microgramme) dans l'eau de mer et dans des solutions provenant de la décomposition de silicates et de plantes marines. Après destruction du réactif organique, l'arsenic est dosé photométriquement au moyen de la méthode au bleu de molybdène.

ZUSAMMENFASSUNG

Zur Bestimmung von Mikrogrammen Arsen in Seewasser und in Lösungen, die durch Zersetzung von Silikaten und Meerpflanzen entstanden, wird die gemeinsame Fällung mit Thionalid in 0.05 *N* schwefelsaurem Medium vorgeschlagen. Nach der Zerstörung des organischen Niederschlages wird das Arsenik photometrisch mit der Molybdänblaumethode bestimmt. Die Ausbeute für den gesamten Prozess beträgt 97–98%. Der Variationskoeffizient betrug bei verschiedenen Materialien 1.3%, 1.7% und 2.6% bei Arsengehalten von 2 µg/l, 1.7 µg/l bzw. 6.6 µg/l.

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SYSTEMATIC ANALYSIS BY SOLVENT EXTRACTION METHODS

PART I. QUALITATIVE ANALYSIS

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(Received May 9th, 1964)

Although the technique of solvent extraction has long been known and exploited, little attempt has been made to apply it systematically to separation schemes in analysis, the notable exception being the scheme developed by WEST AND MUKHERJI[1] for the detection of 35 cations by means of solvent extraction and ring-oven techniques. As most of the species involved in solvent extraction partitions are coloured coordination complexes, their separation should provide a means for both their identification and determination. This paper will describe a qualitative scheme of analysis, and Part II will give some quantitative methods.

Since all systematic schemes of separation are based on a punched-card technique of sorting into groups of substances which possess a common characteristic, and then dividing the members of a group into sub-groups or individuals, the first task was to investigate the extraction of complexes of the ions chosen for investigation. The criteria for choice of complex-forming reagents were cheapness, availability, and ability to form neutral chelate compounds which would be readily soluble in organic solvents. The complexes of four reagents—acetylacetone, dithizone, sodium diethyldithiocarbamate, and 8-hydroxyquinoline—with the common metal ions were investigated. The solvents used were chloroform, carbon tetrachloride, and a mixture of chloroform and acetone. The effect of some common anions (especially those known to form metal complexes) on the extractions was also investigated. An extraction was regarded as analytically useful if it was essentially complete in three successive extractions with volumes of solvent equal to the volume of the aqueous phase (equivalent to a partition coefficient of at least 9).

EXPERIMENTAL

Apparatus

The apparatus used for the extractions was a modification of that described by CARLTON[2]. It consisted of a glass bulb of 20-ml capacity, pulled out to a fine jet at one end and connected to a small splash bulb at the other. The splash bulb was in turn attached to a rubber bulb of 20-ml capacity. By pressure and release of the bulb, the aqueous and organic phases, contained in a beaker, may be drawn into and pushed

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out of the apparatus and so thoroughly mixed. When extraction equilibrium has been reached, the mixture is drawn up into the apparatus, the two layers allowed to separate, and then the lower layer is expelled quantitatively by gentle pressure on the bulb.

Preliminary tests

The pH of 5 ml of the solution to be tested was adjusted by means of dilute ammonia or nitric acid solution and measured on a pH meter. The maximum pH normally used was 10. The solution was extracted with three 5-ml portions of reagent solution and washed once with 5 ml of the organic solvent. The aqueous phase was then tested for any residual cation. The process was repeated at different pH values and cation concentrations and in the presence and absence of chloride, nitrate, sulphate, cyanide, acetate, phosphate, citrate and tartrate. The cations tested were Al, Sb(III), As(III), As(V), Ba, Bi, Cd, Ca, Cr(III), Cr(VI), Co(II), Cu(II), Fe(III), Pb, Mg, Mn(II), Hg(II), Ni, Ag, Sr, Sn(IV) and Zn.

Acetylacetone

The reagent was used as a 20% solution in chloroform. Data for the species extracted are shown in Table I. Extraction occurred over the whole pH range indicated, but was maximal over only part of it. Cations not shown were not extracted. Citrate and tartrate interfered only in large amounts.

TABLE I

EXTRACTION OF ACETYLACETONATES

Cation	*Colour of complex*	*pH range for extraction*	*Maximum extracted (mg)*	*pH range of maximal extraction*	*Anions interfering*
Al	White	5–10	0.5	8–10	Citrate, tartrate
Cu	Blue-green	1–10	2	7–10	Cyanide
Fe	Orange	0–7	1.5	0–4	Citrate, tartrate
Mn	White	6–10	0.5	6–10	Cyanide
Zn	White	5–10	Very little	5–10	

8-Hydroxyquinoline

The reagent was used in chloroform solution. The results are shown in Table II. Citrate and tartrate interfered only if present in large quantity.

Sodium diethyldithiocarbamate

The complexes were formed on addition of an excess of a 1% aqueous solution of the reagent and were then extracted with either chloroform or a mixture of chloroform and acetone (5:2, v/v). The results are given in Table III.

Dithizone

The reagent was used as a saturated solution in chloroform. The results are given in Table IV.

TABLE II

EXTRACTION OF 8-HYDROXYQUINOLINATES

Cation	*Colour of complex*	*Concn. of reagent (%)*	*pH range of extraction*	*Maximum extracted (mg)*	*pH range of maximal extraction*	*Interfering anions*
Al	Yellow	0.5	2.8–10	0.4	4.6–6.5 8.0–10	Citrate[a], tartrate, phosphate
Ba	Yellow	3.0[b]	11–12	0.5	11–12	Citrate, tartrate, sulphate
Bi	Yellow-orange	0.5	1.9–10	0.5	2.2–5.2	Citrate below pH 5.6
Ca	Yellow	0.5[b]	10–12	0.5	10–12	Citrate, tartrate, sulphate
Cd	Yellow-orange	0.5	7.0–10[c]	0.5	8.5–10	Cyanide
Co	Yellow-orange	0.5	2.6–10	0.5	3.6–10	Cyanide
Cu	Yellow-orange	0.5	1.0–10	0.5	1.6–10	Cyanide
Fe	Black	0.5	1.2–5.5	0.5	2.0–3.0	Citrate[d]
Pb	Yellow-orange	0.5	4–10	0.5	7.5–10	
Mg	Yellow	0.5[b]	9–10	0.5	9–10	
Mn	Yellow	0.5	6.4–10	0.5	9.5–10	Cyanide
Hg	Yellow-orange	0.5	4.5–10	0.5	6.5–10	Cyanide, acetate
Ni	Yellow-orange	0.5	2.6–10	0.5	6.5–10	Cyanide
Ag	Yellow	0.5	7.0–10	0.1	8.5–10	Chloride, cyanide, citrate
Sr	Yellow	3.0[b]	11–12	0.5	11–12	Sulphate, citrate, tartrate
Zn	Yellow-orange	0.5	4.0–10[c]	0.25	8–10	Cyanide

[a] Interference eliminated by addition of 10 drops of *n*-butylamine.
[b] In presence of *n*-butylamine (2–3 drops per extraction).
[c] Colour fades rapidly and yellow precipitate appears in organic phase.
[d] Extraction is complete from pH 2 to pH 10 from tartrate solution.

The results obtained are in general agreement with those obtained by other workers[3–11] and can be used as the basis for a systematic scheme of separation. The scheme should satisfy certain conditions:

(*a*) at least 500 μg of any ion should be removable from 5 ml of aqueous solution in not more than 3 extractions with 5-ml portions of reagent or solvent;

(*b*) there should be no subdivision of an ion between groups;

(*c*) there should be no interference from any anions present;

(*d*) exact adjustment of pH should not be necessary.

Such a scheme has been compiled from the extraction data reported above, with some modifications imposed by the mode of preparation of the test solution. Normally, chromium(III) would not be extracted by any of the reagents used and would appear at the end of the analysis in the residual aqueous phase. On addition of ammonia, however, chromium hydroxide is precipitated even in the presence of citrate (added

TABLE III

EXTRACTION OF DIETHYLDITHIOCARBAMATES

Cation	*Colour of complex*	*pH range of extraction*	*Maximum extracted (mg)*	*pH range of maximal extraction*	*Solvent*	*Interfering anions*
Sb	Cream	0–10	3.0	0–7	Mixed	Large amounts of cyanide
As(III)	White	0–9.5	2.0	0–8	Either	
As(V)	White	0–9.5	2.0	0–8	Either	
Bi	Yellow	0–10	0.5	8–10	Chloroform	
				0–10	Mixed	
Cd	White	1–10	1.5	1–10	Mixed	Cyanide
Cr(VI)	Grey-blue	0–7	0.1	1–7	Either	
Co	Green	0–10	1.5	0–10	Mixed	Cyanide
Cu	Brown	0–10	0.5	0–10	Mixed	Cyanide
Fe	Brown	0–5	0.5	0–5	Either	Cyanide
Pb	White	1–10	1.5	1–10	Mixed	
Mn	Wine	1–10	1.0	1–7	Mixed	Cyanide
Hg	White	0–10	0.5	0–10	Either	
Ni	Yellow-green[a]	0–8	1.5	0–8	Either	Cyanide
Ag	White	0–10	0.5	0–10	Mixed	Cyanide
Sn	Orange	1–8	2.5	1–8	Either	
Zn	White	1–10	0.5	1–7	Chloroform	Cyanide
				1–10	Mixed	

[a] Brown-red in presence of nitric acid.

TABLE IV

EXTRACTION OF DITHIZONATES

Cation	*Colour of complex*	*pH range of extraction*	*Maximum extracted (mg)*	*pH range of maximal extraction*	*Interfering anions*
Bi	Red-brown	0.2–1.5 1.5–10[a]	1.0[a]	1.5–10[a]	Chloride, citrate, tartrate
Cd	Red	2.5–10	0.5	5–10	Cyanide, citrate, tartrate
Co	Violet	3.5–10	0.5	6–10	Nitrate, cyanide
Cu	Red-brown	1–10	0.5	1–10	Citrate, tartrate, cyanide
Pb	Red	3–10	0.5	7–10	Sulphate, citrate, phosphate, tartrate
Mn	Deep red	8–10	Very poor		Cyanide
Hg	Orange	1–10	1.5	1–10	Cyanide, chloride
Ni	Violet	4–10	0.5	6–9	Cyanide
Ag	Orange	1–10	2.0	1–10	Chloride, bromide, iodide, cyanide
Sn	Brick red	5.5–10	0.5	8–10	Cyanide
Zn	Red	2.5–10	0.5	6–10	Cyanide, large amounts of chloride, phosphate, citrate, tartrate

[a] From medium containing some citrate.

in small amount to prevent precipitation of hydroxides) unless the test sample is first dissolved in concentrated nitric acid, in which case a stable nitrato complex is formed. If tin(IV) is present, treatment with nitric acid removes it from solution as metastannic acid. If nitric acid is not used to complex the chromium(III) then on addition of ammonia to adjust the pH, chromium hydroxide is precipitated. Chromium(VI) would appear in two groups of the scheme, and must therefore be separately extracted as chromium peroxide. Any interfering anions must be removed by treatment with nitric acid.

Procedure

Prepare the test solution so that it contains no more than 25 mg of total sample or 500 μg of any individual metal in 5 ml of solution. Remove any interfering ions such as cyanide, halide, or large amounts of organic acids which form metal complexes, by adding concentrated nitric acid and evaporating to dryness. Add 50 mg of citric acid to 5 ml of test solution to prevent formation of metal hydroxides (this amount of citrate is not enough to affect the extractions). Proceed according to Table V, and examine the groups obtained, according to the separation schemes described.

TABLE V

SCHEME OF GROUP SEPARATION

Take 5 ml of solution, make ammoniacal, and centrifuge if a precipitate forms.

Group I	Cr(III)	Reduce pH of aqueous solution to about 1.5 with dilute nitric acid. Extract with 20% acetylacetone in chloroform.
Group II	Fe Cu	Extract with saturated solution of dithizone in carbon tetrachloride till no further colour change occurs.
Group III	Ag Hg(II) Bi	Add 2–3 drops 20-vol. hydrogen peroxide. Extract with ethyl acetate.
Group IV	Cr(VI)	Increase pH to 10 with conc. ammonia. Add 1% aqueous sodium diethyldithiocarbamate till no further precipitation. Extract with 5:2 chloroform and acetone.
Group V	Ni Co Mn Zn Sb(III) Pb Cd	Reduce pH to about 5 with dilute hydrochloric acid. Add sodium diethyldithiocarbamate solution till precipitation is complete. Extract with acetone–chloroform mixture.
Group VI	Sn(IV) As(V)	Raise pH to about 10 with ammonia. Add 10 drops *n*-butylamine. Extract with 0.5% oxine in chloroform.
Group VII	Al Mg	
Group VIII	Ca, Sr, Ba, and Cr(III) if solid was dissolved in conc. nitric acid.	

Identification reactions

Group I. Dissolve the precipitate in 1 ml of dilute nitric acid. Place one drop of the solution on test paper, add one drop of concentrated sodium peroxide solution and one drop of benzidine reagent[12]. A blue stain indicates chromium. Limit of identification — 30 μg/5 ml sample.

Group II. Back-extract the organic phase with 5 ml of 6 *N* hydrochloric acid. *Very cautiously* add 2 ml of concentrated sulphuric acid to the aqueous extract. Extract this solution with three 4-ml portions of amyl alcohol. To the organic phase add 2–3 drops of a saturated acetone solution of potassium thiocyanate. A red colour indicates iron. Limit of identification — 25 μg/5 ml. To the aqueous phase add ammonia till the pH has been raised to about 10. Add 2–3 drops of 1% sodium diethyldithiocarbamate solution and extract with 2–3 ml of chloroform. A yellow-brown colour in the extract indicates copper. Limit of identification — 20 μg/5 ml.

Group III. Back-extract the organic phase with two 5-ml portions of 0.2 *N* nitric acid. To the acid phase add 2–3 drops of cinchonine–potassium iodide reagent[14]. Appearance of an orange colour or precipitate indicates bismuth; limit of identification — 30 μg/5 ml. Wash the organic phase with 5 ml of water and then back-extract with 5 ml of *N* sodium chloride at pH 1. Increase the pH of the aqueous phase to 8–10 with dilute ammonia and extract with dilute dithizone solution in carbon tetrachloride. A red-orange colour in the organic layer shows the presence of silver;

TABLE VI

SCHEME OF ANALYSIS FOR GROUP V

<table>
<tr><td colspan="3">Back-extract the organic layer with 5 ml of *N* hydrochloric acid.</td></tr>
<tr><td rowspan="2">*Acid layer*: Increase pH to about 8 with dilute ammonia and add 2 ml 10% potassium cyanide solution. Extract with dilute dithizone in carbon tetrachloride. If organic layer turns red, lead is present. Limit of detection — 20 μg/5 ml.
Decrease pH of solution to about 1 and add formaldehyde till a yellow colour develops. Raise the pH to 8 with dilute ammonia. Extract with dilute carbon tetrachloride solution of dithizone. If a red colour appears in the organic phase then zinc and/or cadmium is present. Extract all of it. Back-extract 5 ml of the organic phase with 5 ml of 0.25% EDTA solution. If no change in colour occurs in the organic phase only zinc is present. If the organic layer turns purple both zinc and cadmium are present. If the organic phase turns green then only cadmium is present. Limits of detection: zinc — 50 μg/5 ml, cadmium — 50 μg/5 ml.</td><td colspan="2">*Organic layer*: Back-extract with two 5-ml portions of 10% potassium cyanide solution.</td></tr>
<tr><td>*Cyanide layer*: Divide into two.
(*a*) Acidify with dilute nitric acid, boil, cool and add 1 ml potassium ethyl xanthate solution and extract with 2 ml chloroform. An orange colour in the organic layer shows nickel present. Limit of detection — 30 μg/5 ml.
(*b*) Add formaldehyde till a yellow colour appears. Add 5 ml concentrated hydrochloric acid. Oxidise with ceric sulphate. Destroy excess oxidant with hydroxylamine hydrochloride. Add 2 ml of rhodamine-B solution and extract with 2 ml of benzene. A purple colour in the organic layer indicates antimony. Limit of detection — 20 μg/5 ml.</td><td>*Organic layer*: Evaporate to dryness.
Dissolve residue in about 1 ml concentrated nitric acid and dilute to about 3 ml.
(*a*) Add one drop to paper, add one drop 2 *N* sodium hydroxide and one drop of benzidine reagent. A blue stain shows manganese present. Limit of detection — 20 μg/5 ml.
(*b*) To 1 ml of the solution add 5 ml of saturated acetone solution of potassium thiocyanate. A blue colour indicates cobalt. Limit of detection — 30 μg/5 ml.</td></tr>
</table>

limit of identification — 20 µg/5 ml. Wash the organic phase left from the sodium chloride extraction with 5 ml of water, and back-extract with 5 ml of *N* potassium iodide solution at pH 1. Increase the pH of the aqueous extract to about 8 with dilute ammonia and extract with a dilute carbon tetrachloride solution of dithizone. An orange colour in the organic phase indicates mercury. The limit of identification is 20 µg/5 ml.

Group IV. No further test is required to prove the presence of chromium(VI). The blue colour in the organic phase is specific; limit of identification — 30 µg/5 ml.

Group V. This is the largest group and its subdivision is described in Table VI.

Group VI. Evaporate the organic layer to dryness and dissolve the residue in concentrated hydrochloric acid. Dilute with an equal volume of water and divide into two. To the first portion add a crystal of mercuric cyanide and 0.5 g of sodium hypophosphite and boil. Add one drop of the solution to a cacotheline test paper. An immediate purple coloration indicates tin. Limit of detection — 30 µg/5 ml. To the second portion add a zinc pellet and hold silver nitrate test paper in the gases evolved. Development of a black stain indicates arsenic. Limit of identification — 20 µg/5 ml.

Group VII. Back-extract the organic phase with 6 *N* hydrochloric acid. Raise the pH to 5–6 with 2 *N* sodium hydroxide and extract with 2–3 ml of chloroform. If the chloroform extract is yellow and has a green fluorescence in ultraviolet light then aluminium is present. Limit of identification — 30 µg/5 ml. Evaporate the aqueous phase to a volume of about 1 ml. Take 5 drops of this solution, and add 1 drop of magneson reagent and 5 drops of 2 *N* sodium hydroxide. Development of a blue colour indicates magnesium. Limit of detection — 20 µg/5 ml.

Group VIII. Evaporate the final aqueous phase to about 1 ml. Carry out the following tests:

(*a*) If the original solution was prepared with concentrated nitric acid, test for chromium by taking on a test paper one drop of the evaporated solution and adding to it 1 drop of concentrated sodium peroxide solution and 1 drop of benzidine reagent. A blue stain indicates chromium. Limit of detection — 30 µg/5 ml.

(*b*) To two drops of solution add 2 drops of concentrated ammonium ferrocyanide solution and 4 drops of alcohol and mix. A white precipitate or turbidity indicates calcium. Limit of detection — 50 µg/5 ml.

(*c*) To 10 drops of solution add 2 drops of 2 *N* acetic acid, 10 drops of 3 *N* potassium acetate and 3 drops of 3 *N* potassium chromate. If a yellow precipitate appears barium is present. Centrifuge and test the centrifugate for strontium. Limit of detection — 50 µg/5 ml.

(*d*) To the centrifugate from (*c*) add 6 drops of concentrated ammonia solution and 2 drops of 3 *N* potassium chromate. Heat to nearly boiling and slowly add 15 drops of alcohol. If a yellow precipitate appears strontium is present. Limit of detection — 100 µg/5 ml.

DISCUSSION

The limits of detection given all refer to the minimum amount of cation that could be detected if it was present in the original 5 ml of test solution. For most of the ions considered the minimum is about 6 µg per ml of solution, the main exceptions being the alkaline earths. On a 25-mg sample this represents about 0.1% of the sample weight. The maximum that can easily be handled is about 500 µg of any ion.

The scheme was tested by analysing various mixtures, first of the ions in Groups I to IV, V and VI, and VII and VIII, and then various alloys and solid mixtures which might contain any combination of the ions in the scheme. The only failures occurred once each with lead and strontium. The lead was present in a mixture containing 9 cations, 4 of which occurred in the lead group. Typical mixtures were:
Cu, Fe, Zn, Mn, Al, Mg alloy; Cu, Pb, Zn, Sb, Sn alloy; Pb, Cd, Zn, Mg, Al, Ca, Sr, Ba; Bi, Co, Mn, Ni, Sb, Cd, Zn, As, Sr; Hg, Bi, Cd, Zn, Sb, Sn, As, Mg, Pb; $K_2Cr_2O_7$, $AgNO_3$, $Hg(OAc)_2$, $NiCO_3$, ZnO, $CdCO_3$, Sb_2O_3, $Pb(OAc)_2$, SnO_2, As_2O_3, Al_2O_2, $Mg(OAc)_2$.

The advantages of the scheme over the classical precipitation methods are as follows.

(*a*) The effect of anions is minimised. Only those forming stable complexes interfere, and these can usually be removed first.

(*b*) Most of the metal complexes used are highly coloured and so easily detected, and completeness of extraction is easily checked.

(*c*) Separations between and within groups are clean, with the exception of the back-extraction of lead in the presence of large amounts of zinc and cadmium. These two metals are preferentially extracted and the lead may be left behind unless two or three further extractions with *N* hydrochloric acid are made.

(*d*) The scheme can be used in conjunction with the classical scheme to provide identification tests, especially as its groups cut across those of the classical scheme. In particular, group 2 of the classical scheme can be handled in this way without the notoriously unsatisfactory division into sub-groups.

(*e*) For many of the ions the method can be made quantitative by spectrophotometric measurements on the extracts. This aspect will be dealt with in Part II.

SUMMARY

A systematic scheme of separation by solvent extraction methods is described for 19 metals.

RÉSUMÉ

Une méthode systématique est décrite pour la séparation de 19 métaux, par extraction au moyen de solvants.

ZUSAMMENFASSUNG

Es wird ein systematisches Schema zur Trennung von 19 Metallen durch Lösungsmittelextraktion beschrieben.

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RUTHENIUM COMPLEXES OF LIGANDS CONTAINING THE FERROIN GROUP AS FLUORESCENT PRECIPITATION INDICATORS FOR IODIMETRY

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(Received April 8th, 1964)

The blue color of the complex formed when iodine is added to a solution containing starch and iodide is one of the most familiar of all titrimetric end-points. The widespread use of direct and indirect iodimetry must be considered to be due in part to the sensitivity and sharpness of the starch–iodine reaction. Starch, however, cannot be used under a number of conditions; these include titrations in highly colored or strongly acidic solutions or at elevated temperatures. Also, the preparation of starch solutions and their limited stability as aqueous dispersions are inconvenient, as is the necessity of adding the indicator near the end-point in indirect titrations to prevent the formation of irreversible starch–iodine complexes.

A variety of new indicators and numerous modifications of existing procedures have been suggested in attempts to circumvent these problems and have been summarized by KOLTHOFF AND BELCHER[1]. Most commonly the color of free iodine either in aqueous solution or extracted into CCl_4 or $CHCl_3$ has been used where starch will not function, but the faint yellow color of free iodine is not very satisfactory and extraction end-points are slow and tedious.

Complexes of ruthenium(II) with 2,2′-bipyridine, 1,10-phenanthroline and several methyl-substituted derivatives have been recently suggested as fluorescent oxidation–reduction indicators[2]. The methyl-substituted compounds have now been found to form very insoluble triiodide salts, and can be used as iodimetric indicators. The end-point in titrations with iodine is indicated by disappearance of the orange-red fluorescence of the ruthenium chelate and the concurrent appearance of a precipitate. These indicators have been investigated under a variety of conditions, and have been found to make possible rapid, accurate, visual titrations in several cases where starch is not applicable. They are stable in solution, sensitive and reversible.

EXPERIMENTAL

Chemicals and special reagents

Preparation of the ruthenium complexes of 1,10-phenanthroline (Ru(Ph)), 5-methyl-1,10-phenanthroline (Ru(5-MPh)), 5,6-dimethyl-1,10-phenanthroline (Ru-(5,6-DMPh)), and 4,4′-dimethyl-2,2′-bipyridine (Ru(DMBP)), has been previously described[2]. Solutions of the nitrate salts, 0.001 *M*, were used. Tris(2,2′-bipyridine) ruthenium(II) chloride (Ru(BP)) was obtained from the G. Frederick Smith Chemical Co., recrystallized, and a 0.001 *M* solution was prepared. Iodine and arsenic(III) solutions were prepared by weight from primary standard iodine and arsenic(III) oxide and checked against each other. A 0.2% starch solution was prepared from soluble starch and a trace of mercury(II) chloride added to retard spoilage. Other chemicals were reagent grade.

Apparatus

The apparatus used for the fluorescent titrations consisted of a mercury lamp (General Electric H-4) excitation source, blue filter (Corning No. 4304, maximum transmittance — 470 mμ) and condensing lens arranged to focus a narrow beam of radiation on the titration vessel, which was located in a black, open-top compartment. Magnetic stirring was used.

Sensitivity of the ruthenium complexes

A visual measure of the sensitivities of the complexes to triiodide was made by adding 3–4 drops of 0.001 *M* indicator solutions to approximately 25 ml of a series of successively more dilute solutions of iodine (prepared by dilution of a solution of 0.001 *N* iodine in 0.002 *N* KI with distilled water). Fluorescence is absent and a turbidity readily apparent at iodine concentrations down to about $4 \cdot 10^{-5}$ *N* for the methyl derivatives. This value is comparable to the values reported for starch, $2 \cdot 10^{-5}$ *N*, and free iodine, $4.5 \cdot 10^{-5}$ *N* (both viewed through a solution depth of 8 cm)[1].

Triiodide salts of the unsubstituted 1,10-phenanthroline and 2,2'-bipyridine ruthenium chelates are more soluble and show only partial fluorescence quenching at comparable iodine concentrations.

Titration procedure

Iodine titrations comparing the end-points of starch, free iodine, and the ruthenium indicators were carried out by pipetting portions of arsenite or thiosulfate solutions into a 100-ml beaker, adjusting conditions as required, adding indicator (2 ml of starch solution or 3–6 drops of fluorescent indicator) and titrating with 0.1 *N* iodine. Reverse titrations of iodine with thiosulfate were done in a similar manner.

For the studies at low concentrations, approximately 10^{-3} *N* solutions of thiosulfate and iodine were prepared by quantitative dilution of 0.1 *N* solutions that had been standardized against each other. Portions of 10^{-3} *N* thiosulfate were pipetted into a 100-ml beaker, indicator was added, and the solutions were titrated with iodine. Indicator blanks were run on 10-ml portions of distilled water. Two drops of ruthenium indicator or 0.2 ml of starch solution were used per titration. For the extraction end-points a 2-ml volume of CCl_4 was used.

RESULTS AND DISCUSSION

Results of titrations of arsenite and thiosulfate with iodine using various indicators are given in Table I. Fluorescence of all the ruthenium compounds diminishes at the equivalence point, but only with the methyl-substituted derivatives is the change satisfactory for indicator use. Here the first slight excess of iodine causes precipitation of the complex as the triiodide salt. The presence of a turbidity in the fluores-

TABLE I

COMPARISON OF INDICATORS FOR TITRATIONS OF ARSENITE AND THIOSULFATE WITH 0.1004 *N* IODINE

Indicator	*Arsenite found (mequiv.)*	% *Error rel.*[a]	*Thiosulfate found (mequiv.)*	% *Error rel.*[a]
Starch	0.995	—	0.929	—
	0.994		0.930	
	0.995		0.929	
Iodine	0.997	0.2	0.929	0
	0.998		0.930	
	0.997		0.929	
Ferroin	0.996	0.13	0.929	0.03
	0.997		0.929	
	0.995		0.929	
Nitroferroin	0.994	0.06	0.927	0.10
	0.995		0.928	
	0.997		0.930	
$Ru(BP)_3Cl_2$	0.998	0.3	0.929	0.07
	0.999		0.930	
	0.998		0.931	
$Ru(Ph)_3(NO_3)_2$	0.995	0.16	0.929	0.03
	0.996		0.930	
	0.998		0.930	
$Ru(5\text{-}MPh)_3(NO_3)_2$	0.995	0.03	0.928	0.10
	0.995		0.928	
	0.995		0.929	
$Ru(5,6\text{-}DMPh)_3(NO_3)_2$	0.995	0.10	0.928	0.06
	0.997		0.929	
	0.995		0.929	
$Ru(DMBP)_3(NO_3)_2$	0.995	0	0.930	0.07
	0.995		0.929	
	0.994		0.931	

[a] Error of average compared to starch.

cence excitation beam is very marked, and in combination with the disappearance of fluorescence provides an easily seen end-point. All the methyl-substituted ruthenium compounds, Ru(DMBP), Ru(5-MPh), and Ru(5,6-DMPh), give satisfactory end-points and were further investigated under a variety of conditions.

Indirect titrations

The methyl-substituted chelates can be added at the beginning of titrations of iodine with thiosulfate. This is not possible with starch because of the formation of irreversible reddish reaction products when iodine is present in greater than trace quantities. The triiodide salts dissolve rapidly at the equivalence point, giving sharp end-points that coincide with those of free iodine and starch (added just before the equivalence point).

Titrations in colored solutions

Comparisons of the various indicators in titrations of thiosulfate and arsenite in 0.02 *N* potassium cobalt(III) ethylenediaminetetraacetate (KCoEDTA) are given in Table II. Starch or free iodine end-points are obscured by the intense red color of the $CoEDTA^-$ anion at this concentration, while the fluorescent end-points are quite discernible.

TABLE II

COMPARISON OF VARIOUS INDICATORS FOR TITRATIONS WITH IODINE IN COLORED SOLUTIONS
(Solutions approximately 0.02 *N* in KCoEDTA at end-point)

Indicator	*Thiosulfate found (mequiv.)*	*Arsenite found (mequiv.) (1.001 mequiv. taken)*
Starch	1.015	1.017
	1.017	1.013
	1.015	
	1.011[a]	
Ru(5-MPh)	1.011[b]	1.001
	1.010[b]	1.001
	1.010[b]	
Ru(5,6-DMPh)	1.011	1.002
	1.011	1.001
	1.011	
Ru(DMBP)	1.011	1.002
	1.012	1.001
	1.011	
	1.011[a]	

[a] KCoEDTA not added.
[b] End-point poor but discernible.

Titrations at elevated temperatures

Starch is not used in titrations above room temperature because of reduced sensitivity. Ru(DMBP) is satisfactory to 75°, and Ru(5,6-DMPh) and Ru(5-MPh) to about 70° in titrations of arsenite with iodine. At higher temperatures the end-points are late because of the combined effects of increased solubility of the indicator triiodide salts and diminished fluorescence intensity.

Titrations in acid solutions

At high acid concentrations starch is hydrolyzed to glucose. The upper limit of acid concentration at which starch gives accurate end-points if the starch is added immediately before the equivalence point is about 4 *N* in sulfuric acid and 2.5 *N* in hydrochloric acid. All 3 ruthenium complexes function satisfactorily in thiosulfate titrations of iodine solutions up to 6 *N* in sulfuric acid or 4 *N* in hydrochloric acid. Thiosulfate rather than iodine was used as titrant at high acidities because thiosulfate decomposes to sulfite in acid solution. Results are accurate if stirring is efficient enough to avoid a local accumulation of thiosulfate, and if the acid is deaerated prior to titrating to avoid air-oxidation of iodide. At high acidities the ruthenium indicators must be added near the equivalence point rather than initially, otherwise the triiodide precipitates are slow to dissolve.

Titrations in dilute solutions

Results of titrations of 0.001 *N* thiosulfate with 0.001 *N* iodine are shown in Table III. Although the end-point is not as sharply defined as at higher concentrations, the appearance of a turbidity is readily seen and gives accurate and precise results. Neither starch nor carbon tetrachloride extraction of iodine is accurate at this dilution.

TABLE III

COMPARISON OF INDICATORS FOR TITRATIONS OF 10^{-3} *N* SODIUM THIOSULFATE WITH 10^{-3} *N* IODINE

Indicator	*Blank (μequiv. iodine)*	*Thiosulfate taken (μequiv.)*	*Thiosulfate found (μequiv.)*
Starch	1.09	10.34	10.03
	1.10		10.04
	1.09		10.01
Iodine	0.17	10.34	10.41
(CCl_4 extraction)	0.15		10.44
	0.16		10.43
Ru(5,6-DMPh)	0.36	10.34	10.34
	0.36		10.38
	0.36		10.34
Ru(5-MPh)	0.41	8.53	8.55
	0.41		8.54
	0.43		8.55
Ru(DMBP)	0.38	8.53	8.52
	0.37		8.49
	0.38		8.52

Miscellaneous titrations

In some cases starch cannot be used as an indicator, apparently because it acts as a negative catalyst. The iodimetric determination of hydrazine is an example of such a system. With the procedure of KOLTHOFF[1], in which hydrazine is titrated in sodium bicarbonate solution with iodine, Ru(DMBP) and free iodine end-points were compared: the amount of hydrazine found with the Ru(DMBP) end-point was 5.40 mequiv. and for the free iodine end-point 5.41 mequiv. Ru (5-MPh) and Ru-(5,6-DMPh) did not give sharp end-points with this system.

Starch also will not function in non-aqueous organic solvents, but attempts to use the ruthenium indicators in such solvents were not very successful. In some solvents the nitrate salts of the indicators were insoluble, while in others, though the nitrate salts were soluble and the triiodide salts insoluble, the formation and dissolution of the precipitates was too slow to be of practical value.

Interferences

Any compound insoluble in the titration medium interferes, as do anions forming insoluble salts with the ruthenium chelates. In general anions of large diameter such as perchlorate, periodate, persulfate, ferrocyanide, etc. are the least soluble; of this group only perchlorate is likely to be present under normal titration conditions and can be tolerated at concentrations up to 0.1 *M*.

Compounds which absorb light in the wavelength region corresponding to that of fluorescence excitation (450–465 mμ) also partially interfere; in such cases the end-point must be determined by precipitate appearance alone. Though accuracy is unaffected, the end-point is not as easily detected.

SMITH[4] measured the solubility of the perchlorate salts of the ferrous complexes of 1,10-phenanthroline, 5-bromo-1,10-phenanthroline and 5-nitro-1,10-phenanthroline (nitroferroin) both in water and in dilute solutions of perchloric acid. Nitroferroin is the least soluble ($3.3 \cdot 10^{-4}$ *M* in pure water, $6 \cdot 10^{-6}$ *M* in 0.01 *M* $HClO_4$), and is suggested as a precipitating agent for the separation and determination of perchlorate, periodate, persulfate, and molybdate. Iodate, sulfate, and phosphate do not interfere. We found that nitroferroin also gives a precipitate with triiodide, and can be used as a precipitation indicator. Accurate results were obtained in titrations of arsenite and thiosulfate (Table I), but the absence of fluorescence made the end-points more difficult to see.

Of the ruthenium complexes studied, Ru(5-MPh) displays the most intense fluorescence, but Ru(DMBP) is recommended for general use because it is applicable to a wider range of conditions. An added advantage of Ru(DMBP) is that it may also be used as a fluorescent oxidation–reduction indicator for sulfatocerate and permanganate titrations (reduction potential = 1.05 V *vs.* the hydrogen electrode). In general, these iodimetric indicators are useful under a variety of conditions, and are especially valuable where end-points formerly have had to be determined potentiometrically or by iodine extraction into carbon tetrachloride or chloroform.

SUMMARY

Chelates of ruthenium(II) with several methyl-substituted derivatives of 1,10-phenanthroline and 2,2'-bipyridine were studied as fluorescent–precipitation indicators for iodimetry. Accurate results were obtained under various conditions where starch will not function. The indicators are stable in solution, sensitive and reversible, and are particularly useful for titrations in colored or very dilute solutions.

RÉSUMÉ

Les auteurs ont examiné les chélates du ruthénium(II), obtenus avec plusieurs dérivés méthylés de la 1,10-phénanthroline et de la 2,2'-bipyridine, comme indicateurs fluorescents en iodométrie. Des résultats exacts ont été obtenus dans des cas où l'amidon ne convient pas. Ces indicateurs sont stables, sensibles, réversibles et particulièrement recommandables pour des titrages en solutions colorées ou très diluées.

ZUSAMMENFASSUNG

Chelate des Rutheniums(II) mit einigen methylsubstituierten Derivaten des 1,10-Phenantrolins und 2,2'-Bipyrridins wurden als Fluoreszenz-Fällungs-Indikatoren für die Jodometrie untersucht. Unter verschiedenen Bedingungen, bei benen Stärke sich nicht eignet, wurden genaue Ergebnisse erhalten. Die Indikatoren sind in der Lösung stabil, empfindlich und reversibel und eignen sich besonders für Titrationen in gefärbten oder sehr verdünnten Lösungen.

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LIQUID-LIQUID EXTRACTION WITH LONG-CHAIN QUATERNARY AMMONIUM HALIDES

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(Received March 20th, 1964)

The extraction of iron, cobalt and nickel by long-chain alkyl amines has been described in some earlier publications[1-3]. It was postulated that the extraction process occurs through "liquid anion exchange", since the exchange of the chloro-metal complex anions for the simple anion occurs mainly at the interface and the distribution ratio when plotted against the electrolyte molarity, produces curves which are similar to those observed with anion-exchange resins[4,5].

It was observed that in most cases, high-molecular-weight quaternary ammonium halides were more efficient than the corresponding secondary or tertiary amines for the extraction of metal ions from aqueous halide media. This is reasonable if the extraction mechanism is that of ion association (or ion exchange) to produce neutral species, since the quaternary ammonium compounds are known to charge-neutralize anionic metal complexes, thus causing an increase in the metal extraction percentage. This property of the quaternary ammonium halides has been used in many analytical procedures with advantage[6-8]. WILSON *et al.*[9] have reported the results of studies on the solvent extraction of some metal complexes with quaternary ammonium halides which indicate some further possible analytical uses for these compounds.

The present study was undertaken to investigate the effect of the anion, the structure and the size of the quaternary compound on the optimum conditions for the extraction of a few typical anionic metal complexes. The extraction of cobalt(II) and iron(III) was extensively investigated. The solvents chosen were chloroform, trichloroethylene and toluene, which do not normally permit the extraction of the simple inorganic metal complexes. A few of the commercially available quaternary ammonium halides were employed; others were prepared in the laboratory.

EXPERIMENTAL

Apparatus

The activity of the aqueous and organic phases was determined by counting aliquots in a well-type scintillation counter. All counting was done using a Hamner Electronics Co., manual scintillation spectrometer—Model No. S-2000, in conjunction with a 1 3/4" × 2" NaI well-crystal in a Hamner model A-18 probe.

Materials

All inorganic chemicals used were of Analytical Reagent grade. Chloroform, toluene and trichloroethylene (practical grade) were redistilled. Most of the quaternary ammonium halides used were prepared from the corresponding amines and purified by recrystallization or extraction. The amines used were the following: tri-*n*-hexylamine—Eastman Kodak white label; triisooctylamine—Gulf Research Development Chemical; tricaprylamine—General Mills commercial compound (Alamine 336); di-*n*-decylamine—Eastman Kodak yellow label; 2,2′-diethyldihexylamine—Eastman Kodak yellow label. Methyltricaprylammonium chloride was a General Mills product (commercial quality; marketed as Aliquat 336).

Isotopes used as tracers were cobalt-58 with a half-life of 71.3 days, iron-59 with a half-life of 44.3 days, gallium-72 with a half-life of 14.2 h and indium-114 with a half-life of 50.0 days. All of these were obtained from the Oak Ridge National Laboratory, as processed high specific activity isotopes, as the chlorides in hydrochloric acid solution.

Procedure

A 0.2 *M* solution of the appropriate quaternary ammonium halide in the organic solvent (chloroform, toluene or trichloroethylene) was prepared. The cobalt, iron, indium and gallium solutions were made up 0.025 *M* (or any other concentration as required) in Co(II) chloride, Fe(III) chloride, In(III) chloride or Ga(III) chloride respectively in the appropriate hydrochloric acid or lithium chloride solutions. A small countable amount of ^{58}Co, ^{59}Fe, ^{114}In or ^{72}Ga activity in the form of cobalt(II) chloride, iron(III) chloride, indium(III) chloride or gallium(III) chloride was added to each of the respective metal ion solutions. Equal volumes of the organic quaternary salt solution and the aqueous metal ion solution were mixed together in a 25-ml round-bottom flask and shaken on a mechanical shaker for 30 min. This period of time was chosen to insure complete equilibration of the two phases. Equal aliquots of each phase were removed, after allowing the mixtures to stand for some time, and the activity was counted in a well-type scintillation counter. The distribution ratio, D_m, of the metal ion was calculated as:

$$D_m = \frac{\text{activity in the organic phase}}{\text{activity in the aqueous phase}}$$

The values of D_m have a precision of approximately ± 2% up to 25, after which it falls sharply. The error may be as much as ± 15% at values $\sim 10^3$. The average values are reported. There was no significant change in the distribution values with variations in the concentration of the metal ion.

The extraction isotherms for a few typical quaternary ammonium halides were obtained following the same procedure except that the concentration of the metal ion was varied from 0.01 to 0.15 *M* and the concentration of the quaternary salt was kept constant.

RESULTS AND DISCUSSION

Distribution ratios of the metal ions

The distribution of the metal ions from the aqueous chloride media into the pure solvents used was found to be practically zero. Thus the metal ion cannot distribute itself in the absence of the quaternary ion in the organic solvent. The effect of the metal ion concentration on the distribution ratio was also very insignificant and a concentration of 0.025 M of the metals was chosen for the experiments.

Effect of anion concentration on the distribution

The dependence of extraction on anion concentration was investigated by using hydrochloric acid and lithium chloride solutions of different concentrations. The value of D_m increases with increasing ligand concentration owing to the formation of an extractable complex anion. Several evidences[1-3,10,11] point to the fact that, in the case of the metals studied, there is only one predominant species which is rapidly extracted from the aqueous chloride media by these quaternary ammonium halides, *viz.*, the tetrachloro metal complex anion. In the case of iron, the extraction goes on increasing till it becomes almost complete between 8.5 and 10 M hydrochloric acid. However, in the case of quaternary iodides which are strikingly poor extractants compared to bromides and chlorides, a maximum is not reached before 12 M hydrochloric acid. In the case of cobalt, maximum extraction occurs around 8.5 M hydrochloric acid; here also, the iodides exhibit maximum extraction of the metal complex at a higher acid concentration, usually at or above 10 M. The extraction curves generally show some maximum at high acid concentration (from 8.5 M to 11 M depending on the system) beyond which the extraction coefficient decreases with increasing acidity. If lithium chloride is used in place of hydrochloric acid as the aqueous electrolyte, the distribution continues to increase until it reaches a maximum value, and then it becomes constant. The curves do not usually regress after a maximum has been reached. Thus, it appears that this regression in the distribution curves is caused not by the chloride ion, but by the hydrogen ion. This effect due to hydrogen ions may be seen clearly in Fig. 1 where the distribution ratio of cobalt(II) has been plotted against varying hydrogen-ion concentrations, the chloride concentration being fixed. A reasonable explanation may be that at higher acid concentra-

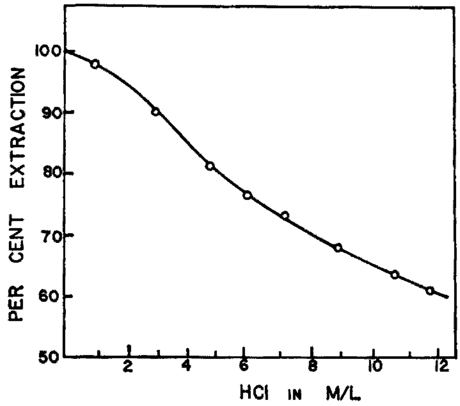


Fig. 1. Extraction of cobalt(II) by 0.176 M methyltricaprylammonium chloride in toluene as a function of HCl molarity (total [Cl^-] is 12 M and [Co(II)] is 0.025 M).

tions, the hydrogen ion competes more favorably than the quaternary ammonium ion for the anionic metal complex to form hydrogen-associated complex anions, which as a result of (and depending on) the number of hydrogen ions associated, have their effective negative charge suppressed. These weak complex acid species then would associate with little or no quaternary ammonium ions resulting in the decreased solubility of the metal complex and thereby causing a decrease in the metal extraction ratio. Also, it has been shown[12] that at high acid concentrations, considerable amounts of the hydrogen dichloride ion (HCl_2^-) are extracted into the organic phase. These ions may be favorably competing for the quaternary ions thus reducing the extraction of the complex metal anions. This effect has been emphasized and investigated in detail[12].

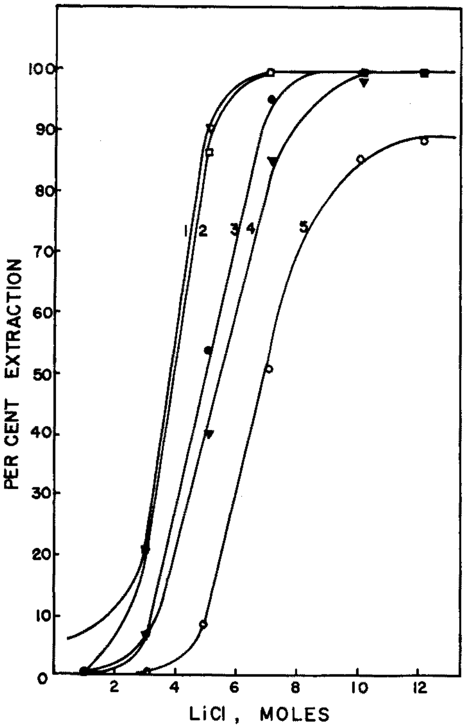


Fig. 2. Extraction of cobalt(II) from lithium chloride solutions by various quaternary ammonium halides (0.2 *M*) in toluene. Curve 1, methyltriisooctylammonium bromide; curve 2, methyltri-*n*-hexylammonium bromide; curve 3, dimethyl-2,2'-diethyldihexylammonium bromide; curve 4, methyltricaprylammonium iodide; curve 5, dimethyl-2,2'-diethyldihexylammonium iodide.

Several extractions of cobalt(II), iron(III), indium(III) and gallium(III) as a function of hydrochloric acid and lithium chloride concentrations were carried out and some of the typical results are represented graphically in Figs. 2–6. The concentration of chloride is plotted against per cent extraction rather than the distribution ratio. The values of the latter are so far separated in different cases that it is not

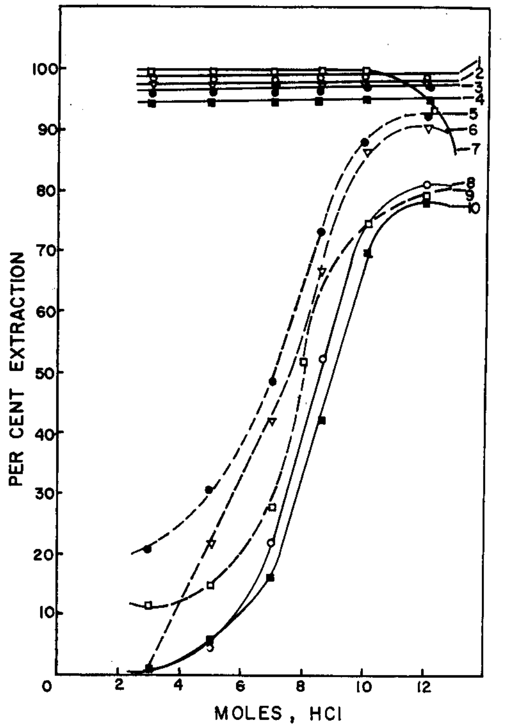


Fig. 3. Extraction of iron(III) from hydrochloric acid solutions by various quaternary ammonium halides (0.2 *M*) in toluene. Curve 1, methyltricaprylammonium bromide; curve 2, methyltricaprylammonium chloride; curve 3, methyltriisooctylammonium bromide; curve 4, dimethyldi-*n*-decylammonium bromide; curve 5, methyltriisooctylammonium iodide; curve 6, methyltricaprylammonium iodide; curve 7, dimethyl-2,2′-diethyldihexylammonium bromide; curve 8, dimethyldi-*n*-decylammonium iodide; curve 9, dimethyl-2,2′-diethyldihexylammonium iodide; curve 10, dimethyldiisooctylammonium iodide.

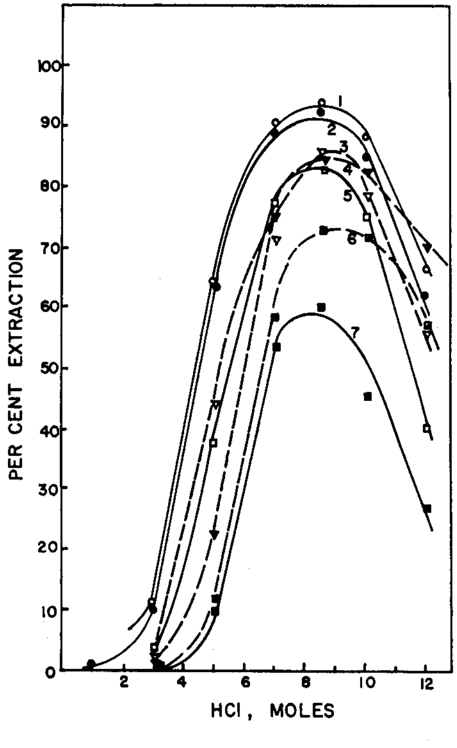


Fig. 4. Extraction of cobalt(II) from hydrochloric acid solutions by various quaternary ammonium halides (0.2 *M*) in toluene. Curve 1, methyltricaprylammonium bromide; curve 2, methyltricaprylammonium chloride; curve 3, methyltricaprylammonium iodide; curve 4, dimethyldi-*n*-decylammonium iodide; curve 5, methyltriisooctylammonium iodide; curve 6, dimethyldiisooctylammonium iodide; curve 7, dimethyl-2,2′-diethyldihexylammonium iodide.

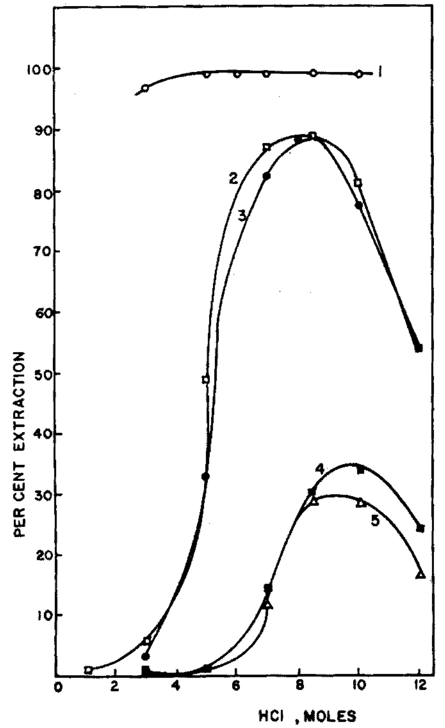
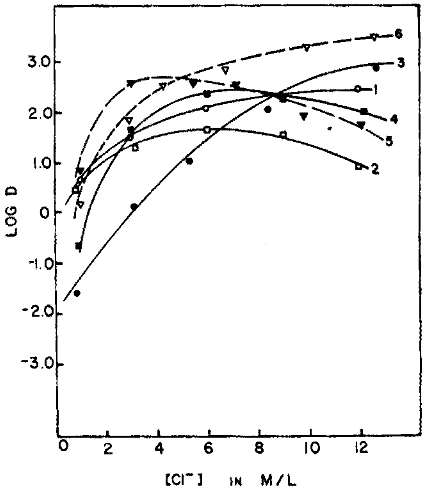


Fig. 5. Extraction of cobalt(II) and iron(III) from hydrochloric acid solutions by various quaternary ammonium halides (0.2 *M*) in chloroform. Curve 1, 0.025 *M* Fe(III) with methyltricaprylammonium chloride; curve 2, 0.025 *M* Co(II) with methyltricaprylammonium chloride; curve 3, 0.025 *M* Co(II) with methyltricaprylammonium bromide; curve 4, 0.025 *M* Co(II) with methyltricaprylammonium iodide; curve 5, 0.025 *M* Co(II) with methyltriisooctylammonium iodide.

Fig. 6. Variation of the distribution ratio with chloride concentration in the extraction of indium(III) and gallium(III) from aqueous chloride media by various quaternary ammonium halides. Curve 1, 0.022 *M* In(III) *vs.* 0.176 *M* methyltricaprylammonium chloride in toluene (lithium chloride); curve 2, 0.022 *M* In(III) *vs.* 0.176 *M* methyltricaprylammonium chloride in toluene (HCl); curve 3, 0.025 *M* In(III) *vs.* 0.176 *M* methyltricaprylammonium chloride in chloroform (lithium chloride); curve 4, 0.028 *M* Ga(III) *vs.* 0.176 *M* methyltricaprylammonium chloride in toluene (HCl); curve 5, 0.021 *M* Ga (III) *vs.* 0.2 *M* methyltricaprylammonium chloride in toluene (lithium chloride); curve 6, 0.021 *M* Ga(III) *vs.* 0.2 *M* methyltricaprylammonium chloride in chloroform (lithium chloride).



feasible to present them graphically together. Moreover, the values of per cent extraction seem to be of greater analytical interest. Toluene as well as chloroform has been employed as the organic diluent. The extraction is poorer in the case of chloroform, as of course would be expected.

Effect of various quaternary ammonium halides on the distribution ratio

The same general shape of metal distribution *vs.* hydrochloric acid or lithium chloride molarity curves was noticed for all the quaternary ammonium halides studied. The results are described in Table I, which also shows the concentration of the aqueous electrolyte at which the value of the distribution ratio is maximum. The procedure as described earlier in the experimental section was followed. Typical curves are shown in Figs. 2–6.

TABLE I

EFFECT OF VARIOUS QUATERNARY AMMONIUM HALIDES ON COBALT(II) AND IRON(III) DISTRIBUTION RATIOS

(Concn. of the metal ion, 0.025 *M*; concn. of the quaternary salt, 0.20 *M*)

Type of R groups	*No. of carbons*	*Maximum* D_{m}	
		Co(II)	*Fe(III)*
		Solvent: toluene	
1. Methyltricaprylammonium bromide	25	14.4 (8.5 *M* HCl) 213.8 (7.0 *M* LiCl)	959.5 (10 *M* HCl) —
2. Methyltricaprylammonium chloride	25	10.9 (8.5 *M* HCl) 28.7 (7.0 *M* LiCl)	294.5 (12 *M* HCl) —
3. Methyltricaprylammonium iodide	25	5.6 (8.5 *M* HCl) 85.9 (12 *M* LiCl)	10.1 (12 *M* HCl) —
4. Methyltriisooctylammonium bromide	25	7.5 (7 *M* HCl) 718.8 (12 *M* LiCl)	204.1 (10 *M* HCl) —
5. Methyltriisooctylammonium iodide	25	5.5 (8.5 *M* HCl) 92.8 (12 *M* LiCl)	11.2 (12 *M* HCl) —
6. Dimethyldi-*n*-decylammonium bromide	22	519.3 (8.5 *M* HCl)	222.3 (10 *M* HCl)
7. Dimethyldi-*n*-decylammonium iodide	22	6.0 (8.5 *M* HCl) 73.1 (12 *M* LiCl)	4.3 (12 *M* HCl) —
8. Methyltri-*n*-hexylammonium bromide	19	455.1 (10 *M* LiCl)	204.1 (10 *M* HCl)
9. Methyltri-*n*-hexylammonium chloride	19	403.8 (8.5 *M* LiCl)	—
10. Methyltri-*n*-hexylammonium iodide	19	0.89 (8.5 *M* HCl) 62.8 (10 *M* LiCl)	5.8 (12 *M* HCl) —
11. 2,2′-Diethyldihexyldimethylammonium bromide	18	3.6 (8.5 *M* HCl) 298.0 (10 *M* LiCl)	204.3 (7 *M* HCl)
12. 2,2′-Diethyldihexyldimethylammonium iodide	18	1.2 (8.5 *M* HCl) 8.0 (12 *M* LiCl)	4.0 (12 *M* HCl)
13. Dimethyldiisooctylammonium iodide	18	3.1 (8.5 *M* HCl) 47.1 (12 *M* LiCl)	3.1 (12 *M* HCl)
		Solvent: chloroform	
1. Methyltricaprylammonium bromide	25	7.7 (8.5 *M* HCl)	1079.4 (8.5 *M* HCl)
2. Methyltricaprylammonium chloride	25	8.6 (8.5 *M* HCl) 21.8 (12 *M* LiCl)	831.1 (8.5 *M* HCl) —
3. Methyltricaprylammonium iodide	25	0.5 (10 *M* HCl)	5.5 (12 *M* HCl)
4. Methyltriisooctylammonium iodide	25	0.4 (10 *M* HCl)	7.3 (12 *M* HCl)

The data presented in this paper are not sufficient to derive any decisive conclusions about the effects due to the structural configurations of the quaternary ammonium halide ions, but a few generalizations may be made on the basis of the results obtained. The extraction efficiency of the molecule increases with the increasing number of carbon atoms and it seems that very poor extraction occurs if the number is less than 18. Also, extraction is favored if the molecule has relatively short bulky aliphatic groups rather than a long chain with smaller groups. For example, the quaternary ammonium salts prepared with bulky tertiary amines have shown better extraction efficiencies than the salts prepared with relatively long-chained secondary amines as is shown in Table I.

Extraction isotherms

A quantitative approach to the mechanism of solvent extraction with quaternary ammonium halides was also attempted. To determine the stoichiometry of the extracting species, extraction isotherms were determined for a few typical quaternary compounds in some representative extraction systems. Figure 7 shows the loading curves for some cobalt(II) and iron(III) systems with different quaternary ammonium halides. Figure 8 represents the loading curves in which methyltricaprylammonium chloride was used to extract the gallium(III) and indium(III) complex anions. The curves with toluene as a solvent and with the bromide or chloride quaternary ammonium salts have been utilized to derive information on the stoichiometry of the

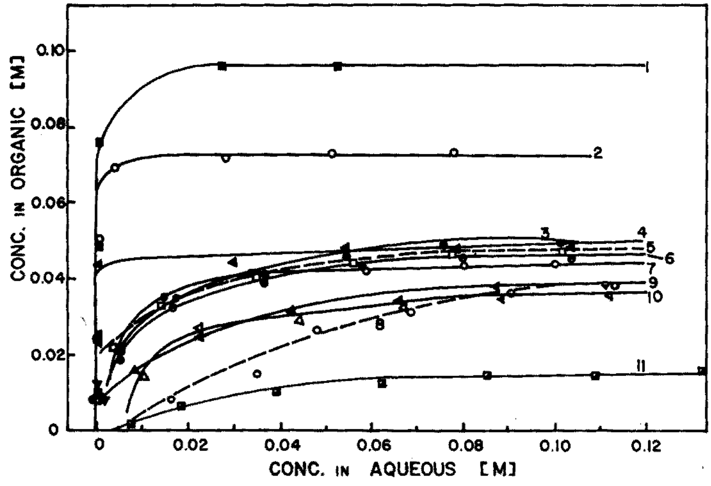


Fig. 7. Extraction isotherms for the extraction of chloride complexes of iron(III) and cobalt(II) from hydrochloric acid solutions by various quaternary ammonium halides (0.1 *M*) in different organic solvents. *Fe(III) extractions.* Curve 1, methyltricaprylammonium bromide in toluene—6 *M* HCl; curve 2, methyltriisooctylammonium bromide (0.088 *M*) in toluene—5 *M* HCl; curve 4, methyltricaprylammonium chloride (0.05 *M*) in toluene—5 *M* HCl; curve 8, dimethyl-2,2'-diethyldihexylammonium iodide in $CHCl=CCl_2$—6 *M* HCl. *Co(II) extractions.* Curve 3, methyltriisooctylammonium bromide in $CHCl=CCl_2$—8.7 *M* HCl; curve 5, methyltricaprylammonium bromide in toluene—8.7 *M* HCl; curve 6, methyltricaprylammonium bromide in $CHCl=CCl_2$—8.7 *M* HCl; curve 7, methyltricaprylammonium chloride in toluene—8.5 *M* HCl; curve 9, methyltriisooctylammonium bromide in chloroform—8.7 *M* HCl; curve 10, methyltricaprylammonium bromide in chloroform—8.7 *M* HCl; curve 11, dimethyl-2,2'-dimethyldihexylammonium iodide in $CHCl=CCl_2$—6 *M* HCl.

extracted species. The limiting mole ratio of the quaternary ammonium halide to metal chloride complex is 1 : 1 in all these cases except in the case of cobalt(II) where it is 2 : 1. This leads to the assumption that a tetrachloro metal anionic species is being extracted in every case which can be formulated as $CoCl_4^{2-}$, $FeCl_4^-$, $GaCl_4^-$ and $InCl_4^-$. Sufficient evidence seems to be in favor of the predominance of these extracting species. Some of these results have been discussed previously[1-3,10]. The ultraviolet and infrared absorption spectra of the extracted species provide fairly conclusive evidence for the existence of these entities.

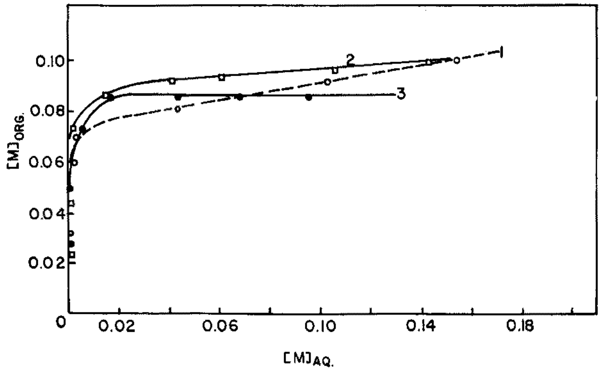


Fig. 8. Extraction isotherms for the extraction of chloride complexes of indium(III) and gallium-(III) from aqueous chloride media by 0.088 *M* methyltricaprylammonium chloride in toluene. Curve 1, In(III) from 6 *M* HCl; curve 2, In(III) from 6 *M* LiCl; curve 3, Ga(III) from 6 *M* HCl.

Dependence of extraction on the free quaternary ammonium halide concentration

A number of log–log plots of the free quaternary salt concentration *vs.* the distribution ratio of the metal ion were determined in order to explore the dependence of the latter on the former, if any. Where log–log plots were determined, the metal cation was added as the "carrier-free" isotope (concentration $\gtrsim 10^{-6} M$). Thus, it was assumed that the concentration of the quaternary ammonium halide in the organic phase was not changed significantly by the extraction of the cation into the organic phase.

The results indicate that, in general, the log–log plots of the free quaternary salt concentration *vs.* the distribution ratio do not give reliable predictions for the stoichiometry of the extracted metal chloride–quaternary salt species, as emphasized by other workers[13]. The curves obtained for different total chloride concentrations give different slopes indicating a change in the extracting species. Usually at low chloride concentrations, the log–log plot gives a straight line curve, the slope of which corresponds approximately to the stoichiometric ratio of the quaternary salt and the metal complex anion, but as the chloride concentration is increased, the slope decreases. A typical plot is shown in Fig. 9. In some cases, the plots do not give straight lines and estimates of the slopes for particular regions of the quaternary ammonium halide concentration do not give satisfactory results. This fact is more remarkable in the case of indium(III) and gallium(III) than in iron(III) and cobalt(II). A detailed study of this aspect will be published later[11].

The results presented above indicate that if equilibrium is established, the distribution ratio of the metal ion is almost independent of the metal ion concentration, which leads to the assumption that probably no polymeric species of the extracted compound are formed in the organic layer.

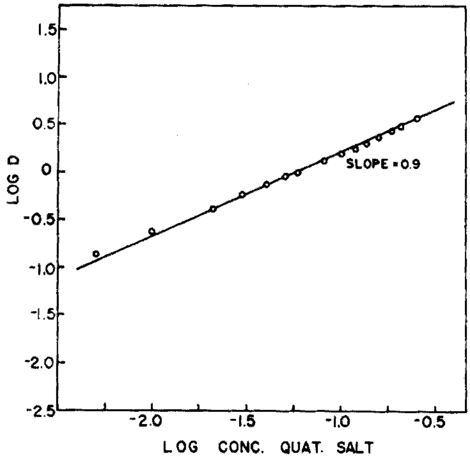


Fig. 9. Variation of the distribution coefficient for indium tracer in 0.98 M HCl as a function of the methyltricaprylammonium chloride concentration in toluene.

The mechanism of the reactions seems to proceed as follows:

$$nR_4N^+A^-_{(org)} + (MB_x)^{n-}_{(aq)} \rightleftharpoons (R_4N^+)_n(MB_x)^{n-}_{(org)} + nA^-_{(aq)}$$

Although there are other possibilities, the one formulated above seems to be reasonable and in agreement with the presented data.

The behavior of the quaternary ammonium halides is different from the simple amine hydrochlorides, probably owing to a difference in the dielectric constant of the two systems. Since the dielectric constants of the quaternary ammonium halides are greater than those of the amine hydrochlorides and since the quaternary ammonium halides can charge-neutralize the anionic chloro-metal complexes with greater ease, it may be logical to assume that the quaternary ammonium salts behave truly as "liquid anion exchangers".

Support for this work from the United States Atomic Energy Commission under Contract No. AT-(40-1)2576 is gratefully acknowledged.

SUMMARY

The extraction of anionic chloro-complexes of certain metal ions using various long-chain quaternary ammonium halides in toluene and chloroform is described. The investigation has concerned itself mainly with cobalt(II) and iron(III); a few extractions have also been carried out with indium(III) and gallium(III). The ion association of chloro-anionic complexes of iron, cobalt, indium and gallium in aqueous chloride media (hydrochloric acid or lithium chloride) with the quaternary ammonium ion in the organic phase is responsible for the extraction of the metal ion into the organic phase. The extraction efficiency varies with the nature of the metal ion system involved as well as with the distribution of the quaternary compound and the size, shape and nature of the organic groups substituted in the quaternary compound.

RÉSUMÉ

Les auteurs décrivent un procédé d'extraction de chlorocomplexes anioniques de certains cations (Co, Fe(III), In et Ga) dans le toluène et le chloroforme, en utilisant divers halogénures d'ammonium quaternaire, à longue chaîne. Les divers facteurs pouvant influencer le rendement de l'extraction ont été examinés.

ZUSAMMENFASSUNG

Die Extraktion anionischer Chlorokomplexe bestimmter Metallionen mit verschiedenen langkettigen quaternären Ammoniumhalogeniden in Toluol und Chloroform wird beschrieben. Die Untersuchung beschäftigt sich neben Indium(III) und Gallium(III) hauptsächlich mit Cobalt(II) und Eisen(III). Die Ionenassoziation chloroanionischer Komplexe von Eisen, Kobalt, Indium und Gallium in wässrigem Chloridmedium mit dem quaternären Ammoniumanion in der organischen Phase ist verantwortlich für die Extraktion der Metallionen in die organische Phase. Die Extraktionswirksamkeit ist abhängig vom Metallionensystem, von der Verteilung der quaternären Verbindung, und der Grösse, Form und Natur der organischen Gruppen.

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A RAPID RADIOCHEMICAL METHOD FOR ANTIMONY AND ARSENIC

PART I. FORMATION OF STIBINE AND ARSINE BY FLASH ELECTROLYSIS

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(Received May 5th, 1964)

In order to obtain nuclear data concerning the short-lived antimony and arsenic isotopes with half-lives down to about 5 sec a very rapid method of separation from fission products is necessary. The present methods available[1] include only one capable of giving the desired speed of separation. This method, described by GREENDALE AND LOVE[1,2], is based on the evolution of stibine and arsine from a zinc–sulphuric acid medium. With the optimum quantities of zinc and sulphuric acid and a temperature of 100°, a very rapid evolution of stibine and arsine is achieved.

In the present instance a method which could be operated under normal laboratory conditions, or remotely in a neutron flux, was required. The method of separating antimony and arsenic by formation of their hydrides gives a clean, one-step separation from other fission products and was previously adopted for our purpose. However, it was considered that the generation of stibine and arsine by electrolytic means, would be more suitable for remote operation than the use of zinc and sulphuric acid.

Only one previous description of an efficient electrolytic method of stibine formation has been given in the literature[3]. The parameters affecting stibine generation by this method have been thoroughly studied[4] and appear to be similar to those necessary for efficient arsine formation[5]. However the method as it stands was far too slow (chemical yield: 45% in 5 min)[4] for our requirements.

In the present paper a very rapid electrolytic method of forming stibine and arsine (chemical yield: 45% in 10 sec) is described. The effects of the ratio of cathode area to electrolyte volume and pH are also reported. The valency state of antimony and arsenic formed in fission cannot be predicted and it was therefore necessary to investigate the efficiency of hydride formation from the different valency states. A second paper will describe the radiochemical application of this method to the separation of antimony and arsenic.

EXPERIMENTAL

Apparatus

In a previous study[4], it was shown that the rate of electrolytic stibine formation is directly proportional to the current flow, but independent of temperature, electrode area, and stirring rate. Similar considerations appear to hold in the electrolytic formation of arsine[6]. It should therefore be possible to obtain a very high yield of hydride in a short time by using a much higher current than has been used hitherto. The limit in increasing the current will be set by the time taken to bring the liquid to boiling point, the resistive heating being proportional to the current squared. To obtain a high rate of electrolysis with minimum heating, a cell of low electrical resistance with a large ratio of cathode area to solution volume is therefore necessary. Such a cell is illustrated in Fig. 1.

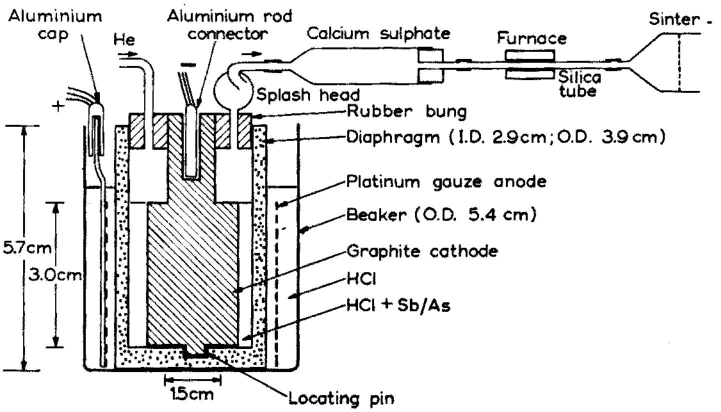

Fig. 1. A cell for rapid stibine and arsine generation.

Both cell compartments contained hydrochloric acid of the same concentration, with the antimony and/or arsenic present only in the cathode compartment. The anode consisted of a cylinder of 48-mesh platinum gauze (wire diam. 0.006 in.), spot-welded onto a 7-cm length of 0.128 in. diameter platinum rod. Cathodes were machined from a high-density graphite (Morgan's H X 12) which is completely impervious to aqueous solutions. By using cathodes of 1.90-cm and 2.49-cm diameter, the volume of liquid in the cathode compartment could be either 11.0 ml or 5.5 ml respectively, whilst the liquid depth was maintained constant at 3.0 cm. In a previous study it was shown that the efficiency of hydride formation is generally unaffected by the nature of the cathode material[4]. As it was intended to irradiate the cell in a beam of neutrons, a cathode material of low neutron-capture cross-section was desirable. For this reason, graphite was chosen. Other materials which do not displace antimony or arsenic from solution would have performed equally well, and any electrode coated with a layer of mercury would have been more efficient[4]. However, mercury was avoided in the present instance, because of its very high neutron-capture cross-section.

Currents up to 100 A were supplied by four 12-V batteries in series and controlled by two 1.8-ohm rheostats coupled in parallel. Electrical connection to the electrodes was by means of several thick aluminium wires welded to aluminium rod. The resistance of the 11-ml cell containing 1 *N* hydrochloric acid was initially 0.50 ohms but this decreased to a final value of about 0.38 ohms, as current was passed and the temperature rose. The average resistance during an experiment was about 0.44 ohms in 1 *N* hydrochloric acid and 0.25 ohms in 4 and 6 *N* hydrochloric acid. The 5.5-ml cell containing 5 *N* hydrochloric acid had an average resistance of about 0.25 ohms.

High-purity helium was passed through the cell, the flow-rate being controlled by a needle valve and measured with a rotameter. On leaving the cell the gases were dried by a 10-cm long, 1.1-cm diameter column of calcium sulphate (−7 +12 mesh B.S.S.) as recommended by GREENDALE AND LOVE[2]. The gases were finally passed through a 4-mm diameter silica tube heated over a length of 5 cm by a small furnace. To decompose stibine completely a temperature of 480° was needed, while 950° was required for arsine; 75% of the metal deposited on the cool region of the tube adjacent to the furnace whilst the remaining 25% passed on in particulate form and was completely removed by the sintered glass filter. The sinter used was a No. 3 (20–30 μ pore size) of 40 mm diameter. Coarser filters were found to allow some of the fine metal particles to pass through.

Preparation of tracers

The yields of stibine and arsine were measured by a radioactive tracer method. Antimony tracer solutions were prepared from ^{124}Sb (60 day), received as $SbCl_3$ dissolved in 5 *N* hydrochloric acid, from the Radiochemical Centre, Amersham, England. Antimony(III) solutions were prepared as described previously[4]. Antimony(V) tracer was prepared by adding excess bromine water to antimony trichloride in 1 *N* hydrochloric acid. Excess of bromine was removed by heating and bubbling argon through the solution for 20 min.

Arsenic tracer was prepared by irradiating "AnalaR"-grade arsenic trioxide in a neutron flux of 10^{12} n/cm^2/sec, to form ^{76}As (26.5 h). The oxide was then dissolved in concentrated sodium hydroxide solution, neutralised with hydrochloric acid and divided into two portions. One portion was diluted as required to give arsenic(III) solutions while the other portion was oxidised to arsenic(V) with bromine in an identical manner to the preparation of antimony(V).

Procedure

The porous diaphragm was placed in the beaker containing hydrochloric acid electrolyte and allowed to soak up the latter for about 30 min before an experiment. This excluded all air from the fine pores of the diaphragm. Tracer solution was then added to the cathode compartment and the cell assembled. Prior to electrolysis, the cell was flushed with helium for several minutes to remove all traces of air. A steady flow of helium of 250 ml/min was then maintained during the electrolysis.

Antimony and arsenic deposits on the silica tube and sinter were dissolved with a hydrochloric acid–hydrogen peroxide mixture[4] and made up to a standard volume. The activity of these solutions was measured either with a liquid beta-counter as described elsewhere[4], or with a gamma-scintillation counter coupled to a Laben 512-channel analyser. In each experiment the following quantities were determined: the concentration of tracer in solution before and after electrolysis; the amounts of tracer deposited on the cathode, silica tube and sinter. A mass balance was then carried out. On average, 6% of the tracer was lost in each experiment, primarily by diffusion into the porous diaphragm.

RESULTS AND DISCUSSION

Stibine — 11-ml cell

With the cathode compartment of this cell containing 0.5 mg of antimony dissolved in 1 *N* hydrochloric acid, the effects of current, time and antimony oxidation state on the yield of stibine were measured. The results are shown in Table I. The 10-sec electrolyses with antimony(III) and antimony(V) were repeated to check the reproducibility of the method. It can be seen from the Table that in these cases the reproducibility was ±3%. The electrolysis time shown was about the maximum which could be used before the liquid in the cathode compartment reached boiling point. If boiling was allowed to commence, liquid was ejected from the cell, blocking the splash head and drying tube and causing an increase in the electrical resistance of the cell. As the heating was virtually adiabatic, the quantity of heat required to cause boiling at different current flows was about the same (*ca.* 12 kw-sec — Table I).

TABLE I

11-ml CELL: YIELDS OF STIBINE

Oxidation state of Sb ions	*Current (A)*	*Time (sec)*	*% Sb in solution converted to SbH_3*	*Heat generated (kw-sec)*
III	52	10	29.2	11.7
III	52	10	27.8	11.6
III	77	5	15.6	12.9
III	93	3	11.5	11.1
V	51	10	19.7	12.7
V	50	10	19.2	12.0

The effect of the antimony oxidation state on the relative yields of stibine (Table I) was approximately the same as in a low-current cell[4], *i.e.* stibine was generated 1.5 times more rapidly from antimony(III) than from antimony(V) solutions. Previous results indicated that stibine is produced by a two-step process involving firstly the deposition of antimony on the electrode followed by reduction of the latter to stibine[4]. Unless the electrode is completely covered with antimony (and this is unlikely in the present instance), then the rate of stibine formation will depend on the rate of antimony deposition. The latter will depend on the condition of the antimony ions in solution. PITMAN, POURBAIX AND DE ZOUBOV[7] state that in 1 *N* hydrochloric acid, antimony(III) will be present almost entirely as SbO^+ while antimony(V) will be present as equal numbers of SbO_2^+ and $Sb(OH)_6^-$ ions. Thus the rate of deposition of antimony from antimony(III) solutions would be expected to be higher than from antimony(V) solutions, since in the latter case only half the antimony is present as positive ions. The rate of stibine formation should therefore also be lower from antimony (V) solutions than from antimony(III) — as found experimentally.

According to the data of PITMAN *et al.*[7], if the pH is reduced below 0, the condition of the antimony(III) remains virtually unchanged while the proportion of antimony(V) which is present as SbO_2^+ increases substantially. If the above postulates are correct, then one would expect the rates of stibine generation from antimony(III) and antimony(V) solutions to become less dissimilar as the pH is reduced. This is in agreement with the experimental findings which are plotted in Fig. 2. Because of the difference in electrical resistance it was possible to use a current of about 60 A in 4 and 6 *N* hydrochloric acid electrolyte, but only 50 A in 1 *N* hydrochloric acid. In order to compare the results, the yield of stibine per A, was therefore plotted. It can be seen that when the acid concentration is increased to about 5 *N*, the rate of stibine formation is independent of the oxidation state of the antimony.

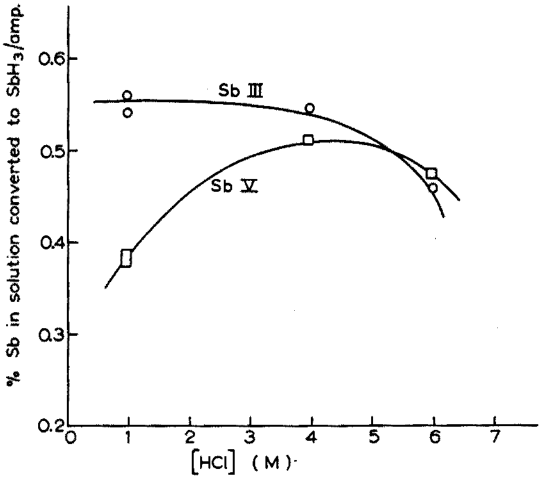

Fig. 2. Effect of [HCl] and antimony oxidation state on the yield of stibine. 0.5 mg Sb initially in solution; electrolysis time, 10 sec.

Stibine — 5.5-ml cell

In an attempt to increase the rate of stibine generation, a cell with a larger ratio of cathode area to electrolyte volume was used. In all experiments the electrolyte was 5 *N* hydrochloric acid; the results are listed in Table II. Two of the 10-sec electrolyses were repeated and showed a reproducibility of ±7%. By comparing the results in Table II with those in Table I and Fig. 2, it can be seen that with an electrolysis

TABLE II

5.5-ml CELL: YIELDS OF STIBINE

Electrolyte composition	*Current (A)*	*Time (sec)*	*% Sb in solution*		*Heat generated (kw-sec)*
			Converted to SbH_3	*Found on electrode*	
1 mg Sb(III)	36	20	55.8	0.4	8.7
1 mg Sb(III)	46	10	41.5	0.1	6.5
1 mg Sb(III)	51	10	38.8	0.1	7.2
1 mg Sb(III)	61	5	23.2	0.1	4.6
0.5 mg Sb(III): 0.5 mg As(III)	53	10	46.3	1.9	7.4
0.5 mg Sb(III): 0.5 mg As(III)	54	10	43.9	1.2	8.1
0.5 mg Sb(V): 0.5 mg As(III)	54	10	46.5	0.02	7.6

time of 10 sec the stibine yield rose from about 30% for the 11-ml cell, to 40–45% for the 5.5-ml cell. By using a mixture of antimony and arsenic, it was shown that the presence of arsenic does not affect the percentage yield of stibine (Table II). The absence of any effect of the antimony oxidation state at this acid concentration was also confirmed.

Arsine — 5.5-ml cell

By using arsenic tracer and non-radioactive antimony, the yield of arsine from an arsenic–antimony mixture, was measured. The results are shown in Table III for an electrolysis time of 10 sec. It can be seen that arsine is generated about 7 times more rapidly from arsenic(III) than from arsenic(V) solutions.

TABLE III

5.5-ml CELL: YIELDS OF ARSINE

Electrolyte composition	*Current (A)*	*% As in solution*		*Heat generated (kw-sec)*
		Converted to AsH_3	*Found on electrode*	
0.25 mg Sb(III); 0.25 mg Sb(V); 0.5 mg As(III)	54	49.7	1.5	8.1
0.25 mg Sb(III); 0.25 mg Sb(V); 0.5 mg As(V)	53.5	7.3	<0.1	8.0

If it is accepted that the mechanism for arsine formation is similar to that for the formation of stibine[4], *i.e.* a two-step process involving the deposition of metallic arsenic on the cathode followed by reduction of the latter to arsine, then one can consider possible reasons for the effect of the arsenic oxidation state on the yield of arsine. SAND[5] has reviewed the electrolytic deposition of arsenic and concludes that in hydrochloric acid solutions, arsenic is more easily deposited from arsenic(III) than from arsenic(V) solutions. It is suggested that this is due to the smaller arsenic(V) ions being present in solution as heavily hydrated neutral species or negative ions such as $As(OH)_6^-$ while the larger arsenic(III) ions are present in a less hydrated form such as AsO^+. Evidence from a study of the As(III)–As(V) exchange reaction, indicates that arsenic(V) is present in hydrochloric acid solutions as a hydrated polymer[8]. Alternatively, the actual discharge of arsenic(V) at the electrode may be energetically unfavourable compared with the discharge of arsenic(III). It is unlikely that the second step in the process, the reduction of deposited arsenic to arsine, will depend on the oxidation state of arsenic in solution.

Contrasting with these results in hydrochloric acid solutions, it has been found that in a sulphuric acid electrolyte, both arsenic(III) and (V) are reduced efficiently at a mercury or zinc/mercury amalgam cathode[5,9]. It is concluded therefore that by judicious selection of the experimental conditions it should be possible in the future to devise a cell in which arsine, like stibine, can be generated at a very high rate and independently of the oxidation state of the ions in solution. This would then obviate the need for the usual oxidation–reduction procedures which are a feature of present radiochemical methods for arsenic.

The author is indebted to Mr. G. N. WALTON for discussions during this work and for correcting the manuscript.

SUMMARY

The formation of stibine and arsine affords a clean, one-step, method of separating antimony and arsenic from fission products. The development of a high-current electrolytic cell for the rapid formation of these hydrides from a hydrochloric acid electrolyte, is described. A chemical yield of 45% was achieved for both antimony and arsenic in 10 sec. The effects of pH and antimony and arsenic oxidation states were also studied. In 5 *N* hydrochloric acid, the chemical yield is independent of the antimony oxidation state. For arsenic however, the yield of arsine is 7 times greater for As(III) than for As(V).

RÉSUMÉ

L'auteur décrit une méthode radiochimique rapide pour la séparation de l'antimoine et de l'arsenic d'avec des produits de fission, par formation de stibine et d'arsine. Un rendement chimique de 45% est obtenu, en 10 sec, soit pour l'antimoine, soit pour l'arsenic. L'influence du pH et du degré d'oxydation de ces éléments a également été examinée.

ZUSAMMENFASSUNG

Zur Abtrennung von Antimon und Arsen als Stibin und Arsin von Spaltprodukten wurde eine elektrolytische Zelle zur schnellen Bildung der Hydride entwickelt. Die chemische Ausbeute, der Einfluss des pH-Wertes und der Oxydationsstufe von Antimon und Arsen wurden untersucht. Die chemische Ausbeute in 5 *N* Salzsäure ist beim Antimon unabhängig von der Oxydationsstufe. Für Arsen jedoch ist die Ausbeute des Arsins sieben mal grösser für As(III) als für As(V).

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DETERMINATION OF CERIUM IN FERROUS ALLOYS

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(Received April 14th, 1964)

Previous investigations have shown that the rare-earth elements can be adsorbed on strongly basic anion-exchange resins from methanol–nitric acid media[1,2] as well as from isopropanol–nitric acid media[3]. Consequently it became possible to separate the rare-earth elements from each other[2] and from other elements[3,4]. Detailed investigations concerning the separability of cerium from other metal ions have, however, not been carried out, especially in respect of the possible analytical applications.

The use of cerium as a deoxygenating agent in the metallurgy of iron and steel presents an analytical problem, the solution of which requires a close study of the separation possibilities of cerium from all the elements usually present in such materials. In the present paper such investigations together with related factors influencing the adsorption of cerium and other elements on the strongly basic anion-exchange resin Dowex 1-X8 in media consisting of methanol–nitric acid are described.

Earlier papers dealing with the separation and determination of cerium and the rare-earth elements in ferrous alloys have involved the fluoride precipitation[5,6] and coprecipitation of the rare earths with thorium fluoride with subsequent ion-exchange removal of thorium[7]; coprecipitation with calcium fluoride[8] or lanthanum fluoride[9] as collectors has also been employed.

EXPERIMENTAL

Reagents and solutions

Ion-exchange resin. The strongly basic anion-exchange resin Dowex 1-X8 (100–200 mesh, nitrate form) was used.

Standard solutions of cerium and other elements. The reagent-grade nitrates of cerium and of the other investigated elements were dissolved in 5 *N* nitric acid to give solutions containing exactly known quantities of these elements (mostly 5 mg element/ml).

Methanol. Reagent grade.

Apparatus

The column operations were carried out in columns of the same type and dimensions as described earlier[10]; the height of the resin bed was 10 cm and its diameter 0.6 cm.

Determination of cerium

Cerium (and other investigated elements such as lead, bismuth, etc.) in the eluates or filtrates (after removal of the resin by filtration) was determined titrimetrically. The solution containing the cerium was diluted to *ca.* 100 ml with distilled water and 1 ml of an aqueous 0.05% solution of xylenol orange indicator was added. Solid hexamethylene tetramine was then added until the solution assumed the red-violet colour of the cerium–dyestuff complex. Subsequent titration with 0.01 *M* or 0.001 *M* EDTA produced a sharp colour change at the end-point from this colour to yellow.

Determination of distribution coefficients

The weight distribution coefficients were determined by employing the batch equilibrium method (batch method)[1].

Working procedure (analysis of test and steel samples)

Pretreatment of resin bed. The resin was introduced into the ion-exchange column from a suspension of the resin in the same solvent mixture as was later to be used as the sorption solution. For further pretreatment 50 ml of this solution was passed through the resin bed to establish exactly the same conditions as those existing during the sorption step.

Sorption. For the separation of cerium from other elements, 20 ml of a solution (test solution) consisting of 1 ml of 5 *N* nitric acid and 19 ml of methanol containing cerium and the elements from which cerium was to be separated, was employed.

For steels, the method was as follows. After dissolution of the steel sample (usually 1 g) in nitric acid and evaporation of the solution to dryness the residue was taken up in 5 *N* nitric acid. From this solution 1 ml was taken and diluted to 20 ml with methanol (the solubility of iron(III) nitrate in 5 *N* nitric acid was found to be around 100 mg of iron/ml).

This solution or the test solution was passed through the pretreated resin bed at a flow-rate of 0.25 to 0.3 ml/min, cerium, lead and bismuth being strongly retained by the resin. To remove iron completely the column was washed portionwise with a solution consisting of 95% methanol–5% 5 *N* nitric acid until no more iron could be detected in the effluent (see Fig. 1).

Elution. To separate cerium from the co-adsorbed lead and bismuth, 50 ml of a mixture consisting of 90% methanol–10% 6 *N* hydrochloric acid was passed through the column; cerium was thus quantitatively eluted and could then be determined directly in this eluate by titration with EDTA as described above. Lead and bismuth which were still adsorbed on the resin, could then be desorbed by elution with 50 ml of 1 *N* hydrochloric acid and 50 ml of 1 *N* nitric acid respectively (see Fig. 1).

RESULTS AND DISCUSSION

In Table I the values for the distribution coefficients of cerium and several other metal ions in 95% methanol–5% 5 *N* nitric acid medium are shown. The volumes required for the complete elution of weakly adsorbed elements are also included in this Table. From these results it can be seen that except for lead and bismuth, only cerium was strongly adsorbed on the resin under these experimental conditions; all the other

TABLE I

DISTRIBUTION COEFFICIENTS AND ELUTION VOLUMES IN 95% METHANOL–5% 5 *N* NITRIC ACID

Metal ion	*Distribution coefficient (5 mg/20 ml load)*	*Elution volume*[a] *(ml) (volume of elution peak)*
Ce(III)	843	—
Fe(III)	<1	40 (15)
Co(II)	<1	65 (15)
Ni(II)	<1	40 (15)
Mn(II)	<1	40 (15)
Cr(III)	<1	40 (15)
Mo(VI)	<1	65 (20)
Bi(III)	3,100	—
V(V)	<1	55 (15)
Pb(II)	81	—
Ti(IV)	<1	50 (20)
Zr(IV)	<1	50 (15)
Al(III)	<1	45 (15)
Ga(III)	<1	45 (15)
In(III)	<1	60 (20)
Mg(II)	<1	60 (15)
Ca(II)	<1	70 (20)
Sr(II)	1.0	90 (40)
Zn(II)	<1	45 (15)
Cd(II)	<1	65 (25)
Cu(II)	<1	40 (15)

[a] On 10-cm column with 5-mg load.

investigated elements showed practically no (or only negligible) adsorption so that a separation of cerium from these elements could easily be accomplished.

In Table II the results of several of such separation experiments are recorded. These separations were performed by the procedure described above and from the results it can be seen that in all cases quantitative recovery of cerium of 5, 10, 50,

TABLE II

SEPARATION OF CERIUM FROM IRON, LEAD AND BISMUTH

Separated elements	*Amount of cerium taken (mg)*	*Amount of cerium recovered (mg)*
Ce + Fe (100 mg)	0.5	0.49
Ce + Fe (100 mg)	1.0	1.00
Ce + Fe (100 mg)	2.5	2.51
Ce + Fe (100 mg)	5.0	4.98
Ce + Fe (100 mg)	10.0	10.03
Ce + Fe (100 mg) + Pb (5 mg)	5.0	5.02
Ce + Fe (100 mg) + Bi (5 mg)	5.0	4.99
Ce + Fe (100 mg) + Pb (5 mg) + Bi (5 mg)	5.0	5.00

and 100 mg showed that the distribution coefficient of cerium decreased from 843 to 415, 158 and 19.2 respectively, so that quantitative adsorption of cerium could be ensured when not more than 50 mg of cerium was present in the sorption solution.

Based on all these results, the working procedure described above was developed and then applied to the analysis of 5 steel samples to which varying amounts of cerium were added before the ion-exchange separations were carried out. From the results of these analyses (Table III), it can be seen that in all cases a quantitative recovery of cerium was achieved.

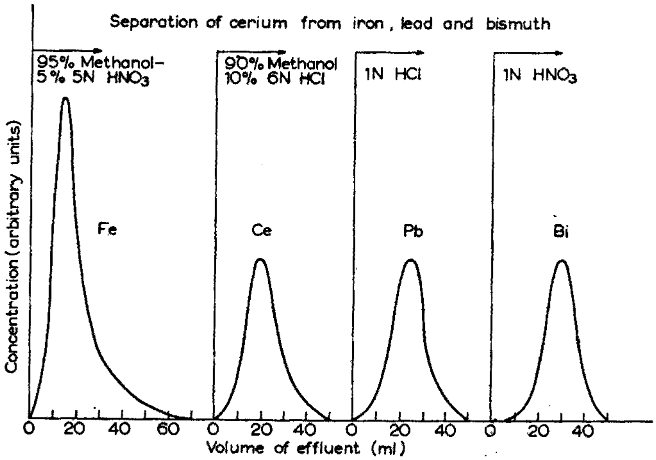

Fig. 1

TABLE III

DETERMINATION OF CERIUM IN STEEL SAMPLES

Steel sample (composition)	*Amount of cerium added (mg)*	*Amount of cerium recovered (mg)*
1. C (0.2%), Mn (0.5%), Si (0.3%), P (0.05%)	0.5 2.5 5.0	0.51 2.52 5.04
2. C (0.2%), Mn (1.0%), Si (0.4%), P (0.02%), Ni (25.5%)	0.5 2.5 5.0	0.48 2.50 5.03
3. C (0.31%), Mn (0.6%), Si (0.15%), Cr (2.8%), Ni (2.6%), W (9.3%), V (0.34%)	0.5 2.5 5.0	0.46 2.48 5.02
4. C (0.15%), Mn (0.3%), Si (0.15%), P (0.02%), S (0.043%)	0.5 2.5 5.0	0.52 2.50 5.00
5. C (0.4%), Mn (1.0%), Si (0.2%), P (0.04%), S (0.02%), Cu (0.4%)	0.5 2.5 5.0	0.50 2.46 5.03

Acknowledgement is made to the donors of The Petroleum Research Fund administered by the American Chemical Society, for partial support of this research (PRF-grant No. 1587–A3).

SUMMARY

A method for the determination of cerium in ferrous alloys is described. Cerium (with lead and bismuth) is separated from other elements by anion exchange in a medium consisting of 95% methanol and 5% 5 *N* nitric acid; cerium alone is then eluted with 90% methanol–10% 6 *N* hydrochloric acid and determined in the eluate by titration with EDTA to xylenol orange indicator. Application of the method to several steel samples was successful.

RÉSUMÉ

Une méthode est décrite pour le dosage du cérium dans des alliages ferreux. Le cérium (avec Pb et Bi) est séparé au moyen d'un échangeur d'anions, en milieu méthanol/acide nitrique 5 *N* (95:5), élué par un mélange méthanol/acide chlorhydrique 6 *N* (90:10) et titré au moyen d'EDTA, en présence de xylénolorange. Ce procédé a été appliqué avec succès à plusieurs échantillons d'acier.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Cer in Eisenlegierungen beschrieben. Cer (zusammen mit Blei und Wismut) wird mit einem Ionenaustauscher aus einer Lösung von 95% Methanol und 5% 5 *N* Salpetersäure abgetrennt und nach dem Eluieren mit einem Gemisch aus 90% Methanol und 10% 6 *N* Salzsäure mit EDTA und Xylenolorange als Indikator titriert.

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THE DETERMINATION OF ZINC IN ROCKS BY NEUTRON ACTIVATION ANALYSIS

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(Received March 7th, 1964)

Various colorimetric determinations of zinc in rocks and minerals using dithizone or zincon have been described[1–5]; several common elements interfere and interferences in the dithizone method in particular are often serious[3]. Another common source of error is contamination, particularly since zinc is a common impurity in reagents and water; it is often this contamination that sets the sensitivity limit for the chemical determination of zinc. Many of the geochemical data for zinc may be in error and there is a need for an accurate and sensitive method for the determination of zinc in rocks and minerals.

Neutron activation analysis has been used for a number of elements in geological materials and has the advantage of being very sensitive and virtually contamination-free. Zinc has been determined by neutron activation analysis in high-purity silicon[6], aluminium[7], germanium[8] and in sea water[9]. A general method for the determination of zinc by neutron activation analysis using 52-min zinc-69 has also been described[10].

The neutron activation method described in this paper for the determination of zinc in rocks is based on the use of 13.8-h zinc-69m and was used to determine the zinc contents of the standard rocks, granite G-1 and diabase W-1.

Data for the thermal neutron-capture reactions of the zinc isotopes[11] are shown in Table I. The ^{68}Zn(n,γ)^{69m}Zn reaction was used in preference to ^{68}Zn(n,γ)^{69}Zn because ^{69m}Zn can be measured by γ-spectrometry and has a more convenient half-life than ^{69}Zn.

TABLE I

THERMAL NEUTRON-CAPTURE REACTIONS OF THE ZINC ISOTOPES

Isotope	*Abundance (%)*	*Cross-section (barns)*	*(n,γ) reaction product*	*Mode of decay*	*Half-life*	*Gamma-energies (MeV)*
^{64}Zn	48.89	0.44	^{65}Zn	EC,β^+,γ	245 d	1.12
^{68}Zn	18.61	0.1	^{69m}Zn	IT,γ	13.8 h	0.44
^{68}Zn	18.61	1.0	^{69}Zn	β^-	52 m	None
^{70}Zn	0.65	0.09	^{71m}Zn	β^-,γ	3.0 h	0.38,0.49
^{70}Zn	0.65		^{71}Zn	β^-,γ	2.2 m	0.12,0.51

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Samples and standards were packed in aluminium foil and irradiated in the JEEP reactor, Institute for Atomic Energy, Kjeller, Norway for 3 days at a flux of $2.5 \cdot 10^{12}$ n/cm^2/sec.

Samples were decomposed with a mixture of hydrofluoric, sulphuric and perchloric acids. Zinc was separated by anion exchange by adsorption from 1.2 *M* hydrochloric acid followed by elution with 0.01 *M* hydrochloric acid. Elements such as In(III), U(VI) and Pb(II)[12] which, if present, might interfere and accompany zinc were removed by iron(III) hydroxide scavenging from an ammoniacal solution. Zinc was then precipitated as zinc oxinate from an acetate-buffered solution. Yields ranged from 85 to 98%.

Zinc oxide was used as a standard and experiments showed that self-absorption of neutrons was insignificant. Copper and nickel activities, produced by the fast neutron reactions ^{64}Zn(n,p)^{64}Cu and ^{68}Zn(n,α)^{65}Ni, and activated impurities were removed by anion exchange after addition of carriers.

Measurement of radioactivity

A γ-scintillation counter and single-channel pulse-height analyzer were used to measure the γ-activity of ^{69m}Zn and measurements were made on the 0.44 MeV ^{69m}Zn photopeak. Gamma-spectra were recorded and ^{69m}Zn half-life values were determined to check the radiochemical purity of sample and standard zinc oxinates.

EXPERIMENTAL

Apparatus and reagents

A single-channel pulse-height analyzer and scintillation counter with a 2 × 2″ NaI(Tl) well-type crystal (Nuclear Chicago Corp.) was used.

Ion-exchange columns. Amberlite CG-400 in chloride form, pretreated with 1.2 *M* hydrochloric acid. Column dimensions: 15 × 0.75 cm.

Zinc carrier solution. 5 mg of zinc per ml, prepared from analytical-grade zinc sulphate. The zinc content was verified by gravimetric determination as zinc oxinate.

Holdback carrier solution. Solution containing 0.5 mg of copper and 0.5 mg of nickel per ml in 1.2 *M* hydrochloric acid.

Zinc-65 solution. Radiochemically pure ^{65}Zn. An aliquot was taken in a counting vial (integral γ-count approximately 20,000 counts/min).

Preparation and irradiation

Dry the powdered rock samples at 110° for 1 h (do not use brass sieves). Weigh out 0.5 g of the sample on to a 5-cm square of aluminium foil (washed with water followed by acetone) and wrap the sample carefully in the foil. Wrap the envelope in a further piece of foil. Prepare standards in a similar manner using 10 mg of "Specpure" zinc oxide (Johnson, Matthey and Co., Ltd.). Pack the samples and 3 standards in an irradiation can and irradiate in a thermal neutron flux of $2.5 \cdot 10^{12}$ n/cm^2/sec for 3 days. After irradiation allow the samples to stand for 2 h.

Treatment of samples

Unwrap the envelope and transfer the sample to a platinum dish. Rinse the foil with a little water and then add 10 ml of perchloric acid, 5 ml of sulphuric acid, 15 ml of hydrofluoric acid and 10 ml of the zinc carrier solution. Place the dish on a hot plate and evaporate the solution nearly to dryness. Add 5 ml of concentrated hydrochloric acid and 10 ml of water and warm to dissolve the residue. Cool the solution, dilute to 50 ml with water and transfer to the ion-exchange column. Wash the dish with 5 ml of 1.2 *M* hydrochloric acid. Adjust the flow-rate through the column to 2 ml per min and after the solution has passed through wash the column with 50 ml of 1.2 *M* hydrochloric acid. Elute the zinc with 50 ml of 0.01 *M* hydrochloric acid at a flow-rate of 2 ml per min. Add 1 ml of a 1% solution of iron(III) chloride and 1 g of ammonium chloride to the eluate and heat nearly to boiling. Add 5 ml of ammonium hydroxide, heat to boiling and place on a steam bath for 5 min. Filter the solution, and discard the precipitate. Neutralize the filtrate with acetic acid, add 3 ml in excess and 5 g of ammonium acetate and slowly add a slight excess of a 2% solution of 8-hydroxyquinoline in 5% acetic acid. Place on a steam bath for 10 min to complete the precipitation. Filter the solution through a sintered glass filter, wash the precipitate with hot water and dry at 140° for 1 h. Transfer the oxinate to a weighed glass counting vial and re-weigh.

Treatment of standards

Transfer the zinc oxide to a 100-ml beaker and wash the foil with 1.2 *M* hydrochloric acid. Add 25 ml of 1.2 *M* hydrochloric acid and when the solid has dissolved transfer the solution to a 1000-ml volumetric flask and make up to volume with 1.2 *M* hydrochloric acid. Take a 2-ml aliquot (pipet) of the solution, add 10 ml of zinc carrier solution and 10 ml of the holdback carrier solution and proceed with the chemical treatment as described for the samples.

Measurement of radioactivity

Set the scintillation counter and pulse-height analyzer to record γ-energies from 0 to 2 MeV and record γ-spectra for the samples and standards. Set the pulse-height analyzer window to record counts within the 0.44 MeV ^{69m}Zn photopeak from 0.35 to 0.55 MeV. Count the samples, standards and the ^{65}Zn solution and record at least 10,000 counts for each measurement. Re-position the analyzer window to record counts within the 1.12 MeV ^{65}Zn photopeak from 1.0 to 1.2 MeV. Count samples, standards and the ^{65}Zn solution and record at least 1000 counts for each measurement. From the data for the ^{65}Zn solution calculate the ratio count rate 0.35 to 0.55 MeV/count rate 1.0 to 1.2 MeV and multiply the 1.12 MeV photopeak readings for samples and standards by this ratio to give values for the background on the 0.44 MeV readings for samples and standards. Subtract the background values from the 0.44 MeV readings. Apply corrections to the ^{69m}Zn count rates for decay during counting, if necessary, and calculate the zinc content of the sample from the expression:

$$\% \text{ zinc in sample} = \left(\frac{R_{sa} \times m_s \times w_{st}}{R_{st} \times m \times w_{sa}}\right) 100$$

where R_{sa} = count rate of sample zinc oxinate,
R_{st} = count rate of standard zinc oxinate,
m_s = weight of zinc in standard solution aliquot (2 ml) originally taken (mg),
m = weight of rock sample (mg),
w_{st} = weight of standard zinc oxinate (mg),
w_{sa} = weight of sample zinc oxinate (mg).

RESULTS AND DISCUSSION

A synthetic sample containing 100 p.p.m. of zinc (in silica matrix) and the standard granite G-1 and diabase W-1 were analyzed by the method. The results are shown in Table II together with results obtained by other authors. The results for G-1 and W-1 agree well with the recommended values[13] and with the only previously reported activation figures[10].

TABLE II

VALUES FOR ZINC IN A SYNTHETIC STANDARD, G-1 AND W-1

Sample	*Neutron activation value (p.p.m.)*	*Standard deviation*	*Previous values (p.p.m.)*	*Half-life of ^{69m}Zn[a] (h)*
	45.1			
	45.7		40[13]	
G-1	45.9		45.1[10]	
	46.3		43.9[10]	
	Mean 45.7	0.44		13.7
	81.7			
	82.5			
	82.7			
W-1	82.8			
	83.0		82[13]	
	83.1		86.1[10]	
	83.8		84.7[10]	
	Mean 82.8	0.64		13.7
	97.0			
100 p.p.m.	99.2			
standard	100			
	103			
	104			
	Mean 101	—	—	13.8

[a] Half-life of ^{69m}Zn is accepted as 13.8 h.

Sources of error

Zinc has a thermal neutron-capture cross-section of 1.1 barns[11] and self-shielding in the zinc oxide standards is thus negligible.

Errors in the results may be caused by the formation of ^{69m}Zn by other nuclear reactions. Reactions that give rise to ^{69m}Zn are ^{69}Ga(n,p)^{69m}Zn and ^{72}Ge(n,α)^{69m}Zn which occur with fast neutrons. The extent of interference from the former reaction may be estimated from data given by GREEN, HESLOP AND WHITLEY[14], who found that for the irradiation of gallium in a thermal neutron flux of $1.5 \cdot 10^{12}$ and a fast flux (>1 MeV) of $2.1 \cdot 10^{11}$ n/cm^2/sec, the apparent zinc content due to the (n,p) reaction was 530 p.p.m. Thus assuming a similar proportion of fast neutrons, the apparent zinc contents of G-1 and W-1 due to gallium (G-1, 18 p.p.m. Ga; W-1, 16 p.p.m. Ga[13]) would be 0.0096 p.p.m. and 0.0085 p.p.m. respectively. Interference from this source can be ignored except for samples very high in gallium.

Yields of (n,α) reactions are usually lower than those of (n,p) reactions and thus interference from ^{72}Ge(n,α)^{69m}Zn may be ignored for normal silicate rocks (G-1, 1.0 p.p.m. Ge and W-1, 1.6 p.p.m. Ge[13]).

Thermal neutron fission of ^{235}U does not produce ^{69m}Zn so that errors with samples high in uranium may be ignored.

Radiochemical purity of the G-1 and W-1 zinc oxinates was checked by examination of the γ-spectra (Fig. 1); it can be seen that the spectra are essentially identical to the standard spectrum. Further evidence that only ^{69m}Zn was being measured was provided by the half-life values for ^{69m}Zn obtained from the decay curves (Table II).

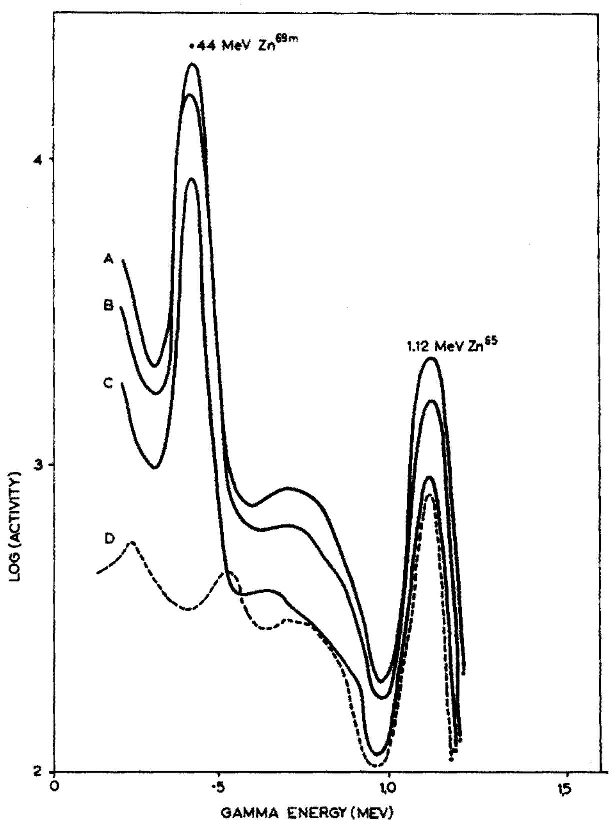

Fig. 1. γ-Ray spectra of ^{69m}Zn and ^{65}Zn. (A) G-1 zinc oxinate. (B) W-1 zinc oxinate. (C) zinc standard. (D) ^{65}Zn spectrum of zinc standard.

Sensitivity and precision

The sensitivity of the method for the experimental conditions employed was estimated to be 0.01 p.p.m. of zinc for irradiation of a 1-g sample in a flux of 10^{13} n/cm^{2}sec for 3 days with measurement 14 h after irradiation.

The precision of the method can be estimated from the G-1 and W-1 data shown in Table II. Relative deviations are 0.96% for G-1 and 0.77% for W-1.

SUMMARY

A neutron activation method for the determination of zinc in rocks and minerals is described. The method is precise, accurate and has a sensitivity of 0.01 p.p.m. of zinc. An ion-exchange separation of zinc together with precipitation of zinc as oxinate, gives good yields. Interference from conflicting (n,p), (n,α) and ^{235}U(n,f) reactions is negligible. The zinc contents of G-1 and W-1 determined by the method were 45.7 and 82.8 p.p.m. of zinc respectively.

RÉSUMÉ

Une méthode par activation au moyen de neutrons est décrite pour le dosage du zinc dans des roches et des mineraux. Elle est précise, exacte et d'une sensibilité de 0.01 p.p.m. de zinc. On procède à une séparation par échangeur d'ions et précipitation du zinc sous forme d'oxinate. L'influence des réactions (n,p), (n,α) et ^{235}U(n,f) est négligeable.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Zink in Gesteinen und Mineralien mit der Neutronenaktivierungsanalyse beschrieben. Die Methode arbeitet richtig, genau und besitzt eine Empfindlichkeit von 0.01 p.p.m. Zink. Eine Abtrennung des Zinks mit einem Anionenaustauscher in Kombination mit einer Fällung des Zinks als Oxinat ergibt gute Ausbeuten. Störungen durch (n,p), (n,α) und ^{235}U(n,f) Reaktionen sind vernachlässigbar.

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DOSAGE SPECTROGRAPHIQUE DE L'OXYGENE DANS LE PLUTONIUM ET SES COMPOSES

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(Reçu le 28 avril, 1964)

L'application de la méthode spectrographique de FASSEL[1,2] permet d'effectuer dans de bonnes conditions le dosage des gaz (oxygène, azote, hydrogène) dans les métaux. Ces impuretés ont une très grande importance pour les métallurgistes. Ceux-ci admettent en effet que la présence de certains gaz dans les métaux en modifie les propriétés mécaniques et physiques. Ainsi, l'oxygène augmente la fragilisation du zirconium, l'azote diminue sa résistance à la corrosion par l'eau[3], tandis que des teneurs gazeuses supérieures à 50 p.p.m. s'opposent au laminage du niobium.

Dans le même esprit, le développement de l'énergie atomique a conduit à étudier l'influence de l'oxygène sur les propriétés nucléaires du plutonium. Son dosage s'inscrit dans le cadre de l'élaboration d'un métal de haute pureté. Les analyses ont été effectuées sur des échantillons de provenance extrêmement variée: plutonium brut d'élaboration, alliages, carbures mixtes. De ce fait, les teneurs rencontrées vont de quelques centaines de p.p.m. à plusieurs milliers. Le Tableau I des résultats met en évidence l'influence de la nature de l'échantillon sur la teneur en oxygène.

TABLEAU I

Nomenclature de l'échantillon	*O_2 (p.p.m.) pour une prise d'essai 200 mg*
Pu refondu sous vide	400
Pu électro raffiné	425
Pu électro raffiné	585
UC PuC	1500
UC PuC	2500
UC PuC	3000
UC fritté	445
UC fritté	820
UC fritté	1630
UC UN(20%) fritté	3580
UC UN(60%) fritté	5710

En dehors des produits métallurgiques tels que le vanadium[4], la méthode FASSEL a vulgarisé le dosage des gaz dans les matériaux entrant dans le domaine nucléaire[2,3,5]. Elle est simple dans son principe, mais d'application délicate; elle présente des avantages de rapidité, de sensibilité et de précision par rapport aux méthodes conventionnelles de fusion sous vide[6] ou aux méthodes chimiques[7]. Elle consomme une quantité modérée de produit (200 mg environ) par rapport au prix qu'il convient d'attacher à la détermination de la teneur de cet élément. Il ne faut cependant pas perdre de vue qu'une analyse spectrographique courante d'une trentaine d'impuretés consomme à peine plus de produit (500 mg: Carrier Distillation Method). La méthode FASSEL est applicable aussi bien à un morceau de métal qu'à une pastille de carbure correctement échantillonné. Ce n'est pas toujours possible avec d'autres méthodes spectrographiques qui exigent de fabriquer une électrode avec le produit à analyser: c'est, par exemple, le cas du dosage de l'oxygène dans le titane au moyen de l'étincelle condensée dans le vide[8].

La méthode FASSEL se trouve concurrencée sur le plan de la rapidité par une variante de mesure fondée sur la conductimétrie. Dans l'analyseur L.E.C.O (Conductimetric Oxygen Analyzer), l'oxygène est dégagé par une fusion en creuset de graphite et entraîné par un gaz inerte. Cette technique offre un intérêt tout particulier dans le cas de matériaux inactifs disponibles en assez grande quantité[9,10]. Mais pour le plutonium, l'utilisation d'un tel appareil nécessite une adaptation extrêmement complexe de la cellule de dosage aux impératifs de sécurité.

La spectrographie de masse trouve un nouveau champ d'application dans le domaine de l'analyse élémentaire; elle permet d'obtenir en général une limite de sensibilité très faible, de l'ordre de 10^{-2} p.p.m. pour beaucoup d'impuretés. Cependant, dans le cas du dosage des gaz dans le plutonium, ce n'est qu'après une extraction des gaz par une fusion sous vide dans un creuset de graphite que la spectrométrie de masse intervient comme une variante de la technique de mesure[11].

PRINCIPE DE LA MÉTHODE ET DISCUSSION

La littérature fournit une documentation précise et abondante sur la description de la méthode[1-3,5,12]. Nous nous bornerons donc à un résumé très succint de celle-ci, à titre de rappel. La méthode FASSEL allie les techniques de la spectrographie classique d'émission à des techniques physico-chimiques récentes et d'application délicate, telles que la fusion réductrice sous argon et une application des techniques du vide.

L'extraction de l'oxygène correspond à la première opération au cours de laquelle l'échantillon est soumis, sous l'effet de la décharge d'un arc continu, à une microfusion en présence d'un bain de platine jouant le rôle de fluidifiant. Le composé métallique oxygéné se trouve réduit par le creuset en graphite (Electrode United Carbon Nr. 5795); l'oxygène extrait se recombine sous forme d'oxyde de carbone qui devient alors une impureté de l'argon. En considérant le cas de l'oxyde de cuivre qui est utilisé pour la préparation des étalons synthétiques, il se produit une réaction à température relativement peu élevée qui résume cette première étape[3]:

$$CuO + C \rightarrow Cu + CO$$

Ensuite, dans la seconde phase de la manipulation, le mélange gazeux d'oxyde de carbone et d'argon se trouve excité, à la faveur de conditions opératoires adéquates:

(*1*) faible pression du mélange gazeux, (*2*) arc continu sous intensité élevée, (*3*) nature de l'anode par suite de l'utilisation d'une électrode auxiliaire en graphite pur.

La réaction suivante résume cette deuxième étape[3]:

$$CO \xrightarrow[\text{d'arc}]{\text{colonne}} C + O \text{ excité}$$

Il suffit alors de photographier les radiations émises et de les mesurer au densitomètre. On utilise la raie 7771.928 Å, la plus sensible du triplet dont les voisines sont la raie 7774.138 Å et la raie 7775.433 Å.

L'enregistrement des raies d'oxygène et d'argon a lieu dans des conditions favorables à l'excitation des niveaux élevés de ces atomes, du fait de l'absence ou de la pauvreté en éléments métalliques de la colonne d'arc (technique de l'anode auxiliaire). De plus, dans la région du rouge lointain où l'on opère, le plutonium donne un spectre pauvre en raies.

La décharge d'un arc continu à haute intensité de courant répond bien à l'impératif de température élevée exigée par la réduction des composés oxygénés du plutonium ou de l'uranium, même inclus dans un mélange de carbures.

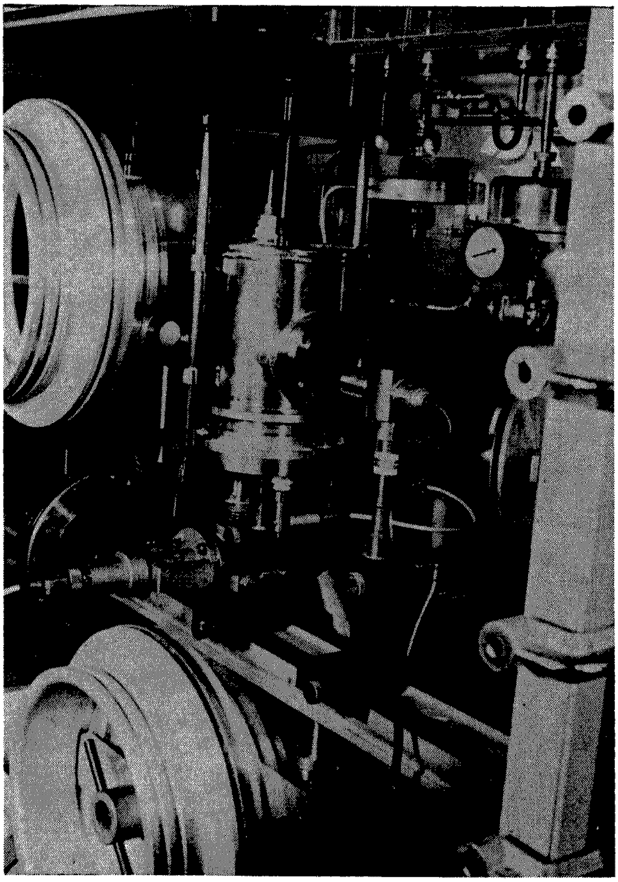

Fig. 1.

Les publications de certains auteurs font état d'une limite de sensibilité de quelques dizaines de p.p.m. et d'une précision de l'ordre de ± 10% pour des matériaux inactifs et technologiquement bien connus tels que les aciers. Il nous est apparu d'une manière évidente que les résultats obtenus dépendent des caractéristiques de la chambre FASSEL.

La première version (Fig. 1) a été conçue avant tout dans un souci de protection au détriment de la facilité d'exploitation et de la sensibilité. Elle nous a permis de parvenir à des teneurs nettement plus élevées que celles des éléments dits spectrographiques dosés habituellement dans le plutonium ou dans l'uranium. Cependant, comparée aux autres méthodes, elle reste satisfaisante par sa sensibilité, compte tenu de la quantité de produit consommé. La limite inférieure de détection de l'oxygène dépend pour une grosse part de la dispersion des résultats pour un même

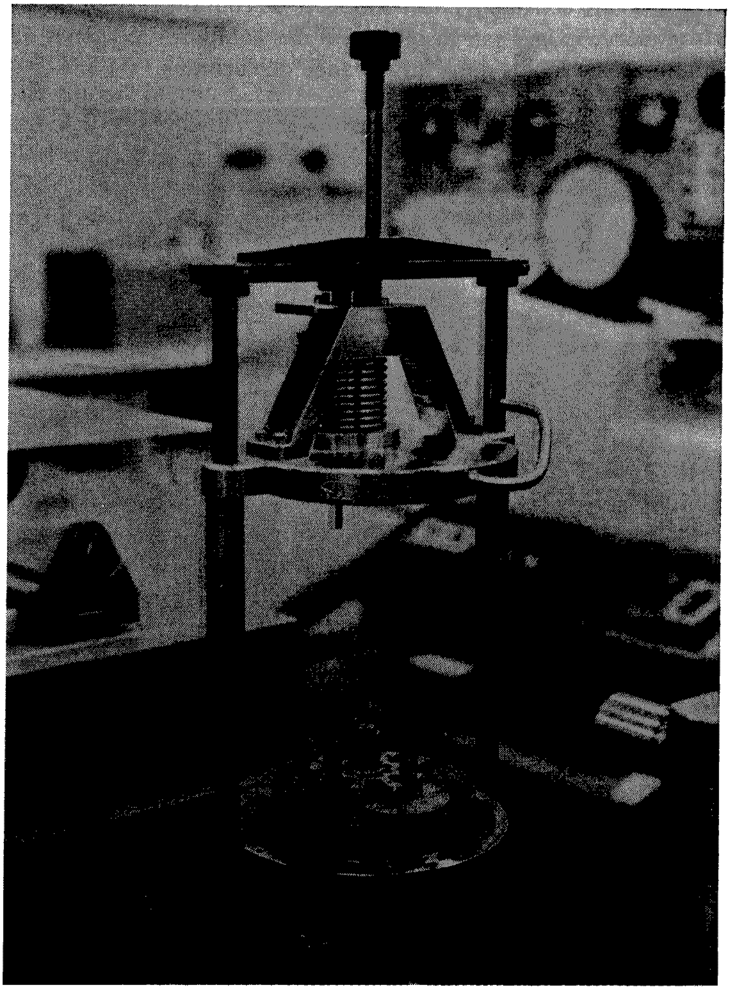

Fig. 2.

échantillon ou un même étalon dans le domaine des faibles teneurs. Dans l'état actuel d'avancement de nos essais, elle est de l'ordre de 50 μg.

La faible précision s'explique par l'impossibilité de régler l'electrode, et par la nécessité de recourir à une source lumineuse non cohérente (image sur la fente d'entrée). Cette méthode conduit à un gain appréciable de lumière par rapport à la formation de l'image sur le réseau, mais est incompatible avec la conception de l'appareil disperseur et avec son utilisation rationnelle.

Un nouveau porte-électrode (Fig. 2) a été étudié et construit pour remédier au premier inconvénient en alliant à un volume réduit une plus grande facilité d'exploitation. Il est essentiellement constitué d'une chambre de pyrex et de deux flasques d'acier inoxydable facilement séparables et nettoyables. Il est dans ces conditions possible d'éliminer le dépôt de carbone pulvérulent qui se produit au fur et à mesure des manipulations et tend à retenir des gaz incompatibles avec une bonne reproductibilité.

DONNÉES EXPÉRIMENTALES

La toxicité et l'activité du plutonium impliquent des conditions particulières de travail en boite à gants; en outre, les propriétés chimiques, en particulier l'affinité pour l'oxygène tant du métal que des carbures, exigent de prendre tout au long de l'analyse des précautions spéciales. Les gaz atmosphériques représentent une cause de pollution dont les effets peuvent considérablement fausser par excès les résultats. En vue d'y remédier, la boite à gants et la chambre FASSEL sont sous atmosphère d'argon.

Description de l'appareillage utilisé

Chambre Fassel. Ce porte-électrodes conditionne par sa conception les caractéristiques de sensibilité et de reproductibilité de la méthode. La première réalisation se compose d'une cloche en acier inoxydable. Deux fenêtres sont ménagées sur l'axe optique: l'une, de grandes dimensions, permet par l'arrière de voir et de régler la position des électrodes; l'autre, plus petite, permet le cheminement des rayons lumineux vers la fente du spectrographe. Cette cloche, mobile verticalement le long de deux colonnes, coiffe un flasque inférieur qui joue le rôle de support d'un barillet dont les douilles peuvent recevoir un maximum de 9 électrodes. Un aimant permet de faire tourner ce barillet à travers la paroi et de placer successivement chacune des électrodes sur l'axe optique. Celles-ci jouent le rôle d'anode et sont électriquement isolées du chassis du porte-électrodes, tandis que la contre-électrode est fixe.

Boite à gants. De forme parallélépipédique et de construction courante, elle est mécaniquement solidaire du spectrographe. Le banc optique traverse la paroi par un passage étanche et supporte le porte-électrodes. En légère dépression, elle est à atmosphère d'argon. Le système de régulation et de purification de ce gaz est de modèle courant. Cette disposition permet de bénéficier des avantages d'un circuit fermé de l'atmosphère de la boite à gants, en particulier en ce qui concerne l'humidité.

Banc à vide. Le dispositif de pompage se trouve tout entier sous la boite à gants. La pompe à diffusion d'huile est boulonnée au fond de celle-ci. La pompe à palettes aspire sur le circuit par l'intermédiaire d'un filtre de papier qui assure la protection contre les poussières radioactives. Ce banc permet d'obtenir un vide de 10^{-5} Torr dans la chambre Fassel préalablement à un rinçage et à un remplissage par de l'argon purifié.

Argon. L'alimentation et la purification de l'argon destiné au remplissage du porte-électrodes sont effectuées sur un appareil indépendant de la boite à gants. L'argon provenant d'une bouteille de gaz comprimé est admis lentement par une microfuite dans un four empli de tournures d'alliage titane–zirconium et chauffé à une température supérieure à 800°. Il remplit un réservoir jusqu'à une pression voisine de 3 atmosphères. Pour éviter des pollutions, toutes les tuyauteries et l'ensemble du système de purification sont en surpression jusqu'à la vanne d'admission au porte-électrodes.

Spectrographe. L'appareil utilisé est un spectrographe Hilger and Watts à réseau concave du type E 730. Ce modèle, relativement ancien, n'a pas une très grande luminosité. A l'intérieur de l'appareil, la propagation des rayons lumineux subit trois réflexions, d'abord sur un miroir plan, puis sur le réseau lui-même; les rayons diffractés sont renvoyés à nouveau par le miroir sur une chambre photographique. La surface focale courbe de l'appareil permet difficilement l'usage de plaques, c'est pourquoi tous nos essais ont été effectués sur film.

Les caractéristiques du réseau sont les suivantes: "Blaze" à 5000 Å premier ordre — 650 traits par mm.

Application de la méthode

Réglages optiques. La distance fente–source de 38 cm prévue par le constructeur rendait difficile l'adaptation d'une boite à gants à cet appareil, tout en nécessitant le système d'illumination par l'image de la source sur le réseau. Cette disposition est en effet favorable à l'analyse quantitative par la cohérence de l'image, mais nous lui avons préféré le système de l'image sur la fente, peut-être moins homogène, mais dont la concentration lumineuse assure une meilleure sensibilité; par ailleurs, nous avons utilisé une fente d'entrée relativement large (environ 50 à 60 μ). L'atténuation

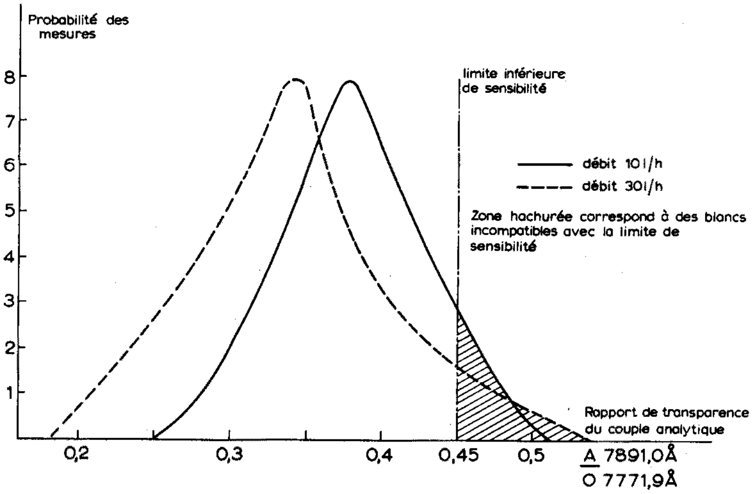

Fig. 3.

du fond continu a été obtenue en plaçant une préfente de forme triangulaire pour éviter de former l'image des électrodes sur la fente d'entrée.

Excitation de l'arc. Celle-ci se trouve étroitement liée aux caractères très particuliers des atomes mis en jeu dans ce dosage. En effet, ces éléments non métalliques, en raison de leurs niveaux d'excitation et d'ionisation élevés, réclament de fortes puissances d'alimentation de l'arc, inhabituelles dans les méthodes d'analyse courantes: elle est obtenue par deux dynamos couplées en parallèle, capables de débiter 40 A sous 220 V. Il est alors permis de penser que l'extraction de l'oxygène est quantitative avec le plutonium en raison de la température mise en jeu dans l'arc, d'autant plus qu'au cours d'une seconde manipulation après vide et rinçage de la cloche, sur le même étalon synthétique à base d'oxyde de cuivre, on trouve par photométrie un rapport analytique inclus dans la zone de dispersion des essais à blanc (Fig. 3). En revanche, une réserve peut être formulée à l'encontre de l'intégralité de l'extraction sur les combustibles à base de céramiques, ainsi que l'avait déjà signalé FASSEL à propos de certains sels métalliques[12]. Il est probable que les améliorations visant à l'extraction totale de l'oxygène doivent s'orienter vers l'obtention de températures plus hautes, plutôt que vers l'étude d'autres paramètres tels que le positionnement de l'échantillon dans l'anode ou le poids ou la forme de la pastille de platine.

Mesures photométriques. Dans le domaine spectral étudié, le nombre limité des raies du triplet de l'oxygène dans le rouge lointain facilite le repérage. Les raies 7771.928 de l'oxygène et 7891.075 de l'argon représentent le couple analytique.

Seule l'émulsion Kodak I *N*, en raison de sa rapidité, permet d'enregistrer les raies émises par de faibles teneurs d'impuretés. Par souci de commodité, nous avons utilisé le support pellicule de préférence aux plaques. Comparativement, nous avons remarqué une sensibilité supérieure de celles-ci, mais la modification des conditions opératoires qu'elles entraînent limite le domaine d'application de la méthode.

La rapidité et les caractéristiques de l'émulsion donnent un grain de fort diamètre, favorable à des phénomènes secondaires de diffusion de la lumière lors de la mesure du flux lumineux transmis. La quantité de lumière reçue par unité de surface n'offre plus un caractère d'homogénéité et la photométrie ne devient plus que relativement représentative, même avec une fente d'entrée fine. Il est certain que la substitution du photomultiplicateur à l'émulsion photographique, telle qu'elle est abondamment effectuée aux Etats-Unis, résout cette difficulté. C'est ainsi qu'un système de lecture directe équipe à Oak Ridge un montage analogue au nôtre, destiné à l'analyse de l'oxygène dans des matériaux d'application nucléaire.

Excitation sous atmosphère d'argon

L'importance de la décharge en atmosphère d'argon a été signalée par les auteurs de la méthode[1] et dans d'autres publications[3]. Ce gaz joue plusieurs rôles: en premier lieu, par son inertie chimique vis à vis des matériaux mis en jeu, il permet d'établir dans le porte-électrodes la pression désirée, d'amorcer l'arc dans de bonnes conditions (au détriment il est vrai de sa stabilité), de diluer après extraction les gaz produits. Il intervient ensuite dans un domaine purement spectrographique. Certains auteurs signalent[3] que sa présence rend possible l'excitation de niveaux élevés comme c'est le cas pour l'oxygène. En effet, les valeurs des potentiels d'excitation et d'ionisation, importantes (supérieures à 10 éV) mais voisines les unes des autres, favorisent les transferts d'énergie par un effet de résonance. Ce phénomène augmente l'intensité des raies du triplet d'oxygène. La production en assez grande quantité d'argon de grande pureté s'est avérée nécessaire: l'obtention de résultats nuls ou du moins à teneur résiduelle faible sur des essais à blanc est liée à l'exactitude et à la finesse des dosages. La présence d'impuretés dans l'argon au voisinage du seuil de détection de l'oxygène conduit à des déterminations non reproductibles ou erronées.

A l'heure actuelle, pour une prise d'essai de 200 mg de métal, compatible avec la contenance des électrodes (United Carbon Nr. 5795), la limite de sensibilité de la méthode est voisine de 200 p.p.m. Certaines précautions et modifications de l'installation permettront de l'améliorer. Nous pensons en particulier:

(*a*) employer un détendeur à piston au lieu d'un détendeur ordinaire, car les membranes habituelles sont toujours poreuses, surtout aux faibles débits;

(*b*) propreté rigoureuse des canalisations, en cuivre ou en acier inoxydable sur toute leur longeur, à l'exclusion de toute partie en caoutchouc;

(*c*) purge de l'ensemble de l'appareil, y compris la microfuite et le détendeur de la bouteille, à condition qu'il soit étanche;

(*d*) dessiccation systématique par des absorbeurs à silicagel avant son introduction dans le porte-électrodes.

Le premier type de porte-électrodes s'est avéré beaucoup trop volumineux. Il est certain que la limite de détection de la méthode sera abaissée par la réduction du volume, tandis que la possibilité de régler, de l'extérieur, après verrouillage, l'écartement des électrodes, contribuera à améliorer la reproductibilité. La nouvelle conception de la chambre FASSEL (Fig. 2) s'est attachée à remédier à ces inconvénients. Par ailleurs, le profil tourmenté de la cloche empêche son nettoyage systématique. Or, il se produit un dépôt pulvérulent de carbone que l'on élimine aisément sur les hublots transparents, mais difficilement ailleurs. Le dégazage est long, certainement irrégulier et incomplet. Les gaz adsorbés peuvent être un facteur très nuisible à la précision et à la reproductibilité de la méthode. De plus, l'accroissement de l'opacité des hublots au fur et à mesure des clichés intervient, en jouant le rôle d'écran filtrant, pour modifier les conditions d'illumination de la fente.

RÉSULTATS OBTENUS

Les résultats obtenus avec cette méthode n'ont de valeur que dans la mesure où son application tient compte des impératifs de soin qu'exige l'observation exacte des conditions expérimentales qui viennent d'être énoncées et imposent un certain nombre d'essais.

Essais à blanc

Les essais à blanc ont tout d'abord eu pour but de tester la qualité de l'installation. Un grand nombre de clichés ont été pris avec des électrodes de graphite préalablement grillées et nettoyées par un préflambage sous argon, répété trois fois pendant une minute sous une intensité de 30 A. Ils nous ont permis de remarquer que les mesures ne sont reproductibles que dans un cycle opératoire ininterrompu. En effet, le porte-électrodes maintenu sous vide statique ne s'avère pas étanche indéfiniment à la valeur du vide secondaire, mais néanmoins donne satisfaction dans le temps imposé par la méthode.

Dans le déroulement normal d'une analyse, chaque essai à blanc est effectué obligatoirement avant tout dosage, et son observation au spectroprojecteur constitue une information qualitative qui précède et détermine la suite de l'analyse et des mesures photométriques.

Dans le but d'obtenir des essais à blanc correspondant à des teneurs résiduelles aussi faibles que possible, et de pousser la sensibilité du dosage à un maximum compatible avec le premier modèle de porte-électrodes, nous avons cherché à effectuer une purification efficace de l'argon. Nous avons fait varier la vitesse d'admission du gaz dans le four à titane–zirconium (Fig. 3). Les essais à blanc comparatifs nous ont montré qu'en fonction de cette vitesse, il était nécessaire de chauffer la charge aux environs de 1000°, et ceci pendant plusieurs heures. Quantitativement, les essais à blanc déterminent la limite inférieure de sensibilité de la méthode (50 μg) et se trouvent répartis selon une courbe de Gauss (Fig. 3 et 4). Ils n'ont enfin pas permis de mettre en évidence séparément l'influence de la teneur résiduelle due à la pureté de l'argon et celle du dégazage de la couche de carbone pulvérulent déposé sur les parois de la cloche.

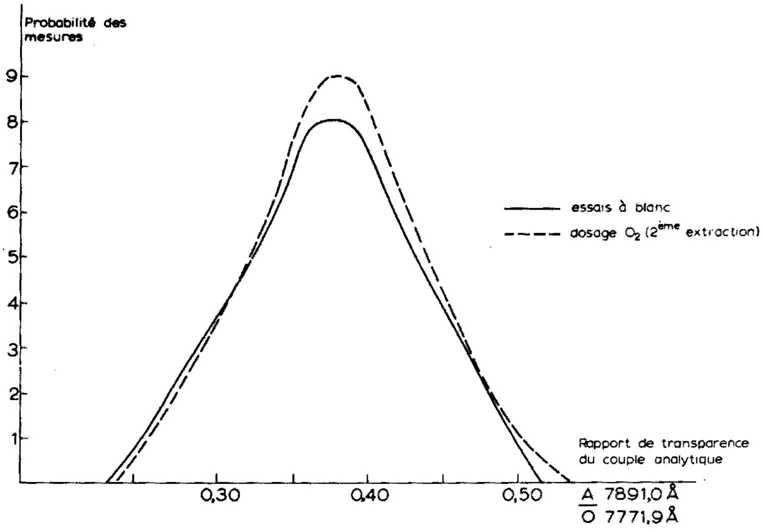

Fig. 4.

Courbe d'étalonnage

Devant l'impossibilité de se procurer des étalons métalliques standard, nous avons adopté la technique des étalons synthétiques, composés d'un mélange d'oxyde de cuivre (Johnson Matthey) et de graphite pastillable, également de qualité spectrographique. L'oxyde de cuivre a été choisi en raison de la parfaite connaissance de sa composition stoechiométrique plus que pour toute autre considération thermodynamique. En effet, la température qui règne dans le creuset de l'électrode (> 2000°) rend la dissociation de tout oxyde quantitative, et la technique d'exposition avec une anode auxiliaire enlève tout intérêt à la constitution d'une gamme d'étalons avec un autre oxyde. Ce n'est pas la nature de l'électrode mais le gaz qui l'entoure qui intervient pour donner le spectre. Un séchage à l'étuve à 100° précède l'homogénéisation du mélange des deux constituants dans un vibro-mélangeur Mixer Mill. On réalise des mélanges-mères qui offrent l'avantage d'éliminer les erreurs de pesées par des prises élevées. Ils sont ensuite dilués avec du graphite.

Le pastillage s'effectue par pressage à froid du mélange pulvérulent avec une presse hydraulique de laboratoire (type L.C.A.). Si la précaution est prise de maintenir la pastille sous une pression de 300 kg/cm^2 pendant 5 min, on évite le lamellage. L'intérêt de la préparation des étalons synthétiques réside dans la possibilité de fabriquer soi-même une gamme complète de témoins. A l'heure actuelle, plusieurs laboratoires mettent sur pied un programme d'élaboration d'étalons métalliques, mais la recherche de l'homogénéité, le prix de revient et la difficulté d'effectuer des confrontations entre laboratoires selon des méthodes différentes constituent des difficultés majeures.

Dans un souci de reproductibilité, nous avons décidé que le poids de la pastille étalon serait constant et indépendant de sa concentration en oxygène. Cela permet d'avoir des électrodes qui ont un profil et un remplissage identique.

Nous avons tracé une droite de dosage en portant en ordonnées les variations du rapport de transparence des raies "argon" par rapport à "oxygène" en fonction des concentrations (Fig. 5). Elle présente une partie linéaire entre 50 et 500 μg avec une zone de sous- et surexposition. La pente est faible et laisse prévoir une reproductibilité médiocre. Nous avons de plus constaté une dérive (difficilement chiffrable) des courbes d'étalonnage (Fig. 6): ceci semble dû à l'impossibilité d'agir sur les paramètres dont il a été fait mention dans les chapitres précédents. L'influence du vieillissement de l'émulsion 1 *N* n'est pas, par ailleurs, à exclure. Dans de telles conditions, une bonne précaution exige de définir la position réelle de la courbe de référence, en encadrant chaque échantillon d'au moins deux étalons en plus de l'essai à blanc.

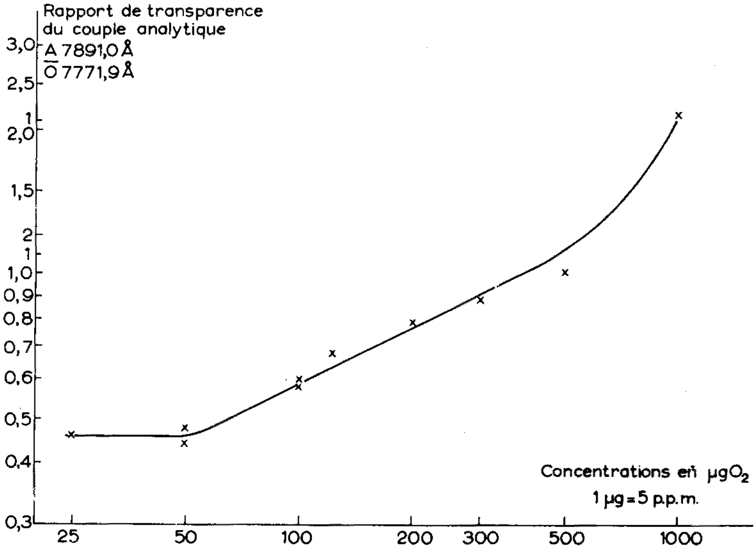

Fig. 5.

Nous avons obtenu un gain de temps appréciable en ce qui concerne l'étalonnage pour constituer une gamme de teneurs aussi complète que possible. Après chaque extraction, un spectre est photographié, puis une nouvelle extraction permet d'ajouter aux précédents les gaz extraits, et ainsi de suite. Elle permet de resserrer à volonté les points sur la droite de dosage.

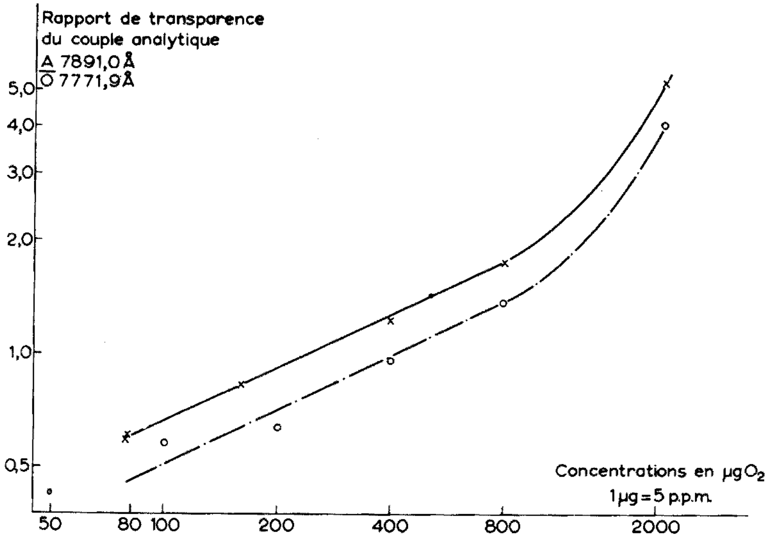

Fig. 6.

Echantillonnage

La forte affinité des composés d'uranium et de plutonium pour l'oxygène par rapport aux métaux courants oblige à effectuer l'échantillonnage avec des précautions rigoureuses. Dans le cas du métal, il est impératif d'avoir la prise d'échantillon, que nous avons fixée à 200 mg, sous une forme massive et non sous forme de copeaux dont la grande surface par rapport au poids favorise l'oxydation de surface, tout en rendant impossible son nettoyage. Nous avons opéré sur des échantillons provenant de lingots élaborés, nettoyés avant prélèvement à l'outil dans une boîte-atelier à atmosphère contrôlée d'argon, aussi sèche que possible.

La préparation des échantillons provenant de mélanges de carbures ou de nitrures a été effectuée sous benzène au mortier d'Abisch par concassage, séchage sur un verre fritté dans un récipient sous vide, et prélèvement à la pince d'un éclat au sein de la pastille. La boite à gants était également maintenue sous circulation d'argon, à partir d'une bouteille de gaz comprimé et ventilation. En aucun cas nous n'avons effectué de décapage électrolytique, car il semble que la présence d'eau, sous quelle forme que ce soit, est un important facteur d'oxydation superficielle des échantillons.

Sensibilité

A l'heure actuelle, pour une prise d'analyse de 200 mg, la sensibilité est de l'ordre de 250 p.p.m. soit 50 μg d'oxygène mis en jeu. L'utilisation d'une nouvelle chambre FASSEL plus petite, mieux appropriée, s'impose pour la recherche d'une sensibilité plus poussée pour de très faibles teneurs. Les améliorations porteront sur une étanchéité plus rigoureuse de l'ensemble des circuits, et l'élimination de toute humidité par absorption chimique. Il semble en effet que des traces d'humidité d'abord nuisibles à l'échantillonnage constituent également le dernier facteur à éliminer pour améliorer les blancs d'analyse, donc pour diminuer le seuil de sensibilité.

Les paramètres sur lesquels nous n'avons pu agir au cours de ces essais: cathode règlable, source cohérente, etc. doivent de plus améliorer la reproductibilité des mesures. L'écart-type relatif, calculé à partir de 8 déterminations effectuées sur des étalons synthétiques d'oxyde de cuivre dégageant 200 μg d'oxygène est voisin de 40% (Tableau II).

TABLEAU II

Numéro d'ordre des mesures	$\varphi_A/\varphi O_2$	O_2 (*p.p.m.*)	X_0	$X - X_0$	$\Sigma_n(X-X_0)^2$	$\sigma = \sqrt{\frac{\Sigma_n(X-X_0)^2}{n-1}}$	$\sigma' = \frac{\sigma \times 100}{X_0}$
1	0.725	1315	1048	267	1,168,561	$\sqrt{\frac{1,168,561}{7}}$	$\frac{0.0408 \times 100}{0.1048}$
2	0.586	760		288			
3	0.664	1040		8		= 408	
4	0.703	1220		172			= 38.93%
5	0.621	870		178			
6	0.656	1010		38			
7	0.659	1020		28			
8	0.689	1150		102			
				$\Sigma_n(X-X_0)$ 1081	Ecart-type voisin de 40%		

Durée d'une analyse

L'observation d'un mode opératoire aussi strict nous conduit à considérer la rapidité et la rentabilité de cette méthode. Le fait de travailler en boite à gants, s'il est d'une part un avantage permettant d'opérer toutes les opérations d'échantillonnage et d'analyse en atmosphère inerte et sèche, contribue d'autre part à accroître la durée d'une analyse et la difficulté de mise en oeuvre. Il convient également d'ajouter les impératifs liés à l'obtention d'un bon vide et d'un argon de grande pureté. Toutes ces opérations, pour être valables, doivent être effectuées sur une installation fonctionnant convenablement, rodée, et avec des droites de dosage préalablement établies. En moyenne, deux jours sont nécessaires pour une analyse; cette durée est longue par rapport à celle d'une analyse spectrographique courante qui implique également les mêmes opérations d'échantillonnage, d'essais à blanc, d'étalonnage et de spectrophotométrie. Cependant, la connaissance de la teneur en oxygène est un précieux renseignement au cours de l'élaboration d'un métal de haute pureté, même avec un écart-type relativement important. Un résultat prend d'autant plus d'importance qu'il est précis, or cette précision est corrélative de soin et implique de ne pas chercher à multiplier les résultats au détriment de leur qualité. L'application au plutonium de la méthode FASSEL est longue et coûteuse, et elle reste dans le domaine des analyses exceptionnelles.

RÉSUMÉ

La méthode FASSEL est appliquée au dosage de l'oxygène par spectrographie d'émission dans divers composés plutonifères. Il s'est agi successivement de métal pur, de carbures ou de carbonitrures.

Son adaptation au travail sur des produits radioactifs comporte de nombreuses difficultés technologiques. Elles nous ont conduit en particulier à la réalisation d'un porte-électrodes dont le volume s'est avéré trop grand pour tirer le maximum des possibilités de la méthode.

Nous avons trouvé une limite de sensibilité inférieure ou égale à 250 p.p.m. pour une prise d'échantillon massive de 200 mg. Les résultats sont déterminés avec une précision (1 σ) de l'ordre de 40%.

SUMMARY

The FASSEL method is applied to the determination of oxygen in various plutonium compounds by emission spectroscopy. Technical difficulties were found in adapting the method for radioactive materials; these were partially overcome by the introduction of a special electrode carrier, but the volume of the carrier was established as too large to enable the full possibilities of the method to be exploited. A lower sensitivity limit of 250 p.p.m. was found for a 200-mg sample; the precision obtainable was of the order of 40%.

ZUSAMMENFASSUNG

Zur Bestimmung von Sauerstoff in verschiedenen Plutoniumverbindungen mittels der Emissionsspektroskopie wird die FASSEL-Methode angewandt. Technische Schwierigkeiten ergaben sich bei der Übertragung der Methode auf radioaktive Materialien. Sie wurden durch die Einführung eines besonderen Elektrodenträgers hervorgerufen. Eine untere Empfindlichkeitsgrenze von 250 p.p.m. wurde bei einer 200-mg Probe gefunden. Die Standardabweichung betrug etwa 40%.

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SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM WITH CHROME AZUROL S

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(Received May 11th, 1964)

Many reagents have been proposed for the spectrophotometric determination of beryllium and these have been reviewed by SMYTHE AND FLORENCE[1]. At a symposium on the analytical chemistry of beryllium in June, 1960 at Blackpool, Great Britain, some of the most important spectrophotometric methods for beryllium were critically discussed by METCALFE AND RYAN[2]. Berillon II and acetylacetone appear to possess many advantages over other reagents. The acetylacetone method is very sensitive and highly selective, but requires an ultraviolet spectrophotometer, and care must be taken to purify all reagents of impurities which absorb in the ultraviolet region. In addition, extraction and washing steps are involved, which are rather time-consuming. The main disadvantage of Berillon II is that the complex does not obey Beer's law.

This paper describes a detailed investigation of chrome azurol S as a chromogenic agent for beryllium. Chrome azurol S is the sodium salt of 3″-sulfo-2″,6″-dichloro-3,3′-dimethyl-4-hydroxyfuchson-5,5′-dicarboxylic acid, also known as al'beron, Solochrome Brilliant Blue B, and Polytrop Blue R (C.I. No. 723). MUSTAFIN AND MATVEEV[3] showed that beryllium may be determined with chrome azurol S at pH 4.6, using EDTA to mask interferences. Other workers[4-6] have used chrome azurol S at higher pH values, but these methods are of limited use in practical analysis since many foreign metals also form coloured lakes. Our comprehensive investigation shows that at pH 4.6, and in the presence of EDTA, chrome azurol S is a highly selective and fairly sensitive reagent for the determination of beryllium and possesses several advantages over Berillon II.

The spectrophotometric method described below has been in use for several years in the author's laboratory, and has given excellent results when applied to a wide range of beryllium samples.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP600 spectrophotometer with 1-cm glass cuvettes was used.

Chrome azurol S solution. Dissolve 0.165 g of chrome azurol S (Geigy (A/sia) Pty. Ltd.) in water and dilute to 100 ml.

Buffer solution, pH 4.60. Dissolve 238 g of sodium acetate trihydrate in 500 ml of water, add 102 ml of glacial acetic acid, and dilute to 1 l. When 5 ml of buffer solution is diluted to 25 ml the pH should be 4.6.

Beryllium solutions. Dissolve 0.983 g of pure beryllium sulphate tetrahydrate in 200 ml of water and 50 ml of 10 *M* HCl, and dilute to 1 l. Prepare a working solution (5 μg Be/ml) by diluting 10 ml of stock solution to 100 ml.

Recommended procedure

Transfer an aliquot of the slightly acidic sample solution (1–80 μg Be) to a 25-ml volumetric flask. On a separate aliquot determine the amount of 10% sodium hydroxide required to neutralise the free acid to methyl orange indicator. Add 1.0 ml of 1% ascorbic acid, 2.00 ml of 10% EDTA, and 5.00 ml of acetate buffer. Add the predetermined amount of 10% hydroxide. Dilute to about 20 ml with water. Add 2.00 ml of the chrome azurol S solution and dilute to volume. Measure the absorbance against a blank at 569 mμ in 1-cm cells.

If aluminium, chromium, or zirconium is present special precautions must be taken (see DISCUSSION).

To determine beryllium in bronze or aluminium alloys proceed as above, except for the addition to the blank of an amount of copper or aluminium approximately equal to that in the sample aliquot. No corrections are necessary.

DISCUSSION

Sensitivity and stability of the method

The beryllium–chrome azurol S lake, when measured against the blank, gives an absorbance peak between 568 and 570 mμ (Fig. 1). With the recommended procedure, the molar absorptivity of the lake is $4.06 \cdot 10^3$ (20°), corresponding to 0.0022 μg Be/cm^2 on the Sandell scale. Beer's law is obeyed to at least 3.0 μg Be/ml, and at 4.0 μg Be/ml there is a 1.5% deviation. The absorptivity varies considerably with

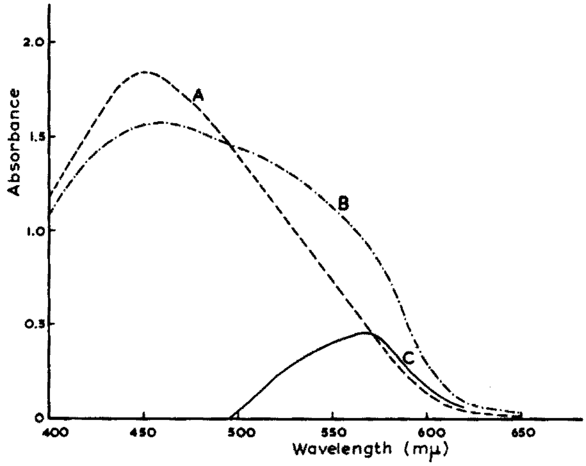

Fig. 1. Absorption spectra for chrome azurol S and its beryllium lake. (A) 2 ml of 0.165% reagent solution. (B) 25 μg of Be^{2+} and 2 ml of 0.165% reagent solution. (C) Difference between the two curves.

change in pH and in the concentrations of buffer, EDTA, and chrome azurol S. The molar absorptivity is $21.7 \cdot 10^3$ (0.00042 μg of Be/cm^2 on Sandell scale) when only 0.05 ml of buffer solution and 2 ml of dye solution in 25 ml are used.

At the specified pH of 4.6 the beryllium–chrome azurol S lake is formed instantly and is stable in the presence of ascorbic acid at normal room temperatures for at least 4 h. After 24 h the absorbance drops slightly (9%), but solutions containing no ascorbic acid are stable for at least 24 h. The lake is stable in the temperature range 15° to 35°. With increasing temperature the absorbance of the complex decreases by 1%/degree.

Effect of varying reagent concentrations

The addition of 1, 2, and 5 ml of 10% EDTA reduces the absorbance of the lake by 9, 13, and 30% respectively. A decrease in the concentration of the buffer solution increases the absorbance. A change from 5 ml to 2 ml of buffer solution increases the absorbance by 55%, and a change from 1 ml to 2 ml of the reagent increases the absorbance of the complex by 90%. However, it is impracticable to raise the dye concentration above 0.014%, because a blank containing 2 ml of the reagent has an absorbance equivalent to 25 μg of beryllium.

Choice of pH, and effect of free acid and free alkali

MUSTAFIN AND MATVEEV[3] used buffered solutions between pH 4.6 and 4.8 because EDTA considerably weakened the colour of the beryllium lake at pH values higher than 4.8. On the other hand, the absorbance of a chrome azurol S blank increased below pH 4.6, but decreased sharply at higher pH values. The pH of 4.6 was retained because it is in the middle of the sodium acetate–acetic acid buffer range and is a good general pH for forming metal–EDTA complexes.

Free acid increased and free alkali decreased the absorbance of the beryllium–chrome azurol S lake when measured against the blank at pH 4.6. Additions were made to solutions containing 2 ml and 5 ml of buffer solution, and from the results obtained (Table I) it was decided to use 5 ml of buffer solution.

TABLE I

RECOVERY OF Be AND CHANGES OF pH AFTER ADDITION OF FREE ACID OR FREE ALKALI

(25 μg of Be taken)

Added	*5 ml Buffer*		*2 ml Buffer*	
	Be found (μg)	*pH*	*Be found (μg)*	*pH*
Nil	25.0	4.60	25.0	4.60
1.0 ml 1 *M* HCl	27.0	4.48	28.6	4.30
2.0 ml 1 *M* HCl	29.0	4.36	29.4	3.98
5.0 ml 1 *M* HCl	34.4	3.95	—	—
1.0 ml 1 *M* NaOH	22.2	4.70	21.6	4.83
2.0 ml 1 *M* NaOH	18.9	4.78	10.4	5.08
5.0 ml 1 *M* NaOH	8.8	5.15	—	—

Interference by various ions

Many elements form strongly coloured chrome azurol S complexes (*e.g.*, Al^{3+}, Cu^{2+}, Fe^{3+}, Th^{4+} and Zr^{4+}) but in the presence of EDTA their interference is masked considerably (Table III). The error is proportional to the concentration of the interfering ions present, and is additive at any beryllium concentration. This permits the determination of beryllium in the presence of large amounts of interfering ions, by adding equivalent amounts of these ions to the blank.

TABLE II

EFFECT OF SALT ADDITION

Gram-equivalent salt added	*Recovery of Be (μg)*[a]				
	NaCl	*Na_2SO_4*[b]	*$NaNO_3$*	*$NaClO_4$*	*NH_4Cl*
0.001	24.6	23.9	25.0	25.2	24.4
0.025	24.4	23.2	24.8	25.4	24.0
0.050	24.2	21.9	24.4	25.6	23.8

[a] 25 μg Be added.
[b] Mol. wt./2.

TABLE III

EFFECT OF DIVERSE ELEMENTS

(25 μg Be added)

Foreign ion added	*Amount taken (mg)*	*Be found (μg)*	*Relative error (%)*
Al^{3+}	2.0	28.0	12[a]
Al^{3+}	2.0	25.5	2[b]
Ca^{2+}	2.0	25.2	1
Cd^{2+}	2.0	25.3	1
Co^{2+}	2.0	25.5	2
Cr^{3+}	2.0	39.3	57[b]
Cu^{2+}	2.0	26.1	4
Fe^{3+}	2.0	25.0	0
Hg^{2+}	2.0	25.3	1[c]
Mg^{2+}	2.0	24.8	—1
Mn^{2+}	2.0	25.3	1
Mo^{6+}	2.0	25.0	0
Ni^{2+}	2.0	25.7	3
Pb^{2+}	2.0	25.3	1
Th^{4+}	2.0	25.7	3
U^{6+}	2.0	26.1	4
V^{5+}	2.0	26.4	6
V^{5+}	2.0	25.0	0[c]
W^{6+}	2.0	25.0	0
Zn^{2+}	2.0	25.3	1
Zr^{4+}	2.0	25.7	3[d]
F^-	0.019	21.2	—15
F^-	0.038	18.5	—26
F^-	0.095	12.8	—51
PO_4^{3-}	1.0	24.5	—2
PO_4^{3-}	2.0	24.1	—4
PO_4^{3-}	4.0	23.4	—6

[a] Measured after 15 min.
[b] After heating.
[c] Without ascorbic acid.
[d] 100 mg meso-tartaric acid added.

Ascorbic acid was used to reduce iron(III) to iron(II) because, when free acid was neutralized with 10% sodium hydroxide, colloidal iron(III) hydroxide was formed which caused erratic absorbance readings. Ascorbic acid can be omitted if iron is absent since it reduces vanadium(V) to vanadium(IV) which forms a blue complex with EDTA and absorbs strongly at 569 mμ. Ascorbic acid cannot be used in the presence of mercury(II) since mercury(II) is reduced to mercury(I), which forms insoluble salts, and metallic mercury.

Aluminium in the presence of EDTA reacts slowly with chrome azurol S and reaches its highest absorbance in 15 min, after which the absorbance drops gradually. There are two alternative procedures: either (*1*) measure the absorbance after 15 min development time (when the correction is large), or (*2*) heat the blank, standard, and sample solutions to boiling before adding chrome azurol S addition (when the correction is small (Table III)).

Chromium reacts slowly with EDTA at room temperature causing a gradual increase in the absorbance. By heating the solution to boiling before the addition of chrome azurol S, a stable chromium–EDTA complex is formed, which absorbs strongly at 569 mμ, but as the absorbance is additive a correction can be made by adding the same amount of chromium to the blank.

Zirconium is complexed only weakly with EDTA at pH 4.6 and interferes seriously; 2 mg of zirconium has an absorbance equivalent to 40 μg of beryllium, but can be complexed with meso-tartaric acid. Addition of 100 mg of meso-tartaric acid (neutralized to pH 4.6) to 2 mg of zirconium results in a positive error equivalent to only 0.7 μg beryllium. It is recommended that a solution of 50 mg of meso-tartaric acid per ml be prepared, neutralised to pH 4.6, and 2 ml of this solution added to the blank, standard, and working solutions.

The interference of different salts was studied at the 25 μg Be level, by measuring the absorbance of the beryllium complex against a blank (Table II).

Reproducibility of the method

Ten replicate determinations were made at the 25 μg Be level by the recommended procedure. At this level the relative standard deviation of the results ($n-1$) was found to be ± 0.4%.

Precision spectrophotometry

The relative standard deviation of the beryllium determination may be improved to ± 0.2% by using a differential technique and measuring the absorbance of the sample (110–150 μg Be) against a reference solution containing about 100 μg Be/25 ml. The recommended procedure is followed except that only 2.0 ml of acetate buffer and 5.00 ml of 0.052% chrome azurol S are used. In this case the calibration curve is not linear.

COMPARISON BETWEEN CHROME AZUROL S AND BERILLON II

The determination of beryllium with Berillon II was similar to that described by HUNT AND MARTIN[7] except that triethanolamine was used instead of ascorbic acid or Nervaniad F (N,N-di-(2-hydroxyethyl)glycine). The following procedure was used. Pipet aliquots containing 4–16 μg of beryllium into a 50-ml volumetric flask, add 2.5 ml of 10% EDTA–6% triethanolamine solution, dilute to 30 ml with water, neutralize, add 2 ml of 10% sodium hydroxide, and dilute to 45 ml. Add 2.00 ml of 0.2% Berillon II and dilute to volume. Measure the absorbance at 630 $m\mu$ in 1-cm cells. Carry a blank through the complete procedure.

Interferences

A comparison of interferences in the two methods is given in Table IV, and for most of the metals there is no great difference in choice of reagent, except for thorium and uranium where chrome azurol S and Berillon II, respectively, are preferred.

TABLE IV

COMPARISON OF INTERFERENCES USING BERILLON II AND CHROME AZUROL S REAGENTS

Foreign ion added	*Amount taken (mg)*	*Berillon II*			*Chrome azurol S Relative error (%)*
		Be taken (μg)	*Be found (μg)*	*Relative error(%)*	
Al^{3+}	2	0	0	0	—
Al^{3+}	2	15.0	15.9	6	3
Al^{3+}	4	15.0	16.8	12	—
Al^{3+}	4	10.0	11.3	13	—
Ca^{2+}	2	15.0	15.0	0	1
Co^{2+}	2	15.0	15.2	1	2
Cr^{3+}	2	15.0	7.0	—53	—
Cr^{3+}	2	15.0	28.0	87	97[a]
Cu^{2+}	2	15.0	15.9	6	8
Fe^{3+}	2	0	0	0	—
Fe^{3+}	2	15.0	15.6	4	0
Fe^{3+}	4	15.0	16.2	8	—
Fe^{3+}	4	10.0	10.8	8	—
Mg^{2+}	2	15.0	15.0	0	—1
Mg^{2+}	4	15.0	15.7	5	—
Mn^{2+}	2	15.0	15.5	3	2
Mo^{6+}	2	15.0	15.0	0	0
Ni^{2+}	2	15.0	15.4	3	5
Th^{4+}	0.5	10.0	9.0	—10	2
Th^{4+}	1	10.0	8.0	—20	4
Th^{4+}	2	10.0	6.7	—33	7
U^{6+}	2	10.0	9.8	—2	11
U^{6+}	4	10.0	9.4	—6	22
V^{5+}	2	15.0	15.4	3	0[b]
W^{6+}	2	15.0	15.4	3	0
Zn^{2+}	2	15.0	15.0	0	2
F^{-}	0.019	10.0	10.0	0	—15
F^{-}	25	10.0	10.0	0	—

[a] After heating.
[b] Without ascorbic acid.

The results show that iron and aluminium do not give colours with Berillon II, but enhance the beryllium absorbance. Other interfering cations give colours with Berillon II and produce a proportional additive error as previously reported by ATKINSON, HUNT AND MACDONALD[8]. In Table V the effect of free acid and free alkali on beryllium determination is shown for each reagent, and the interference of neutral salts is compared in Table VI.

TABLE V

RECOVERIES OF Be (μg) AFTER ADDITION OF FREE ACID OR FREE ALKALI

Added	*Be found (μg)*	
	Berillon II	*Chrome azurol S*
Nil	15.0	25.0
2.0 ml of 1 *M* HCl	25.0	29.0
2.0 ml of 1 *M* NaOH	10.0	18.9

TABLE VI

RECOVERIES OF Be (μg) AFTER ADDITION OF 0.0025 GRAM-EQUIVALENTS OF SALTS

Reagent	*Nil*	*NaCl*	Na_2SO_4	$NaNO_3$	$NaClO_4$
Chrome azurol S	25.0	24.4	23.2	24.8	25.4
Berillon II	15.0	14.1	14.7	13.8	14.6

The disadvantages of the Berillon II method for the determination of beryllium are the limited range (0–0.32 μg Be/ml), the instability of the complex, the high absorbance of the reagent blank, and the failure of the complex to follow Beer's law. By comparison, the beryllium–chrome azurol S lake is stable for at least 4 h, Beer's law is obeyed up to 3.2 μg Be/ml, and the precision is higher because of the relatively smaller absorbance of the reagent blank.

SUMMARY

A comprehensive investigation of the spectrophotometric determination of beryllium with chrome azurol S is described. At pH 4.6, in the presence of EDTA, only chromium(III) and fluoride interfered seriously. A molar absorptivity of 4060 at 569 mμ was found for the complex, with a relative standard deviation of ± 0.4% at the 25 μg Be level. Beer's law was obeyed from 0 to 3.2 μg Be/ml. Chrome azurol S has several advantages over the widely used Berillon II.

RÉSUMÉ

L'auteur a mis au point le dosage spectrophotométrique du béryllium, au moyen de chrome azurol S. Ce réactif présente plusieurs avantages, comparé au bérillon II, généralement utilisé. Au pH 4.6, en présence d'EDTA, seuls le chrome(III) et les fluorures gênent sérieusement.

ZUSAMMENFASSUNG

Eine umfassende Untersuchung über die spektralphotometrische Bestimmung des Berylliums mit Chromazurol S wird beschrieben. In Gegenwart von EDTA stören beim pH-Wert 4.6 nur Chrom(III) und Fluorid ernsthaft. Bei 569 mμ ergab sich ein molarer Extinktionskoeffizient von 4060. Das Beersche Gesetz wurde von 0–3.2 μg Be/ml befolgt. Chromazurol S besitzt verschiedene Vorteile gegenüber dem häufig benutzten Berillon II.

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ETUDE POTENTIOMETRIQUE DES PICOLATES DE LANTHANE, PRASEODYME ET NEODYME

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(Reçu le 28 avril, 1964)

L'étude des picolates cristallisés de lanthane, praséodyme et néodyme[1] a été poursuivie par la détermination de leurs constantes de stabilité ionique en solution aqueuse, par mesures potentiométriques. La méthode de CHABEREK[2] a mis en évidence la formation de complexes de type MA_3 et la détermination des constantes de stabilité a été effectuée par application de la méthode de BJERRUM[3] pour une force ionique faible ($\mu = 0.02$) et à force ionique $\mu = 0.5$ par addition de perchlorate de sodium.

MÉTHODES EXPÉRIMENTALES

Réactifs

L'acide picolique est préparé par oxydation de l'α-picoline[4] et recristallisation dans le benzène.

Les solutions de terres rares sont obtenues par dissolution de quantités connues d'oxydes purs "Pechiney-Saint-Gobain" dans un léger excès d'acide perchlorique. Puisque les cations de terres rares ne subissent pas[5] d'hydrolyse notable à un pH inférieur à 6, il est possible de doser potentiométriquement cet excès d'acide.

Le perchlorate de sodium pur "Prolabo" est recristallisé 2 fois dans l'eau avant son utilisation.

Les neutralisations sont effectuées avec de la soude *N* exempte de carbonate.

Courbes de neutralisation

Les mesures de pH sont effectuées à 25° à l'aide d'un compensateur "METROHM" E 388. L'électrode de référence est une électrode au calomel à remplissage de KCl saturé. L'électrode de mesure est une électrode en verre. Ce couple est étalonné au moyen des tampons de BATES[6]. A force ionique 0.5 l'électrode de référence est munie d'un pont à NaCl saturé. L'étalonnage du couple est alors effectué par addition de quantités connues[7] d'acide perchlorique à une solution de perchlorate de sodium 0.5 *M*: la force électromotrice lue donne directement la concentration en H^+.

Les solutions sont $5 \cdot 10^{-3}$ *M* (Nd) ou 10^{-3} *M* (Pr, La) en cation métallique. On dose par la soude des solutions contenant de l'acide picolique et le cation de terre rare dans les rapports molaires 1/1, 2/1, 3/1, 10/1, 50/1. Le déplacement des courbes de neutralisation des trois premiers rapports montre la formation de complexes successifs du type MA^{2+}, MA_2^{+}, MA_3 ne contenant pas de groupements hydroxyle.

Les rapports 3/1, 10/1, 50/1 sont seuls utilisés pour le calcul des courbes de formation. Les solutions initiales contiennent de l'acide perchlorique libre à la concentration 10^{-2} *N*.

La courbe de neutralisation par la soude d'une solution $5 \cdot 10^{-2}$ *M* en acide picolique et 10^{-1} *M* en acide perchlorique, à force ionique 0.5, est utilisée pour le calcul des constantes de dissociation de l'agent complexant.

COURBES DE FORMATION ET CALCUL DES CONSTANTES

Constantes de dissociation de l'acide picolique

Les constantes de dissociation de l'acide picolique à force ionique faible ont été déterminées précédemment[8] : $pK_1^\circ = 1.60$; $pK_2^\circ = 5.40$. Nous les avons déterminées pour $\mu = 0.5$ par une méthode potentiométrique.

La courbe de neutralisation d'un mélange acide picolique–acide perchlorique permet en effet de calculer pour un pH donné le nombre moyen de protons liés à l'anion A^- de l'acide picolique[9]:

$$\bar{n}_H = \frac{2[H_2A^+] + [HA]}{C_A} = \frac{C_A + E + [OH^-] - [H^+] - C_B}{C_A}$$

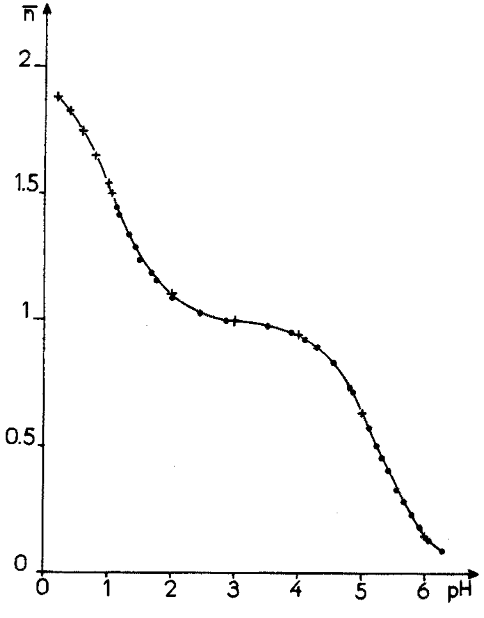

Fig. 1. Acide picolique $\mu = 0.5$. Points calculés +.

C_A représente la concentration totale en acide picolique, E la concentration initiale en acide perchlorique, C_B la concentration de soude ajoutée.

La courbe $\bar{n}_H = f$ (pH) obtenue est représentée Fig. 1. Les deux stades de formation sont nettement séparés et les valeurs du pH correspondant aux demi-valeurs de

$\bar{n}_{\mathrm{H}}$ ($\bar{n}_{\mathrm{H}} = 0.5$ et $\bar{n}_{\mathrm{H}} = 1.5$) nous donnent respectivement les valeurs de pK_2 et pK_1 de l'acide picolique:

$$\mu = 0.5 \quad \mathrm{pK}_1 = 1.07 \quad \mathrm{pK}_2 = 5.25$$

Ces valeurs expérimentales de pK_1 et pK_2 permettent de calculer la courbe de formation théorique, d'après l'expression générale du nombre de formation:

$$\bar{n}_{\mathrm{H}} = \frac{2[\mathrm{H}^+]^2 + K_1[\mathrm{H}^+]}{K_1K_2 + [\mathrm{H}^+]^2 + K_1[\mathrm{H}^+]}$$

Les points ainsi calculés sont représentés par des + sur la Fig. 1. Nous constatons que la courbe calculée coïncide avec la courbe expérimentale ce qui justifie l'extrapolation de cette dernière pour les valeurs de $\bar{n} > 1.45$, où les déterminations directes devenaient impossibles.

Courbes de formation des picolates et calcul des constantes de stabilité

(*a*) *Obtention des courbes de formation.* En chaque point des courbes de neutralisation obtenues en présence de cations de terre rare, nous pouvons calculer le nombre de formation $\bar{n}$, c'est-à-dire le nombre moyen de molécules liées à l'ion métallique

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n[\mathrm{MA}_n]}{T_{\mathrm{M}}}$$

M représente la cation métallique, T_{M} la concentration totale en métal, HA l'acide picolique. Ici $N = 3$.

Pour calculer $\bar{n}$ en fonction des données expérimentales, nous exprimons les concentrations totales en métal et acide picolique:

$$T_{\mathrm{M}} = [\mathrm{M}^{3+}] + [\mathrm{MA}^{2+}] + [\mathrm{MA}_2{}^+] + [\mathrm{MA}_3] \tag{1}$$

$$T_{\mathrm{HA}} = [\mathrm{H}_2\mathrm{A}^+] + [\mathrm{HA}] + [\mathrm{A}^-] + [\mathrm{MA}^{2+}] + 2[\mathrm{MA}_2{}^+] + 3[\mathrm{MA}_3] \tag{2}$$

ou:

$$[\mathrm{MA}^{2+}] + 2[\mathrm{MA}_2{}^+] + 3[\mathrm{MA}_3] = T_{\mathrm{HA}} - [\mathrm{H}_2\mathrm{A}^+] - [\mathrm{HA}] - [\mathrm{A}^-] \tag{2a}$$

La neutralité électrique de la solution s'exprime par l'équation:

$$[\mathrm{H}_2\mathrm{A}^+] + 3[\mathrm{M}^{3+}] + 2[\mathrm{MA}^{2+}] + [\mathrm{MA}_2{}^+] + [\mathrm{Na}^+] + [\mathrm{H}^+] = [\mathrm{OH}^-] + [\mathrm{ClO}_4{}^-] + [\mathrm{A}^-] \tag{3}$$

Si E représente l'acide perchlorique libre initial et si le cation est ajouté sous forme de perchlorate, nous avons d'après (1):

$$[\mathrm{ClO}_4{}^-] = \mathrm{E} + 3T_{\mathrm{M}} = \mathrm{E} + 3[\mathrm{M}^{3+}] + 3[\mathrm{MA}^{2+}] + 3[\mathrm{MA}_2{}^+] + 3[\mathrm{MA}_3] \tag{4}$$

En combinant (3) et (4), nous exprimons le nombre de molécules d'acide picolique liées au métal:

$$[\mathrm{MA}^{2+}] + 2[\mathrm{MA}_2{}^+] + 3[\mathrm{MA}_3] = [\mathrm{Na}^+] + [\mathrm{H}^+] - \mathrm{E} - [\mathrm{OH}^-] - [\mathrm{A}^-] + [\mathrm{H}_2\mathrm{A}^+] \tag{5}$$

La dissociation de l'acide picolique donne les équilibres:

$$K_{2\mathrm{a}} = \frac{[\mathrm{A}^-]\,[\mathrm{H}^+]}{[\mathrm{HA}]} \quad \text{d'où} \quad [\mathrm{HA}] = \frac{[\mathrm{A}^-]\,[\mathrm{H}^+]}{K_{2\mathrm{a}}} \tag{6}$$

$$K_{1\mathrm{a}} = \frac{[\mathrm{HA}]\,[\mathrm{H}^+]}{[\mathrm{H}_2\mathrm{A}^+]} \quad \text{d'où} \quad [\mathrm{H}_2\mathrm{A}^+] = \frac{[\mathrm{A}^-]\,[\mathrm{H}^+]^2}{K_{1\mathrm{a}}K_{2\mathrm{a}}}$$

En identifiant (2a) et (5) et en remplaçant [HA] et $[H_2A^+]$ par leurs valeurs en fonction de $[A^-]$ dans (6), nous obtenons $[A^-]$ en fonction des données expérimentales:

$$[A^-] = \left[T_{HA} - ([Na^+] + [H^+] - E - [OH^-])\right] \frac{K_{1a}K_{2a}}{2[H^+]^2 + K_{1a}[H^+]}$$

$\bar{n}$ s'obtient alors en remplaçant dans (5) $[A^-]$ et $[H_2A^+]$ par leurs valeurs:

$$\bar{n} = \frac{1}{T_M}\left\{[Na^+] + [H^+] - E - [OH^-] - \left[T_{HA} - ([Na^+] + [H^+] - E - [OH^-])\right] \frac{[H^+]^2 + K_{1a}K_{2a}}{2[H^+]^2 + K_{1a}[H^+]}\right\}$$

$[OH^-]$ est négligeable aux pH auxquels nous opérons.

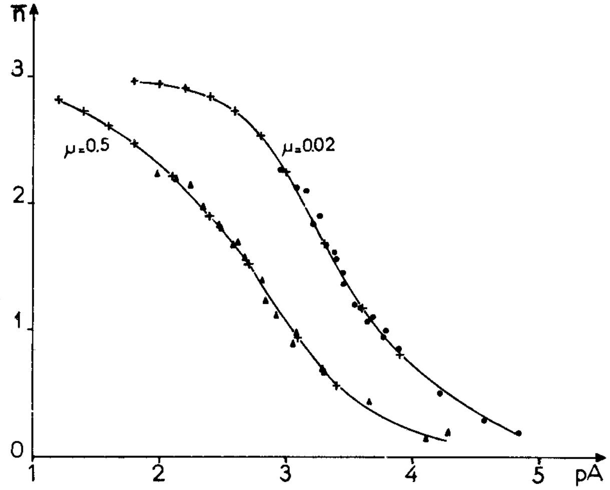

Fig. 2. Courbes de formation du picolate de lanthane. $\mu = 0.02$ ●; $\mu = 0.5$ ▲. Points calculés +.

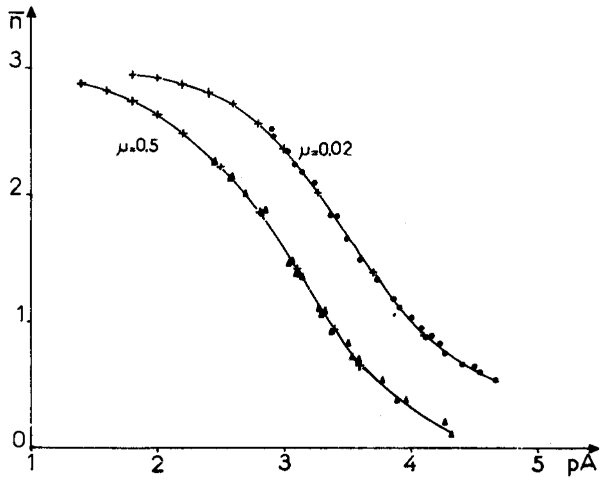

Fig. 3. Courbes de formation du picolate de praséodyme. $\mu = 0.02$ ●; $\mu = 0.5$ ▲. Points calculés +.

Les courbes de formation $\bar{n} = \mathrm{f}\,(\mathrm{pA})$ sont tracées Figs. 2, 3 et 4.

Dans le cas présent, il n'est pas possible d'obtenir avec précision des valeurs de $\bar{n}$ supérieures à 2.2–2.3. L'acide picolique étant relativement dissocié et la stabilité des picolates étudiés relativement faible, la concentration en anions A^- devient importante au voisinage du point d'équivalence. De plus, la faible solubilité des picolates ne permet pas d'employer des solutions plus concentrées.

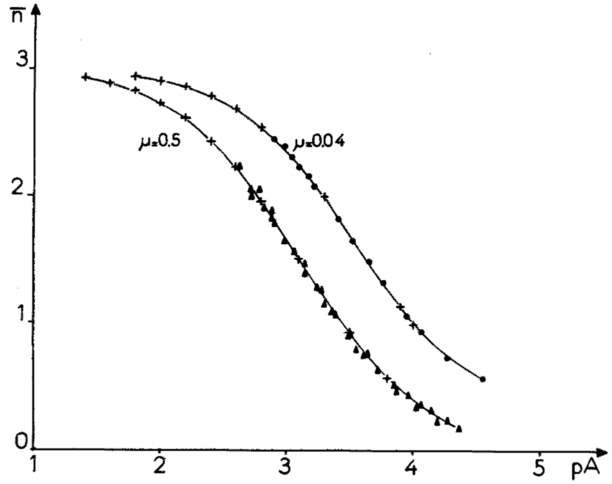

Fig. 4. Courbes de formation du picolate de néodyme. $\mu = 0.04$ ●; $\mu = 0.5$ ▲. Points calculés +.

(*b*) *Détermination des constantes de stabilité.* De ces courbes de formation, nous avons déduit les constantes de stabilité des complexes successifs:

$$\beta_n = \frac{[\mathrm{MA}_n]}{[\mathrm{M}]\,[\mathrm{A}]^n}$$

en choisissant parmi les différentes méthodes possibles:

(*1*) *une méthode algébrique* de résolution d'équations simultanées: pour trois valeurs de $\bar{n} = 0.5$, 1.5, 2.2 nous déterminons pA sur chaque courbe, et les valeurs correspondantes sont introduites dans l'expression:

$$\bar{n} + \sum_{n=1}^{n=3} (\bar{n} - n)\,[\mathrm{A}]^n \beta_n = 0$$

Les valeurs de β_n ainsi calculées sont rassemblées dans le Tableau I.

(*2*) *la "méthode de la pente au point milieu" de la courbe de formation*: dans le cas où $N = 3$ le facteur de répartition x est donné par l'expression

$$\frac{k_n}{k_{n+1}} = 3x^2 \quad \text{avec} \quad k_n = \frac{[\mathrm{MA}_n]}{[\mathrm{MA}_{n-1}]\,[\mathrm{A}]}$$

et la mesure de la pente au point milieu Δ de la courbe permet de calculer x selon:

$$x^2 = \frac{9 - 4\Delta}{12\Delta - 3}$$

Pour les courbes de formation des picolates étudiés, x est voisin de 1, ce qui nous permet d'écrire:

$$\log k_2 = \mathrm{pA}_{\bar{n}=1.5}$$

Connaissant ainsi k_2 et x, nous avons calculé k_1 et k_3 puis les constantes globales de stabilité β_1, β_2, β_3. Les valeurs ainsi obtenues pour les picolates de néodyme et de praséodyme sont rassemblées dans le Tableau II. Elles concordent assez bien avec les valeurs obtenues par la méthode précédente; nous pensons qu'elles sont moins précises, principalement à cause de l'imprécision inévitable sur la mesure de la pente Δ.

TABLEAU I

CONSTANTES DE STABILITÉ DES PICOLATES

Force ionique		*μ faible*	*μ = 0.5*
Lanthane	$\log \beta_1$	4.19	3.21
	$\log \beta_2$	7.20	6.06
	$\log \beta_3$	10.47	7.94
Praséodyme	$\log \beta_1$	4.38	3.43
	$\log \beta_2$	7.90	6.65
	$\log \beta_3$	11.00	8.94
Néodyme	$\log \beta_1$	4.27	3.69
	$\log \beta_2$	7.91	6.80
	$\log \beta_3$	10.95	9.33

TABLEAU II

	μ	*Δ*	*x*	*log β₁*	*log β₂*	*log β₃*
Praséodyme	0.02	0.59	1.26	4.28	7.88	10.80
	0.5	0.78	0.97	3.49	6.53	9.12
Néodyme	0.04	0.62	1.21	4.30	7.95	10.95
	0.5	0.66	1.13	3.69	6.80	9.33

(*c*) *Calcul des courbes de formation.* Les valeurs de β_n calculées sont vérifiées en recalculant les courbes de formation en introduisant ces constantes dans l'expression:

$$\bar{n} = \frac{\sum_{n=1}^{n=3} n\,\beta_n[\mathrm{A}]^n}{1 + \sum_{n=1}^{n=3} \beta_n[\mathrm{A}]^n}$$

Les points obtenus sont représentés par + sur les courbes de formation, Figs. 2, 3 et 4. Nous constatons qu'ils sont en accord avec les valeurs expérimentales, ce qui nous a permis une extrapolation des courbes au delà de $\bar{n} = 2.2$; toutes ces courbes tendent normalement vers $\bar{n} = 3$.

CONCLUSIONS

Les valeurs reproduites dans le Tableau I montrent que la stabilité des picolates étudiés augmente de La à Nd. Nous avons également constaté que la solubilité augmentait dans le même sens. Ces résultats sont en accord avec l'accroissement habituel de la force de la liaison métal–coordinat quand le rayon ionique du cation diminue[10].

Les constantes de stabilité des picolates de terres rares sont légèrement supérieures aux constantes correspondantes des glycinates[11], malgré une basicité plus forte de la glycine ($pK_{2a} = 9.53$ à $\mu = 0.1$). Il est possible que le cycle pyridinique de l'acide picolique entraîne des possibilités de résonance qui peuvent jouer un rôle favorable dans la chélation.

Cependant, les picolates de terres rares sont beaucoup moins stables que les chélates correspondants de l'E.D.T.A.[12] et de ses dérivés. De même les dipicolates de terres rares étudiés par GRENTHE[13] à force ionique 0.5 ($NaClO_4$) ont des constantes de stabilité nettement supérieures à celles des picolates ($\log \beta_1$ de l'ordre de 8–9). Ceci est en accord avec la règle générale selon laquelle l'augmentation du nombre de cycles de chélation possibles entraîne un accroissement corrélatif de la stabilité des chélates formés.

RÉSUMÉ

Les auteurs ont déterminé par une méthode potentiométrique les constantes de stabilité successives des picolates de lanthane, praséodyme et néodyme en solution aqueuse pour deux forces ioniques: $\mu = 0.02$ et $\mu = 0.5$, en milieu perchlorate de sodium à 25°.

SUMMARY

A potentiometric method is used to determine the stepwise stability constants of lanthanum, praseodymium and neodymium picolinates in aqueous solution at two ionic strengths ($\mu = 0.02$ and $\mu = 0.5$; sodium perchlorate medium) at 25°. The stability and the solubility of these picolinates increase from La to Nd.

ZUSAMMENFASSUNG

Mit einer potentiometrischen Methode wurden die Stabilitätskonstanten des Picolinats von Lanthan, Praseodym und Neodym in wässeriger Lösung bei 25° bestimmt. Die Ionenstärken betrugen in $NaClO_4$-Medium $\mu = 0.02$ und 0.5. Die Stabilität und Löslichkeit der Picolinate steigt vom La zum Nd.

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METHYL-2-PYRIDYL KETOXIME AS A COLORIMETRIC REAGENT FOR RHENIUM

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(Received April 4th, 1964)

Although oximes have been extensively investigated as colorimetric reagents for several of the transition metals, their utilization in the analysis of rhenium has not been great. TOUGARINOFF[1] observed the formation of a colored species when dimethylglyoxime and perrhenate ion were treated with tin(II) chloride in an acidic solution, and a quantitative method based on this was developed by KENNA[2]. TRIBALAT[3] used α-benzildioxime as a qualitative reagent. MELOCHE, MARTIN AND WEBB[4] developed a quantitative method with α-furildioxime. KASSNER *et al.*[5] investigated 4-methylnioxime. All of these methods have disadvantages. The dimethylglyoxime procedure is, according to KENNA, accurate to only 5% .The methods involving α-benzildioxime, α-furildioxime, and 4-methylnioxime all require extraction of the colored species into an organic phase prior to photometric measurement, or are subject to interference by many ions.

The method described here has several advantages: methyl-2-pyridyl ketoxime** is readily available by a simple procedure from commercially obtainable methyl-2-pyridyl ketone; it is stable in solution for long periods; the rhenium complex formed with it requires no extraction into an organic phase; the analytical procedure is manipulatively simple; it is subject to only a limited number of interferences. Although lacking the sensitivity of some of the methods listed previously, the method described here is capable of detecting 0.5 p.p.m. of rhenium. Above specified values, the concentrations of the oxime and of tin(II) chloride are not critical.

EXPERIMENTAL

Reagents

Methyl-2-pyridyl ketoxime was prepared from methyl-2-pyridyl ketone by the method of TRUSELL[6] and purified by recrystallization from hot water (m.p. found, 120–121°; reported[7], 120°).

Potassium perrhenate was obtained from the Chase Brass and Copper Company and was further purified by 3 recrystallizations from hot water. The material was dried

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** Although syn- and anti-isomers are to be expected, to our knowledge, resolution of isomers of methyl-2-pyridyl ketoxime has not been effected.

for 24 h at 110° and analyzed[8] by precipitation of $(C_6H_5)_4AsReO_4$; the purity was 99.9%.

All other reagents were reagent grade and all solutions were prepared with distilled water.

Standard solutions

Standard rhenium stock solution (0.001000 *M*) was prepared by dissolving 0.2893 g of purified $KReO_4$ and diluting to 1 l. All working solutions were prepared from this stock. The ligand solution (0.01000 *M*) was prepared by dissolving 1.3615 g of recrystallized methyl-2-pyridyl ketoxime in water and diluting to 1 l. Tin(II) chloride reducing solution (approximately 10%) was prepared by dissolving 12 g of $SnCl_2 \cdot 2H_2O$ in enough concentrated hydrochloric acid to bring the volume to 100 ml.

Apparatus

Quantitative absorption studies were done on a Hitachi Perkin-Elmer Model 139 UV-VIS spectrophotometer using matched 1-cm glass cells. The absorption spectrum trace was obtained with a Beckman DB spectrophotometer equipped with a Sargent Model SRL recorder.

Recommended procedure

To a 50-ml volumetric flask containing 0.1–2.5 mg of rhenium as perrhenate, add 5 ml of aqueous 0.01000 *M* methyl-2-pyridyl ketoxime and 6 ml of 10% tin(II) chloride solution. Dilute to the mark with distilled water. Mix thoroughly and allow to stand for 30 min. Measure the absorbance at 490 mμ against a water blank, and determine the rhenium from a calibration curve or from Beer's law ($\varepsilon = 3836$).

If the rhenium being determined comes from a readily oxidized species, conversion to the perrhenate may be accomplished by treatment with hydrogen peroxide in basic solution. More durable compounds require fusion with sodium peroxide to insure complete oxidation prior to analysis.

RESULTS AND DISCUSSION

The reliability of the method was evaluated by analysis of solutions containing known amounts of rhenium (Table I).

Interference of diverse ions

The interference of diverse ions with the determination of rhenium was investigated

TABLE I

ACCURACY OF THE PROPOSED METHOD

Re present (p.p.m.)	*Re found (p.p.m.)*	*Relative error (%)*
5.00	4.98	−0.4
10.00	10.01	+0.10
15.00	15.11	+0.73
20.00	20.07	+0.35
30.00	30.17	+0.57

by adding 1000 p.p.m. of the ion to a solution containing 20 p.p.m. of rhenium prior to analysis.

It may be noted that the interference of chromium(III), copper(II) and Bi(III) ions may be avoided by using the absorption peak at 630 mμ; the interference of arsenate and arsenite is also reduced considerably at the higher wavelength.

TABLE II

INTERFERENCE OF DIVERSE IONS

(1000 p.p.m. interfering ion)

Ion	*% Error (λ = 490 mμ)*	*% Error (λ = 630 mμ)*	*Ion*	*% Error (λ = 490 mμ)*	*% Error (λ = 630 mμ)*
F^-	0	0	Zn^{2+}	+1	0
Br^-	+1	−1.5	Pb^{2+}	+1.5	+1
I^-	+1	+1	Ca^{2+}	+1	+1
Ac^-	0	0	Sr^{2+}	+1	+0.5
ClO_3^-	−1	+2	Pd^{2+}	+2.5	+25
ClO_4^-	−1	+2	Bi^{3+}	+4	+0.5
SO_4^{2-}	0	0	Sb^{3+}	+3.5	+1.5
Citrate	−1	−0.5	Co^{2+}	+4	−2.5
Al^{3+}	+1	+0.5	Fe^{3+}	+6.5	−7
Na^+	0	0	Fe^{2+}	+6.5	−7
K^+	0	0	$C_2O_4^{2-}$	−5	−3.5
NH_4^+	0	0	Ni^{2+}	+9	−2.5
Cd^{2+}	0	−1	AsO_3^{3-}	−11.5	+1.5
Mn^{2+}	0	+0.5	AsO_4^{3-}	−11.5	+1.5
Cu^{2+}	−6	+0.5	Cr^{3+}	+250	0
Mg^{2+}	+2	+1	EDTA	+2.5	+2

Molybdate interference may be removed by extraction of the perrhenate into pyridine equilibrated with 5 *N* sodium hydroxide and then back-washing with 5 *N* sodium hydroxide equilibrated with pyridine[9]. Thiocyanate interference may be removed by making the sample basic, adding hydrogen peroxide, and heating to destroy excess hydrogen peroxide. Nitrate interference is removed by repeated fuming to dryness with hydrochloric acid after the addition of enough sodium chloride to prevent loss of rhenium as the volatile heptoxide.

Effects of varying amounts of reagents

The rate of color development reached a maximum when 3 ml of ligand solution were used; samples containing from 3 to 10 ml of the ligand solution gave the same absorbance values after 30 min.

Variation of the acidity of the solution has a great effect upon the nature of the colored complex. In solutions which are 1 *M* or greater with respect to hydrochloric acid, the complex has an emerald green color which is stable for at least 48 h. In solutions which are 0.5 *M* or less, with respect to hydrochloric acid, the green complex is formed initially, but begins to fade within 4 h to a purple solution; this transformation may be effected by heating the solution for 1 h in a boiling water bath.

Preliminary studies suggest that the variation in colored forms arises from different chloride complexes of the rhenium species bound to the ligand.

That the differences in color might be attributable to the reduction of the methyl-2-pyridyl ketoxime to the corresponding amine and the formation of a rhenium complex with this was also investigated. A small sample, *ca.* 10 mg, of methyl-2-pyridyl ketoxime was dissolved in 6 ml of 10% tin(II) chloride solution and enough distilled water added to bring the volume to 50 ml. This solution was boiled for 1 h, made basic to litmus with sodium hydroxide, and extracted with diethyl ether. The ether extract was dried over anhydrous sodium sulfate and the ether solution placed in an open vessel. Upon evaporation of the ether, *ca.* 10 mg of white solid remained which gave the same results as did the untreated ligand when used in a rhenium determination. With other substances constant, treated and untreated ligand samples gave the same spectrum in the region 400 to 700 mμ.

The only restriction on the order of addition of reagents is that the tin(II) chloride solution must be added last; low results are obtained otherwise.

If the volume of the rhenium sample taken for color development is large, the solution will have a slight yellow-brown cast in the first minutes after addition of the tin(II) chloride, but this is masked as color development proceeds and the resultant solutions give the expected absorbance readings.

Spectrum of the complex

The spectrum of the rhenium complex formed under the recommended conditions is shown in Fig. 1. The peak at 490 mμ was selected for the quantitative work because of its greater intensity. A Beer's law plot at this wavelength was found to be linear between 10 and 50 p.p.m. rhenium.

The ligand: metal ratio was determined by the method of VOSBURGH AND COOPER[10] and found to be 1:1. The ratio was determined by mixing 0.001000 *M* ligand and 0.001000 *M* potassium perrhenate, in volume increments of 1 ml, so that the total volume of ligand and perrhenate was a constant 10 ml. The VOSBURGH–COOPER plot is shown in Fig. 2.

It is said that the reduction of an acidic perrhenate solution by tin(II) chloride in the presence of a ligand yields rhenium(IV) except where the ligand itself is a reducing

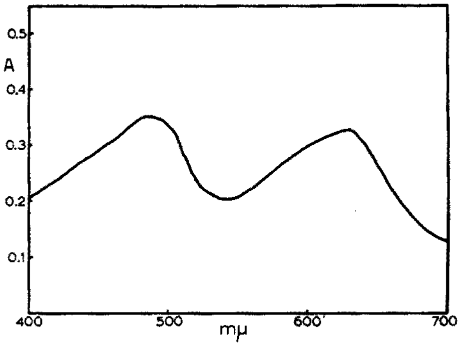

Fig. 1. Absorption spectrum of rhenium complex of methyl-2-pyridyl ketoxime.

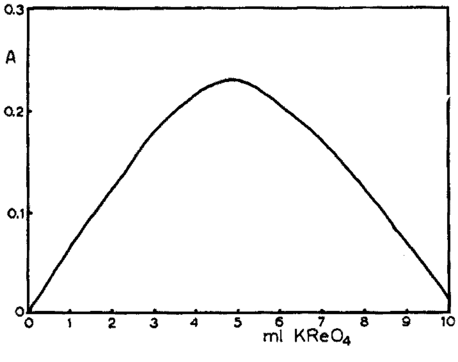

Fig. 2. VOSBURGH–COOPER plot of rhenium complex of methyl-2-pyridyl ketoxime.

agent[11]. It seems likely, therefore, that the complex produced by the reduction of perrhenate ion by tin(II) chloride in acid solution in the presence of methyl-2-pyridyl ketoxime should, by analogy to the behavior noted with α-furildioxime, α-benzildioxime, and dimethylglyoxime[11], also contain rhenium(IV). Basic hydrolysis of hexachlororhenate(IV) ion and analysis of the resulting mixture by the procedure described above gave a rhenium content in agreement with the rhenium taken; this is strongly indicative that a rhenium(IV) complex is formed.

That a complex ion is the species formed with methyl-2-pyridyl ketoxime may be inferred from the fact that the colored species is not extracted by organic solvents such as amyl alcohol. The colored ion is most probably an anion since it is retained by an anion-exchange resin (Dowex 1-X1) and is not eluted by water, but is eluted by 4 *M* hydrochloric acid.

After the submission and acceptance of the above paper, a paper by J. Guyon and R. K. Murmann (Anal. Chem., 36 (1964) 1058) appeared on the spectrophotometric determination of rhenium with syn-phenyl-2-pyridyl ketoxime, in which work of a nature similar to the above is reported.

The authors acknowledge the generous support of the Robert A. Welch Foundation.

SUMMARY

Reduction of the perrhenate ion by tin(II) in hydrochloric acid solution in the presence of methyl-2-pyridyl ketoxime yields a species which has an absorption peak at 490 mμ. Beer's law ($\varepsilon = 3836$) is obeyed in the range 10 to 50 p.p.m. rhenium, and as little as 0.5 p.p.m. rhenium can be detected readily. The ligand solution is stable; the color formation is complete within 30 min and stable for at least 48 h.

RÉSUMÉ

La réduction du perrhénate par l'étain(II), en solution acide chlorhydrique et en présence de méthyl-2-pyridylcétoxime donne un composé présentant un pic d'absorption à 490 mμ. La loi de Beer s'applique de 10 à 50 p.p.m. de rhénium ($\varepsilon = 3836$); on peut déceler facilement jusqu'à 0.5 p.p.m. de rhénium. La coloration est totale après 30 min et est stable 48 h au moins.

ZUSAMMENFASSUNG

Die spektralphotometrische Bestimmung des Rheniums mit Methyl-2-pyridylketoxim wird beschrieben. Das Perrhenation wird in salzsaurer Lösung durch Zinn(II) reduziert und ergibt mit dem Reagenz ein Absorptionsmaximum bei 490 mμ ($\varepsilon = 3836$). Das Beersche Gesetz wird für den Bereich von 10–50 p.p.m. Rhenium befolgt, jedoch können noch 0.5 p.p.m. Rhenium bestimmt werden. Die Farbbildung erfolgt vollständig in 30 Min und ist für wenigstens 48 Std. beständig.

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Short Communications

The rapid separation of rare earth mixtures by thin-layer chromatography

The use of thin-layer chromatography to obtain the rapid separation of the several components of a complex mixture is well known, and the technique has been extensively applied to many problems in organic chemistry[1]. By contrast, thin-layer chromatography has been little used in inorganic chemistry[2,3], although rapid separation of small quantities of solute, as might be achieved by thin-layer chromatography, would clearly be of value to certain inorganic analytical techniques. Recently, selective stationary phases have been developed for inorganic chromatography by immobilizing an organic complexing agent on both powders and paper sheets, and these have been applied to a variety of separations. There is the possibility that this type of reversed-phase partition chromatography could be further extended to provide selective stationary phases for inorganic thin-layer chromatography, thus providing rapid and efficient separations of small quantities of inorganic solutes.

One of the systems to which partition chromatography has been applied has been the separation of the rare earths using di(2-ethylhexyl) hydrogen phosphate (HDEHP) retained on a poly(vinyl chloride/vinyl acetate) copolymer, Corvic, as the stationary phase, and a column separation of the elements has been achieved[4]. In preliminary investigations it was found that the polymer loaded with reagent would adhere to a standard glass plate, without the addition of binder, if the thin layers were heated after the slurry had been spread over the plates. Results obtained by chromatographing rare earths on these thin layers are reported in this paper.

Preparation of thin layers

The method of preparing Corvic powder for retaining HDEHP for use in columns, was described previously[5]. The material prepared in this way was not suitable for thin layers, however, as the size of the particles decreased upon heating, resulting in cracks in the thin layers. To overcome this, and to increase the speed at which the loaded powder could be prepared, diethyl ether was used instead of toluene for dissolving the HDEHP before it was added to the dry Corvic powder.

Thin layers were prepared as follows: 2.5 ml of purified HDEHP were dissolved in a mixture of 25 ml of chloroform and 25 ml of diethyl ether and the solution was added to 50 g of Corvic (the smallest particle size available was passed through a 150-mesh sieve before use) in a beaker. The contents of the beaker were stirred in a current of air to evaporate the organic solvents, and the powder, thus loaded with HDEHP, was slurried with 0.05 M hydrochloric acid. The slurry was applied to the plates in the usual way with commercially available equipment (Unoplan Leveller, Shandon Scientific Company) with the spreader blade set to give a layer 750 μ thick. Surplus aqueous solvent was allowed to evaporate, and the plates were then placed in an oven at 110–120° for 15–20 min. If the plates were heated at too high a temperature, or for too long, the polymer particles tended to sinter and the thin layers gave uneven fronts with the developing solvent.

Development

Ascending, descending and horizontal development were all tried in order to find the most satisfactory method. Horizontal development was finally used as it gave a development time of 10 min, eluting solvent being added to the plates from the solvent trough by a filter paper tongue. The peak shapes of rare earths eluted from HDEHP–Corvic columns were previously found to improve as the temperature of the column was raised; consequently, development of thin layers on to which mixtures of rare earths had been spotted, was carried out at 60–80°, by placing the developing tank in a thermostatted air-batth.

The procedure employed for development was similar to standard thin-layer techniques. A sharply defined margin was made down each side of the plate by removing about 5 mm of the layer, and the mixture to be separated was spotted on to the plates in a small volume of solution. Standards of known composition were also spotted on to the plates to act as controls. After development the plates were dried and the positions of the elements located, either by spraying the plates with a colour-forming agent (1%(w/v) 8-hydroxyquinoline in a 1:1 ethanol–water mixture and exposed to ammonia vapour) or by using radioactive tracers. The latter method enabled the elements to be characterised by means of their γ-ray spectra.

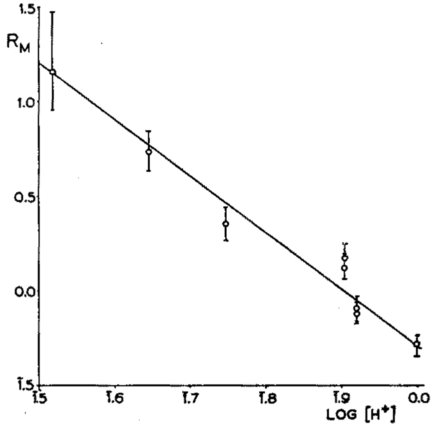

Fig. 1. Dependence of the zone-migration parameter, R_M, upon the acidity of the eluting phase.

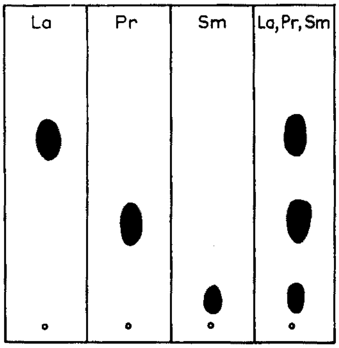

Fig. 2. Separation of 5 μg each of samarium, praseodymium and lanthanum on HDEHP–Corvic thin layers. Mobile phase 0.25 M HCl.

Results and discussion

A plot of the zone-migration parameter, R_M, [log $(1/R_F - 1)$] against the log of the acidity of the mobile phase, (log [H⁺]), has been shown to approach the expected value of -3, when the rare earths are eluted from an HDEHP stationary phase retained on paper sheets[6] or Corvic powder[7]. Figure 1 gives the plot of R_M against log [H⁺] for the elution of europium on HDEHP–Corvic thin layers, with hydrochloric acid at room temperature, results being obtained by scraping off the completed chromatogram 1 cm at a time and plotting a histogram of the europium activity. A line of slope -3 has been drawn through the points, and limits are included to correspond to a variation of 0.5 cm in the estimated position of the activity maximum. All the plates used in these expeiiments were prepared at the same time, from the same batch of material.

Separation of rare earth mixtures proceeded as expected with elements of high atomic number migrating more slowly than elements of low atomic number at any given acidity. An increase in the acidity of the eluting phase caused an increase in the rate of migration of the rare earths along the plate.

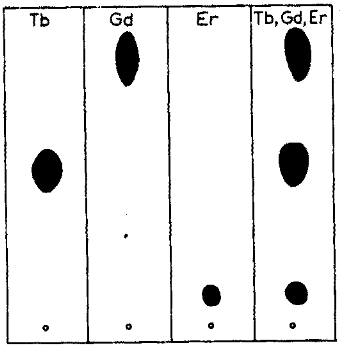

Fig. 3. Separation of 5 μg each of erbium, terbium and gadolinium. 0.80 M HCl mobile phase.

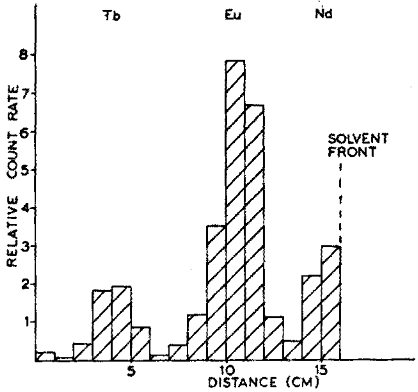

Fig. 4. Histogram of separation of tracer terbium, europium and neodymium. 0.90 M HCl mobile phase.

Thin-layer chromatography is capable of providing rapid separation of small quantities of organic solutes. In these experiments inorganic separations employing a reversed-phase technique were found to be equally fast, 10 min being required for the solvent front to traverse the whole length of the plate. Figures 2, 3 and 4 give typical examples of the separations that have been achieved with pure elements spotted on to the plates alongside the mixture to act as controls, for the actual R_F values were found to depend upon the temperature and to vary slightly from batch to batch of plates. Whilst the separations shown do not include mixtures of rare earths whose migration rates are most similar, separation factors for the components spotted on to the plates are not large, and the very rapid separations achieved would be difficult to obtain by other conventional chromatographic methods.

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(Received May 14th, 1964)

The detection and estimation of the relative amounts of primary and secondary hydroxyl groups using N.M.R.

Hydroxyl groups are usually detected fairly readily in organic compounds by high-resolution proton magnetic resonance spectroscopy. In the 10% solutions normally used, they appear as a single sharp peak that can be moved steadily downfield by successive additions of small amounts of acid to the sample; trifluoroacetic acid is often used for this purpose. This variation in peak position is due to exchange between the hydroxyl group protons of the alcohol and acid, which results in these protons losing their separate identities and appearing as one peak whose position depends upon the concentration of acid added[1,2]. Alternatively, a hydroxyl peak can be recognised by shaking the sample with D_2O whereupon the peak is reduced in intensity and may even disappear. Exchange of the hydroxyl protons is again responsible for this behaviour.

However, because of similar exchange processes, the various chemically different hydroxyl groups that may be present in a molecule or mixture, again give only a single peak; this is illustrated in Fig. 1 where the spectrum of 1,3-butanediol is shown.

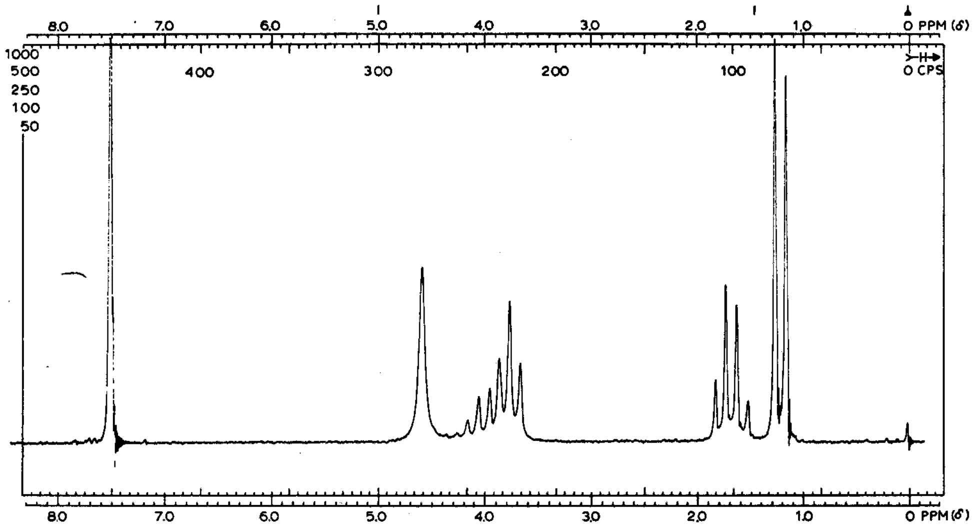

Fig. 1. 1,3-Butanediol in $CHCl_3$ at 60 MC. 1.20 δ due to CH_3—, 1.68 δ due to —CH_2—, 3.60–4.30 δ due to —CH_2OH and >CHOH, 4.70 δ due to OH.

From the area of this peak information can be obtained on the total amount of hydroxyl present, but not on the relative amounts of primary, secondary and tertiary hydroxyl groups. The relative amounts of primary and secondary hydroxyl groups can be obtained in favourable cases from a comparison of the areas of the resonances due to the protons on the carbon atoms carrying the OH groups, *i.e.* —CH_2OH and >CHOH, but in most cases, these resonances give overlapping bands between *ca.* 3 δ and 4 δ. (Throughout this paper the Varian system of chemical shift measurement is used, in which positive δ values refer to the chemical shifts, quoted in parts per million, downfield from an internal reference of tetramethylsilane.) This can be seen in Fig. 1 even in the simple case of 1,3-butanediol. In Fig. 2 the spectrum is shown of the reaction mixture after 1,3-butanediol has been acetylated with excess acetic anhydride. Here it can be seen that the resonances due to those protons on the carbon atoms that originally carried the hydroxyl groups have both been moved downfield and are in fact now separated by about 1 p.p.m. The —$COOCH_2$— multiplet is centred at 4.1 δ whilst that due to —COOCH< is centred at 5.0 δ. The areas of these resonances can then be compared. Hence acetylation of a hydroxyl-containing compound or mixture followed by an N.M.R. examination of the product can yield directly the primary to secondary hydroxyl ratio, provided of course that the acetylation is quantitative.

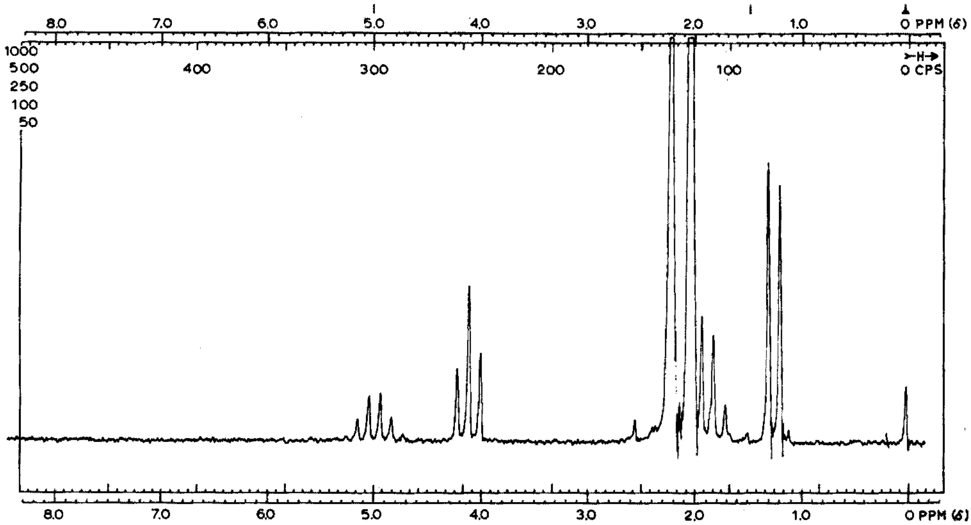

Fig. 2. Reaction mixture (in CCl_4 at 60 MC) after acetylation of 1,3-butanediol with excess acetic anhydride. 1.25 δ due to CH_3—, 1.65–2.50 δ due to —CH_2— and CH_3CO, 4.10 δ due to —$COOCH_2$—, 4.95 δ due to —COOCH<.

Acetylation

Several methods are available for achieving quantitative acetylation[3]. In order that the reaction mixture after acetylation may be examined by N.M.R. immediately, the reagents used in the acetylation must not have any resonances falling in the range of 3.5 δ to 5.5 δ. In fact, this proviso debars none of the usual procedures. Thus excess acetic anhydride either alone or with sodium sulphate or sodium acetate contributes only the resonances of the methyl protons of acetyl groups, which occur between 2 δ and 2.5 δ. Similarly, acetylation with acetic anhydride–pyridine mixtures adds only resonances in the acetyl region, together with the aromatic proton band of pyridine between 7 δ and 8.6 δ.

Accuracy and sensitivity

In order to test the accuracy of this method of determining primary to secondary ratios, a series of test samples was prepared by weighing out mixtures of 1,4-butanediol and 2,3-butanediol (B.D.H., Ltd.). For these samples the following acetylation procedure was found to be satisfactory: 2 ml of sample with a 3-fold excess of A.R. acetic anhydride and about 0.5 g of anhydrous sodium acetate were placed in a 100-ml flask fitted with a condenser and refluxed gently for 30 min. The reagents were examined before use by N.M.R. for trace impurities. After cooling, about 0.5 ml of the reaction mixture was withdrawn and mixed with about 0.5 ml of a standard solution of 1% T.M.S. in CCl_4 and the spectrum recorded using a Varian A-60 N.M.R. spectrometer. The areas of the $—COOCH<$ resonance centred at 4.95 δ (area A) and of the $—COOCH_2$ resonance centred at 4.05 δ (area B) were then obtained using the electronic integrator. A minimum of 4 repeat integrations was performed on each sample. The required ratio was then simply:

$$\frac{\text{(primary OH)}}{\text{(secondary OH)}} = \frac{B}{2A}$$

The factor of two arises since each primary group contributes two protons to B whereas each secondary group only contributes one proton to A.

Table I shows the percentage of primary hydroxyl group calculated from the weighed amounts of diols and the values obtained by acetylation and N.M.R. examination. The agreement between the two sets of data was quite good. The deviations of the experimental values in no case exceeded 1.7%. The average deviation of the experimental values over the whole range of concentration was 0.8%. At first sight it seems possible from the signs of the deviations that the N.M.R. method may have slightly over-estimated the amount of primary hydroxyl. However, a Student *t*-test of significance applied to the data showed that the measured mean value did not differ from zero at the 5% level of significance. The deviations were, in fact, comparable with the limits of accuracy claimed for the electronic integration method of the Varian A-60 spectrometer. The nature of the integration method implies that as the amount of one component becomes smaller with respect to the other, the relative

TABLE I

% Primary OH calculated(X)[a]	*% Primary OH measured(Y)*	*Difference (Y—X)*
97.28	96.4	−0.9
93.67	94.3	+0.6
88.50	89.6	+1.1
76.03	75.3	−0.7
62.98	64.7	+1.7
49.92	50.8	+0.9
39.05	39.8	+0.8
25.36	26.0	+0.6
12.29	12.3	0.0
2.93	3.8	+0.8

[a] $\left[\frac{\text{(primary OH)} \times 100}{\text{(primary OH)} + \text{(secondary OH)}}\right]$.

uncertainty in the estimation of this smaller component must increase. In the present work it was found that samples 1 and 10, with only 2.72% secondary OH and 2.93% primary OH respectively, represented the limits of reliable estimation.

The above accuracy tests of the method were performed on butanediol mixtures where hydroxyl made up 38% by weight of the samples. It was necessary to know the lowest level of OH that could be detected in an unknown sample. For this purpose two ethylene oxide–propylene oxide block co-polymers were used. These polymers of molecular weight about 3500, had terminal OH groups and a mixture of $—OCH_2CH_2OH$ and $—OCH_2CH(CH_3)OH$ chain ends was present. The samples contained 1.46 and 1.70% by weight of OH, determined as 48 mg and 56 mg KOH per gram respectively. The samples (2 ml) were heated for 2 h with 0.5 ml of acetic anhydride and 0.25 g of anhydrous sodium acetate. In both cases, after acetylation, the $—COOCH_2—$ and $—COOCH<$ resonances could be observed on the higher sensitivity scales of the A-60 and a comparison of the relative areas could just be made. This gave 25 ± 5% and 50 ± 5% primary hydroxyl respectively for the 2 samples. These samples therefore, approached the limit at which the presence of primary and secondary hydroxyl groups could be confirmed, but the quantitative estimation became less accurate.

Applicability

The method described may be inapplicable to alcohols containing other functional groups which cause resonances in the region of the N.M.R. spectrum between 3.5 δ and 5.5 δ and hence obscure the $—COOCH_2—$ and $—COOCH<$ bands. Fortunately the number of such proton types is quite small. The only common species are olefinic protons, and protons on ester linkages and alkoxy groups, particularly alkoxy groups on aromatic rings. Also some $>CH—X$ resonances, where X represents nitrogen, a halide or phenyl group, occur in this region. However, even when a resonance is already present, a comparison of the spectra taken before and after acetylation often enables the proportion of the resonance at 4 δ or 5 δ ascribable to the interfering group to be determined and hence the primary to secondary hydroxyl ratio can still be obtained.

This method gives no information concerning tertiary or phenolic OH groups, but no interference is encountered from of these groups. The same is true for any water present in the sample. Amine groups which, of course, seriously affect the chemical determination of hydroxyl groups by acetylation procedures, have no effect on the N.M.R. method, since the acetyl derivatives of the amine groups contribute no resonance to the spectral region under investigation.

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(Received May 30th, 1964)

Book Reviews

Compound Semiconductors, Vol. 1, *Preparation of III–V Compounds*, Edited by ROBERT K. WILLARDSON AND HARVEY L. GOERING, Reinhold Publishing Corporation, New York (Chapman and Hall Ltd., London), 1963. xxii + 553 pp. Price $ 25.

This comprehensive publication will have an appeal to all associated with the manufacture and use of semiconductors.

The book is divided into 10 sections under such titles as *Crystal Structure and Bonding*, *Purification of the Elements*, *Preparation of Compounds*, *Single Crystal Growth*, and *Thermodynamic Properties*. Section III is headed *Detection of Impurities*, and this is sub-divided into several chapters covering the determination of impurities in gallium and gallium arsenide by emission spectroscopy, the determination of impurities (in inorganic substances generally) by spark-source mass spectrometry, the determination of sulphur in Group III–V semiconductors, and the determination of impurities in gallium and aluminium by colorimetric procedures. Separate chapters on *Radioactivation Analysis*, *Residual Resistivity* and *Electrical Analysis* also appear in Section III, which justifies an extended title to indicate that the various analytical techniques cover not only the detection but also the determination of specified impurities. Thus, whilst the book is by no means intended solely for the analyst, the importance of analysis in the semiconductor industry is not overlooked, and about 10% of the publication is devoted to this subject.

The book, which contains a bibliography of nearly 1200 references, is well indexed, and attractively bound.

W. T. ELWELL (Birmingham)

Anal. Chim. Acta, 31 (1964) 602

W. J. POTTS, JR., *Chemical Infrared Spectroscopy. Vol. I. Techniques*, John Wiley and Sons, Inc., New York, 1963, 322 + xvi pp., price 64 s.

The number of books, largely generated by the publication explosion, dealing with spectroscopy allows one to ask of any new book whether it represents a useful addition to the material already available. This book, the first of a two-volume work, survives such examination most convincingly. After brief introductory chapters there follow extensive sections dealing with spectrometer performance, sample handling techniques, special methods, and analytical methods. Although most laboratories evolve procedures suitable to their particular problems, those described by Dr. POTTS will attract general acceptance. These sections are written in a relaxed style and combine lucidity with complete authority. Unfortunately this cannot be said of the final chapter which attempts to compress the theory of vibrations, symmetry rules and group theory into 55 pages. The magisterial tone of this chapter would have been better employed in directing the reader to one of the several adequate treatments of these matters. Nevertheless this book is to be welcomed and the second volume awaited with enthusiasm.

K. J. MORGAN (Lancaster)

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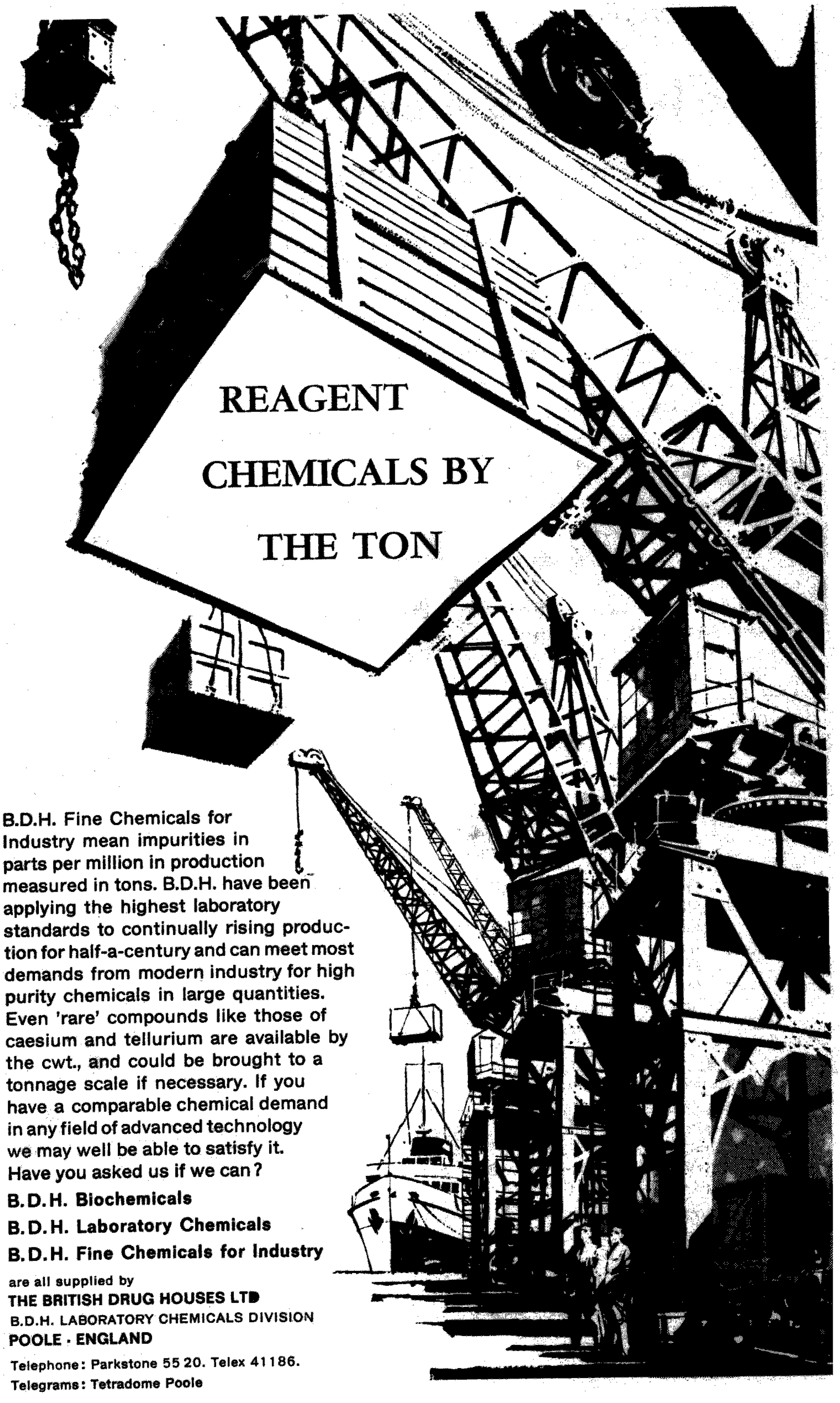
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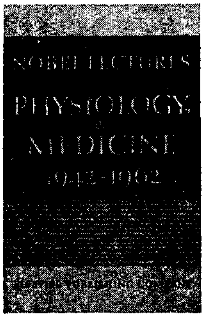
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