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. 41, No. 3, 413–572, June 1968
Published monthly. Completing Vol. 41

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2. F. FEIGL, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

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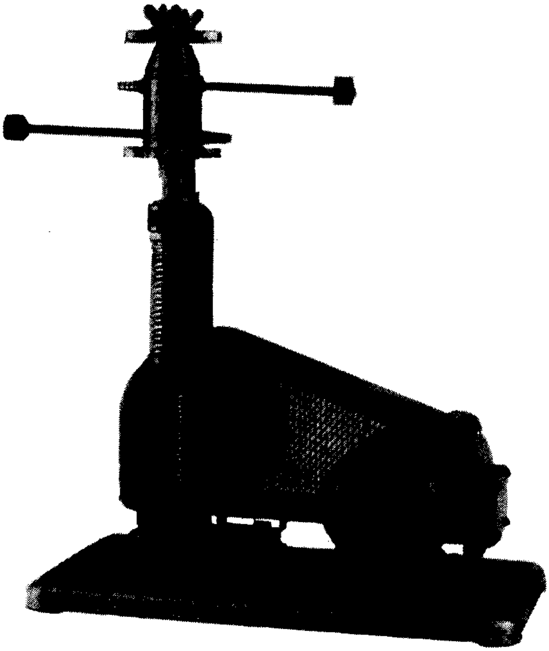

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by J. H. Beynon, R. A. Saunders and A. E. Williams, Research Department,
Imperial Chemical Industries Ltd., Manchester, Great Britain

7 x 10″, ix + 510 pages, 20 tables, 181 illus., 547 lit. refs., 1968, Dfl. 97.50

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MASS SPECTROMETRIC ANALYSIS OF SOLIDS

edited by A. J. Ahearn, Member of Technical Staff, Bell Telephone Laboratories, Inc.,
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5½ x 8½″, viii + 175 pages, 13 tables, 46 illus., 242 lit. refs., 1966, Dfl. 30.00

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ATOMIC-ABSORBTION SPECTROSCOPY

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by J. H. Beynon, R. A. Saunders and A. E. Williams

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by J. H. Beynon and A. E. Williams

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 41, No. 3, June 1968

THE DYNAMIC BEHAVIOUR OF THE SILVER–SILVER HEXACYANOFERRATE(II) ELECTRODE: COULOMETRIC PRODUCTION OF HEXACYANOFERRATE(II)

The electrochemical behaviour of the silver–silver hexacyanoferrate(II) electrode was studied. The reaction $Ag_4[Fe(CN)_6] + 4e^- \rightarrow 4\,Ag + [Fe(CN)_6]^{4-}$ was shown to be useful for the coulometric production of hexacyanoferrate(II) ions in titrations of zinc(II). Coulometric titrations of organometallic compounds such as $R_2Sn(ClO_4)_2$, with electrically generated hexacyanoferrate(II) are also reported.

F. MAGNO AND G. PILLONI,
Anal. Chim. Acta, 41 (1968) 413–418

THE SIMULTANEOUS DETERMINATION OF OSMIUM, RUTHENIUM, IRIDIUM AND GOLD IN PLATINUM BY NEUTRON ACTIVATION ANALYSIS

Osmium, ruthenium, iridium and gold can be determined simultaneously in 100-mg platinum samples after irradiation for 11 days at a thermal neutron flux of $4 \cdot 10^{11}$ n·cm^{-2}·sec^{-1}. An addition method of analysis is used; samples are dissolved in small sealed silica tubes before activation. After irradiation, Os and Ru are distilled from sulfuric acid–sodium bromate, Ru being determined by counting the 498-keV peak of ^{103}Ru; Os is determined after a second distillation. Gold is extracted with ethyl acetate from the residue of the first distillation; the ratio ^{198}Au/^{199}Au is a direct measure for the *gold* content, with appropriate correction for the second-order reaction $^{196}Pt(n,\gamma)^{197}Pt \rightarrow {}^{197}Au(n,\gamma)^{198}Au$. Ir is determined in the residual aqueous phase using the 317-keV peak of ^{192}Ir; a correction for the platinum activity (^{191}Pt) is made. The lower limit of determination is *ca.* 0.5 p.p.m. for ruthenium, *ca.* 0.2 p.p.m. for osmium, *ca.* 0.1 p.p.m. for gold and *ca.* 0.1 p.p.m. for iridium. After a separation of Pt from Ir, the sensitivity for Ir can easily be improved to $<$ 10 p.p.b.

R. GIJBELS AND J. HOSTE,
Anal. Chim. Acta, 41 (1968) 419–429

DETERMINATION OF IMPURITIES IN SINGLE CRYSTALS OF MAGNESIUM OXIDE BY NEUTRON ACTIVATION ANALYSIS

The determination of some trace impurities in single-crystal magnesium oxide is described. Radiochemical separations of iron, cobalt, scandium, manganese and chromium by ion exchange and solvent extraction are applied in conjunction with γ-spectrometry. The impurities that give rise to long-lived γ-emitting isotopes are considered.

H. M. LEE,
Anal. Chim. Acta, 41 (1968) 431–440

THE DETERMINATION OF GOLD BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Gold can be isolated from most other elements other than the platinum metals by the extraction of iron(II) 1,10-phenanthroline tetrabromoaurate in chloroform. After isolation gold can be determined in the organic solvent by atomic absorption spectroscopy or colorimetrically by decomposition of the complex and determination of the iron by bathophenanthroline.

E. N. Pollock and S. I. Andersen,
Anal. Chim. Acta, 41 (1968) 441–446

THE DETERMINATION OF MINOR AMOUNTS OF TELLURIUM IN IRON AND STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

A study was made of the determination of 0.0005–0.030% tellurium in iron and steel by atomic absorption spectrophotometry. Tellurium is separated by precipitation with tin(II) chloride and concentrated by extraction of the diethyldithiocarbamate complex into amyl acetate. The procedure is free from interference by elements which are reduced by tin(II) chloride or from the diethyldithiocarbamates of these elements. The results obtained on standard samples are in agreement with those reported with X-ray spectrometry and cathode-ray polarography.

M. V. Marčec, K. Kinson and C. B. Belcher,
Anal. Chim. Acta, 41 (1968) 447–451

X-RAY DETERMINATION OF TRACES OF HAFNIUM IN ZIRCONIUM METAL OR TRACES OF ZIRCONIUM IN HAFNIUM METAL AFTER SEPARATION BY ION EXCHANGE

A method is proposed for the determination of traces of hafnium in zirconium metal or zirconium in hafnium metal. The trace metals are first separated from the matrix metals on an ion-exchange column and then determined by X-ray analysis.

C. L. Luke,
Anal. Chim. Acta, 41 (1968) 453–458

EMISSION INTENSITY OF CESIUM IN FLAMES OF VARIOUS GAS COMPOSITIONS

The emission intensity of cesium at 852.1 nm has been studied in hydrogen flames burning with various mixtures of oxygen and nitrogen. A significant maximum was observed in the relative emission intensity of cesium at an oxygen to nitrogen ratio of 3:2 in the aspirating gas. The effect of Rb^+, K^+, Li^+, Na^+, and NH_4^+ ions on cesium emission is much less pronounced in this optimum flame than in a pure oxy–hydrogen flame. The optimum flame (60% oxygen) yields a significantly better calibration curve than can be obtained in either the normal air–hydrogen or oxy–hydrogen flame for 0–12 p.p.m. cesium concentrations; the graph is linear over this concentration range.

J. R. Jadamec and N. R. Andersen,
Anal. Chim. Acta, 41 (1968) 459–465

THE RAPID RADIOCHEMICAL SEPARATION OF SILVER BY AMALGAM EXCHANGE

(in French)

A rapid separation of silver on mercury is proposed in order to utilize short-lived isotopes for the determination of silver by activation. The conditions allowing quantitative reduction of silver were studied; a kinetic study showed that after 90 sec, 97% of silver could be transferred to the mercury. The spectrometric analysis of ^{110}Ag was also examined. Only metals with a redox potential greater than that of mercury form amalgams, and under the irradiation conditions these metals produce virtually no activity.

E. Loepfe and D. Monnier,
Anal. Chim. Acta, 41 (1968) 467–474

RAPID RADIOCHEMICAL SEPARATIONS BY EXCHANGE WITH MERCURY

EXCHANGE OF GOLD AND PLATINUM AND SELECTIVE DETERMINATION BY THERMAL NEUTRON ACTIVATION

(in French)

A rapid extraction method of platinum and gold ions by means of a mercury drop is proposed. This is based on the different redox potentials of the various couples present and gives a separation from most other elements. The phenomenon is rapid and quantitative between defined concentration limits. The selectivity is good; silver interferes but this can be avoided. The sensitivity is excellent; with neutron activation in a flux of $7.7 \cdot 10^{12}$ $n \cdot cm^{-2} \cdot sec^{-1}$ for 2 h, the lower limit is about 5 ng/ml.

D. Monnier and E. Loepfe,
Anal. Chim. Acta, 41 (1968) 475–481

THE DETERMINATION OF FREE ACIDITY IN CONCENTRATED AQUEOUS SOLUTIONS OF PLUTONIUM(IV)

(in French)

A method for the determination of free acidity in concentrated aqueous solutions of plutonium(IV) is described. The plutonium–EDTA complex is formed by addition of the calcium–EDTA complex and the neutralization titration with sodium hydroxide is followed potentiometrically, the equivalence point being determined by a graphical method. The relative standard deviation is 1%. Uranium and iron in small amounts do not interfere. The method is applicable to solutions which are *ca.* 1 N in acid and which contain up to 200 g Pu/l.

N. Damien and P. Cauchetier,
Anal. Chim. Acta, 41 (1968) 483–495

THE SPECTROPHOTOMETRIC DETERMINATION OF ALIPHATIC AZO AND HYDRAZO COMPOUNDS

(in German)

Aliphatic azo-compounds after rearrangement to hydrazone in acidic medium can be hydrolyzed and the released aldehyde can be determined quantitatively. 1,2-Disubstituted alkylhydrazines (hydrazoalkanes) can be determined by the same principle after oxidation by mercury(II) sulfate in aqueous sulfuric acid. The lower detection limit for both types of compounds is 0.1–0.2 μmoles. The applicability and specificity of this new analytical method are discussed.

R. Preussmann, H. Hengy, D. Lübbe and A. von Hodenberg,
Anal. Chim. Acta, 41 (1968) 497–504

THE EXTRACTION OF COPPER(I), LEAD(II) AND TIN(IV) FROM HYDROCHLORIC ACID BY SOLUTIONS OF TETRA-*n*-HEXYLAMMONIUM CHLORIDE IN ETHYLENE DICHLORIDE

Copper(I) is strongly extracted from chloride media as the ion-pair $NR_4^+CuCl_3^-$ by solutions of tetra-*n*-hexylammonium chloride ($NR_4^+Cl^-$) in ethylene dichloride. The distribution coefficient decreases from *ca.* 100 in 1 *M* chloride but is still as high as 13 in 10 *M* chloride. The extraction of lead(II) is shown to be due to the partition of the ion-pair ($NR_4^+PbCl_3^-$). The percentage of 0.0018 *M* lead extracted is 98% from 0.58 *M* hydrochloric acid and falls to 38% from 7.8 *M* acid. The distribution coefficient decreases rapidly with the total lead concentration. The extractions of tin(IV) increased to a maximum of 99.5% in *ca.* 5 *M* hydrochloric acid but decreased rapidly above 6 *M* acid. It proved impossible to identify the extractable species.

H. M. N. H. IRVING AND A. H. NABILSI,
Anal. Chim. Acta, 41 (1968) 505–513

VERSATILE HIGH-TEMPERATURE LABORATORY PREPARATIVE GAS–LIQUID CHROMATOGRAPHY MANIFOLD AND TRAPPING ASSEMBLY

A dual manifold preparative GLC trap assembly is described. The design provides a second-pass trap for increased sample recovery. There is a reduction in component loss by aerosol breakup (vaporization) before entry to the second-pass trap. The reduction in gas velocity by dual trap collection of single components results in increased trapping efficiency. Isolation for separate heat control of the hot incoming trap inlet gases and the cool trap outlet gases for continuous temperature readout results in a minimum of thermal degradation of purified sample.

A. B. CAREL,
Anal. Chim. Acta, 41 (1968) 515–521

ELECTROCHROMATOGRAPHIC SEPARATION OF METAL IONS ON TIN(IV) PHOSPHATE PAPERS

Electrochromatographic separations on tin(IV) phosphate papers in 12 background electrolytes are described. Migration distances for 48 ions are given. Many binary as well as ternary separations are readily achieved, *e.g.* Fe–Cr, Sr–Ba, Pt–Ru–Cu and Au–Pd–Cu.

M. QURESHI AND A. H. ISRAILI,
Anal. Chim. Acta, 41 (1968) 523–528

THE QUANTITATIVE SEPARATION OF CALCIUM FROM MAGNESIUM, ALUMINIUM AND OTHER ELEMENTS BY CATION-EXCHANGE CHROMATOGRAPHY IN ETHANOL–HYDROCHLORIC ACID

Magnesium can be separated from calcium by elution with 3.0 *M* hydrochloric acid containing 60% ethanol from a column of AG50W-X8 cation-exchange resin. Calcium is retained and can be eluted with 3.0 *M* hydrochloric acid or 2.0 *M* nitric acid. The separation factor of $\alpha_{Mg}^{Ca} = 5.6$ is considerably higher than that in aqueous hydrochloric acid and comparable to those obtained with organic complexing reagents. Separations are sharp and quantitative; up to 10 mmol of magnesium can be separated from 0.01 mmol of calcium and *vice versa* on a 60-ml column. Al, Fe(III), Mn, Ni(II), Co(II), Zn, Cd, Cu(II), Pb(II), U(VI), Be, Ga, Ti(IV) in the presence of H_2O_2 and many other elements accompany magnesium and can be separated from calcium quantitatively. Sr, Ba, Zr, Hf, Th, Sc, La and the rare earths are retained together with Ca, but can be separated by other methods.

F. W. E. STRELOW AND C. R. VAN ZYL,
Anal. Chim. Acta, 41 (1968) 529–536

SEPARATION OF PLATINUM AND PALLADIUM FROM BASE METALS WITH A WEAKLY BASIC CELLULOSE ION EXCHANGER

Platinum(IV) and palladium(II) are strongly adsorbed on the weakly basic cellulose ion exchanger DEAE from dilute thiocyanate media, while most other metal ions do not show any marked tendency to adsorb from the same media. It is possible to separate and concentrate the noble metal ions from a large quantity of base metals such as iron, cobalt, nickel, copper, zinc and lead. As little as 1 mg of platinum(IV) and/or palladium(II) can be quantitatively separated from as much as 20–25 g of base metals on a small column of DEAE (thiocyanate form). The noble metal ions adsorbed are easily stripped from DEAE.

K. Ishida, T. Kiriyama and R. Kuroda,
Anal. Chim. Acta, 41 (1968) 537–545

THE DETERMINATION OF SILVER IN FINE SILVER BULLION BY ATOMIC ABSORPTION SPECTROSCOPY

L. G. Hickey,
Anal. Chim. Acta, 41 (1968) 546–548

GENERAL FORMULA FOR THE CALCULATION OF THE HYDROGEN-ION CONCENTRATION OF AQUEOUS SOLUTIONS OF SEVERAL POLYVALENT WEAK ACIDS

(Short Communication)

J. Klas,
Anal. Chim. Acta, 41 (1968) 549–550

THE THERMAL AND ATOMIC-FLUORESCENCE EMISSION OF GERMANIUM IN A NITROGEN–OXYGEN–ACETYLENE FLAME

(Short Communication)

R. M. Dagnall, K. C. Thompson and T. S. West,
Anal. Chim. Acta, 41 (1968) 551–554

THE PRECISE DETERMINATION OF LIGHT ELEMENTS BY X-RAY FLUORESCENCE. A COMPARISON OF FUSION METHODS

(Short Communication; in French)

R. Tertian,
Anal. Chim. Acta, 41 (1968) 554–556

CONTROLLED DEACTIVATION-HYDROLYSIS AND DETERMINATION OF ALUMINUM IN ALUMINUM ALKYL COMPOUNDS

(Short Communication)

D. F. Hagen, D. G. Biechler, W. D. Leslie and D. E. Jordan,
Anal. Chim. Acta, 41 (1968) 557–560

QUANTITATIVE SEPARATION OF SELENIUM FROM METAL IONS ON TIN(IV) TUNGSTATE PAPERS

(Short Communication)

M. Qureshi and K. N. Mathur,
Anal. Chim. Acta, 41 (1968) 560–563

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DYNAMIC BEHAVIOUR OF THE SILVER–SILVER HEXACYANOFERRATE(II) ELECTRODE: COULOMETRIC PRODUCTION OF HEXACYANOFERRATE(II)

F. MAGNO AND G. PILLONI*
Istituto di Chimica Analitica, Università di Padova, Padova (Italy)

(Received December 20th, 1967)

The coulometric production of hexacyanoferrate(II) is usually based on the cathodic reduction of hexacyanoferrate(III) at a platinum electrode[1]. Such methods possess the disadvantage, which is also found in titrations where the reagent is electrically produced from a soluble complex[2,3], that the generating reagent must be present in the test solution at a concentration much higher than that of the generated reagent. The generating electrolyte and the compounds which have to be determined, may sometimes interact so that correct titrations are impossible. For this reason, on the basis of the good results previously obtained[4,5] in the investigation of second-order electrodes, such as Ag/Ag_nX, a study was made of the dynamic behaviour of the silver–silver hexacyanoferrate(II) electrode. The reaction $Ag_4[Fe(CN)_6] + 4\ e^- \rightarrow 4\ Ag + [Fe(CN)_6]^{4-}$ has proved to be useful for the coulometric production of hexacyanoferrate(II).

EXPERIMENTAL

Materials

All chemicals were reagent-grade (Merck pro Analysis, and BDH). Twice-distilled water was used in the preparation of solutions. Standard solutions of zinc were prepared by dissolving pure zinc (99.99%) in perchloric acid. Stock solutions of organometallic tin cations (dipropyl and dibutyl) were prepared by dissolving weighed amounts of their oxides in perchloric acid. Nitrogen (99.99%), further purified as described by ARTHUR[6], was employed for the removal of oxygen from the solutions.

Apparatus

For all the experiments, current–voltage curves, diagrams of current *versus* hexacyanoferrate(II) concentration, chronopotentiometric tests and titrations, the apparatus previously described was employed[4,5,7].

The electrical apparatus consisted of a constant-current electronic generator (the stability of which was greater than 0.1%), a Knick electrometer, a Sefram Verispot Galvanometer, a model M.R. Sargent recorder, a standard 1000-ohm Siemens Resistor, a Leeds and Northrup model K-3 potentiometer and a 100-ohm

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* Ricercatore del C.N.R.

Metrohm potentiometer. The rotating platinum disc electrode was silvered for 15 min at 3 mA in a silver cyanide solution. It was then covered with $Ag_4[Fe(CN)_6]$ by anodizing it in a neutral 10^{-2} *F* sodium hexacyanoferrate(II) solution. For the production of hexacyanoferrate(II) ions, a silver spiral electrode with a surface of about 7 cm^2, was employed. The layer of silver hexacyanoferrate(II) on the electrode was obtained by anodic deposition from a neutral 10^{-2} *F* sodium hexacyanoferrate(II) solution. The electrode was then washed with twice-distilled water and used immediately.

Polarization curves

Current–voltage curves were plotted in 0.1 *M* perchloric acid solutions at different concentrations of hexacyanoferrate(II) and silver ions. The potentials (*vs.* S.C.E.) were varied in 20-mV steps. The waiting time, after each potential variation, was 5 min. The counter-electrode was a second saturated calomel electrode.

Chronopotentiometric experiments

The chronopotentiometric experiments were carried out in 10^{-2} *F* sodium hexacyanoferrate(II) solution at different current densities. The working electrode was a silver spiral. The auxiliary electrode, separated by a sintered glass disc, was made of platinum foil. The reference electrode (S.C.E.) was connected by means of a salt bridge. Preliminary tests suggested that the oxidation of hexacyanoferrate(II) to hexacyanoferrate(III) took place together with the formation of the silver hexacyanoferrate(II) layer on the electrode. This was quantitatively checked by the biamperometric technique. Two platinum wire electrodes were dipped in the solution with an interposed potential difference of about 100 mV. Current, indicating the hexacyanoferrate(III) species, was observed. The number of coulombs required for the oxidation of hexacyanoferrate(II) to hexacyanoferrate(III) was calculated in the following manner: the current, flowing through the two platinum wire electrodes, was measured after the anodic polarization time. Then known amounts of hexacyanoferrate(III) were electrically produced on a platinum anode. In consequence, it was possible to determine the initial concentration of hexacyanoferrate(III) by graphic interpolation. The strict proportionality of the biamperometric current to the hexacyanoferrate(III) concentration had been checked previously. As a consequence of the hexacyanoferrate(II) oxidation, the working electrode was made the cathode in another solution (0.1 *M* perchloric acid). The anodic electrolysis time was of arbitrary length; the cathodic one was found by measuring the time required to obtain a rapid linear voltage increase[4].

Coulometric efficiency

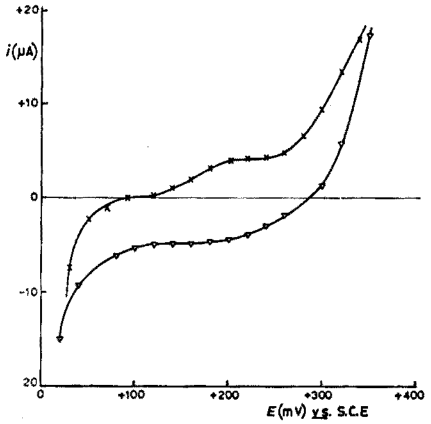
The coulometric production of hexacyanoferrate(II) ions was tested by amperometric titration with zinc(II). Because, as is well known[8], correct results are only obtained when zinc is titrated with hexacyanoferrate(II), the generating electrode was made the cathode in a solution of zinc(II), which was 0.1 *M* in perchloric acid and 0.1 *M* in sodium perchlorate. Only when a pH lower than 3 was used, was it certain that the precipitate corresponded exactly to $Zn_3Na_2[Fe(CN)_6]_2$ [1]. The end-point was detected by the monoamperometric technique. The indicator electrode was the rotating silver–silver hexacyanoferrate(II) electrode, polarized at +200 mV *vs.* S.C.E.

RESULTS AND DISCUSSION

Figure 1 shows the polarization curves, plotted in 0.1 *M* perchloric acid solution; only in a narrow potential range is a plateau obtainable. The anodic wave most probably corresponds to the reaction:

$$4\,Ag + [Fe(CN)_6]^{4-} \rightleftharpoons Ag_4[Fe(CN)_6] + 4\,e^-$$

The potentials at which the cathodic branches are located, correspond rigorously to the potentials measured when the silver–silver hexacyanoferrate(II) spiral is working cathodically. The straight line in Fig. 2, which was constructed by plotting the current at +0.2 V (*vs.* S.C.E.) against the hexacyanoferrate(II) concentration, proves the strict proportionality of the current to the hexacyanoferrate(II) concentration.



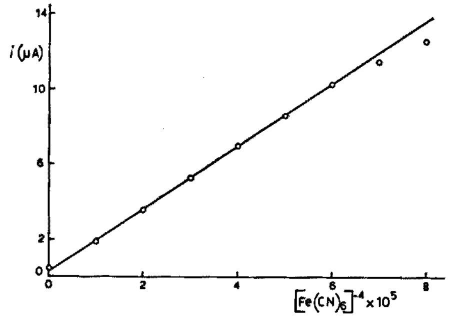


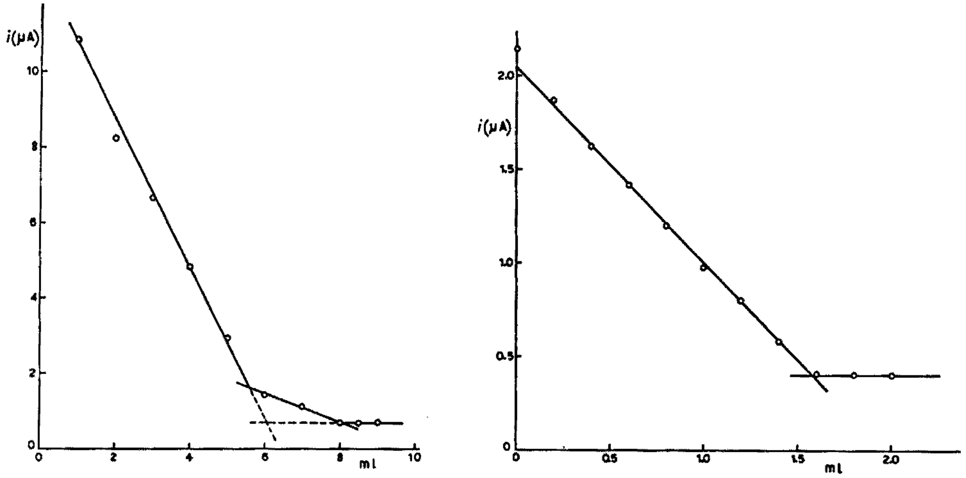
Fig. 1. Polarization curves in 0.1 *M* $HClO_4$. × $5.2 \cdot 10^{-5}$ $Na_4Fe(CN)_6$; ▽ $5.0 \cdot 10^{-5}$ $AgClO_4$.

Fig. 2. Plot of amperometric current against hexacyanoferrate(II) concentration.

The use of an electrode indicating the hexacyanoferrate(II) concentration made it possible to detect the establishment of an equilibrium system in the titration of potassium hexacyanoferrate(II) with zinc in a neutral solution. It is generally assumed that, in acidic media, the precipitate corresponds to the $Zn_3K_2[Fe(CN)_6]_2$ form, and, in neutral media, to $Zn_2[Fe(CN)_6]$. Figure 3 shows that the formation of $Zn_3K_2[Fe(CN)_6]_2$ always takes place at the beginning of the titration. This precipitate is transformed, in neutral solution, with the decrease in the concentration of the free hexacyanoferrate(II), into the more stable $Zn_2[Fe(CN)_6]$ form.

With very low initial concentrations of hexacyanoferrate(II), the $Zn_2[Fe(CN)_6]$ precipitate forms immediately (Fig. 4). In Table I some of the results of the chronopotentiometric experiments are reported; an increase in the current density causes an increase in the formation of the $Ag_4[Fe(CN)_6]$ layer. This had to be borne in mind when the working electrode was prepared.

Table II shows the results of the amperometric titrations of the electrically generated hexacyanoferrate(II). These good results were obtained when the layer on the working electrode was of one form only; when potassium hexacyanoferrate(II)



Figs. 3–4. Amperometric titration of 70 ml of (3) $5.720 \cdot 10^{-5}$ *M*, (4) $1.144 \cdot 10^{-5}$ *M* $K_4Fe(CN)_6$, with $1.0009 \cdot 10^{-3}$ *M* $Zn(ClO_4)_2$. Base electrolyte 0.1 *M* $NaClO_4$.

TABLE I

RESULTS OF CHRONOPOTENTIOMETRIC EXPERIMENTS

Current (mA)	*Coulombs (anodic time)* *A*	*Coulombs (cathodic time)* *B*	*Coulombs of hexacyanoferrate(III) found* *C*	*B + C*	*A − B − C*
0.50	0.150	0.0	0.150	0.150	0.0
0.50	0.150	0.0	0.150	0.150	0.0
2.08	0.624	0.364	0.187	0.551	0.073
2.08	0.624	0.372	0.187	0.559	0.065
4.16	1.248	0.928	0.218	1.146	0.102
4.16	1.248	0.981	0.193	1.174	0.074
8.31	2.493	2.144	0.218	2.362	0.131
8.31	2.493	2.044	0.125	2.169	0.324

TABLE II

AMPEROMETRIC TITRATIONS OF ELECTRICALLY GENERATED HEXACYANOFERRATE(II) WITH ZINC(II)
(Volume in the cell = 80 ml. Base electrolyte 0.1 *M* $NaClO_4$, 0.1 *M* $HClO_4$)

μmole taken	*μmole found*	*Error (%)*
3.169	3.159	+0.33
3.159	3.140	−0.6
6.581	6.580	+0.015
6.318	6.328	+0.16

was used in the preparation of the electrode, incorrect results were obtained. This was due to the formation on the electrode, under dynamic conditions, of the two precipitates $Ag_3K[Fe(CN)_6]$ and $Ag_4[Fe(CN)_6]$*. It is well known that two end-points

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* An apparent formula where the number of silver ions lay between 3 and 4 was found.

are found when potassium hexacyanoferrate(II) is titrated with silver[9]. If the sodium salt is used, the titration curve shows only one end-point which corresponds to the formation of the insoluble $Ag_4[Fe(CN)_6]$; this was checked in the present work. Accordingly, the use of sodium hexacyanoferrate(II) in the preparation of the electrode was critically important.

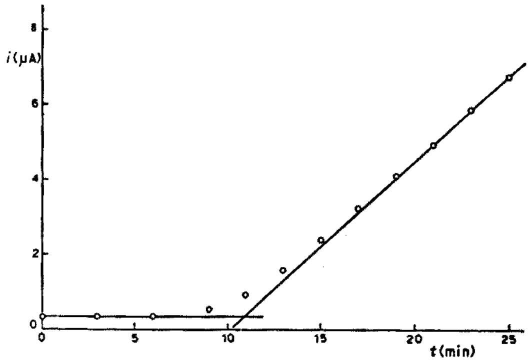

Fig. 5. Amperometric titration of 80 ml of $4.401 \cdot 10^{-5}$ *M* $Bu_2Sn(ClO_4)_2$ with electrically generated hexacyanoferrate(II). Base electrolyte 0.1 *M* $HClO_4$. Generating current 1.03 mA.

TABLE III

AMPEROMETRIC TITRATIONS OF $Pr_2Sn(ClO_4)_2$ AND $Bu_2Sn(ClO_4)_2$ WITH ELECTRICALLY GENERATED HEXACYANOFERRATE(II)

(Volume in the cell = 80 ml. Base electrolyte 0.1 *M* $HClO_4$)

$Pr_2Sn(ClO_4)_2$			*$Bu_2Sn(ClO_4)_2$*		
μmole taken	*μmole found*	*Error (%)*	*μmole taken*	*μmole found*	*Error (%)*
9.850	9.846	−0.04	8.804	8.805	+0.01
4.925	4.947	+0.45	3.521	3.506	−0.43
2.463	2.594	+5.3	0.880	0.960	+9.1

Titrations of compounds, such as $R_2Sn(ClO_4)_2$, were carried out by coulometric generation of hexacyanoferrate(II) (Table III). An example of these titrations is reported in Fig. 5. The end-points were detected amperometrically by the silver–silver hexacyanoferrate(II) rotating electrode. The two large errors, found in the last two titrations, can probably be ascribed to the very low concentrations of organometallic compounds in the test solutions. This technique, unlike the techniques previously described[10], exhibits no limitations from the complicated polarographic behaviour of organometallic compounds. The titrations of organometallic ions with hexacyanoferrate(II) are a good example of the impossibility of using the coulometric production of hexacyanoferrate(II) from hexacyanoferrate(III) at a platinum electrode, for hexacyanoferrate(III) reacts with organometallic ions to form slightly soluble compounds.

Other investigations have suggested the existence of soluble complexes of silver with hexacyanoferrate(II). Such complexes would explain the small error always found in the chronopotentiometric data. The formation of these complexes is at present being investigated.

The authors wish to thank Prof. LUIGI RICCOBONI for helpful discussions and the Consiglio Nazionale delle Ricerche (Roma) for financial support.

SUMMARY

The electrochemical behaviour of the silver–silver hexacyanoferrate(II) electrode was studied. The reaction $Ag_4[Fe(CN)_6]+4\ e^- \rightarrow 4\ Ag+[Fe(CN)_6]^{4-}$ was shown to be useful for the coulometric production of hexacyanoferrate(II) ions in titrations of zinc(II). Coulometric titrations of organometallic compounds such as $R_2Sn(ClO_4)_2$, with electrically generated hexacyanoferrate(II) are also reported.

RÉSUMÉ

On examine le comportement chimique de l'électrode argent–hexacyanoferrate-(II) d'argent. La réaction

$$Ag_4[Fe(CN)_6]+4\ e^- \rightarrow 4\ Ag+[Fe(CN)_6]^{4-}$$

est utile pour la production coulométrique des ions hexacyanoferrate(II) lors du dosage du zinc. On décrit des dosages coulométriques de composés organométalliques tels que $R_2Sn(ClO_4)_2$ à l'aide d'hexacyanoferrate(II) produit coulométriquement.

ZUSAMMENFASSUNG

Das elektrochemische Verhalten der Silber–Silberhexacyanoferrat(II)-Elektrode wurde untersucht. Es konnte gezeigt werden, dass die Reaktion $Ag_4[Fe(CN)_6]+4e^- \rightarrow 4Ag+[Fe(CN)]^{4-}$ nützlich ist für die coulometrische Bildung von Hexacyanoferrat(II)-Ionen bei der Titration von Zink(II). Über coulometrische Titrationen von organometallischen Verbindungen mit elektrisch erzeugtem Hexacyanoferrat(II) wird ebenfalls berichtet.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE SIMULTANEOUS DETERMINATION OF OSMIUM, RUTHENIUM, IRIDIUM AND GOLD IN PLATINUM BY NEUTRON ACTIVATION ANALYSIS

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(Received November 28th, 1967)

The classical determination of impurities in platinum causes many difficulties[1]. Large samples (20 g) are required and chemical separations must be repeated several times. Moreover, concentrations below 0.1–0.01% are difficult to determine accurately.

Several authors have described the determination of impurities such as palladium, gold, silver and/or rhodium in platinum and its alloys by spectrographic analysis[2–11]. Traces of osmium, ruthenium and iridium have seldom been determined[12]. LINCOLN AND KOHLER[7] report for the latter elements and gold the following sensitivities in 50-mg samples: 80, 10, 5 and 0.5 p.p.m. respectively. Owing to the insufficient sensitivity of the spectrochemical method, several authors have applied neutron activation analysis (see Table I).

TABLE I

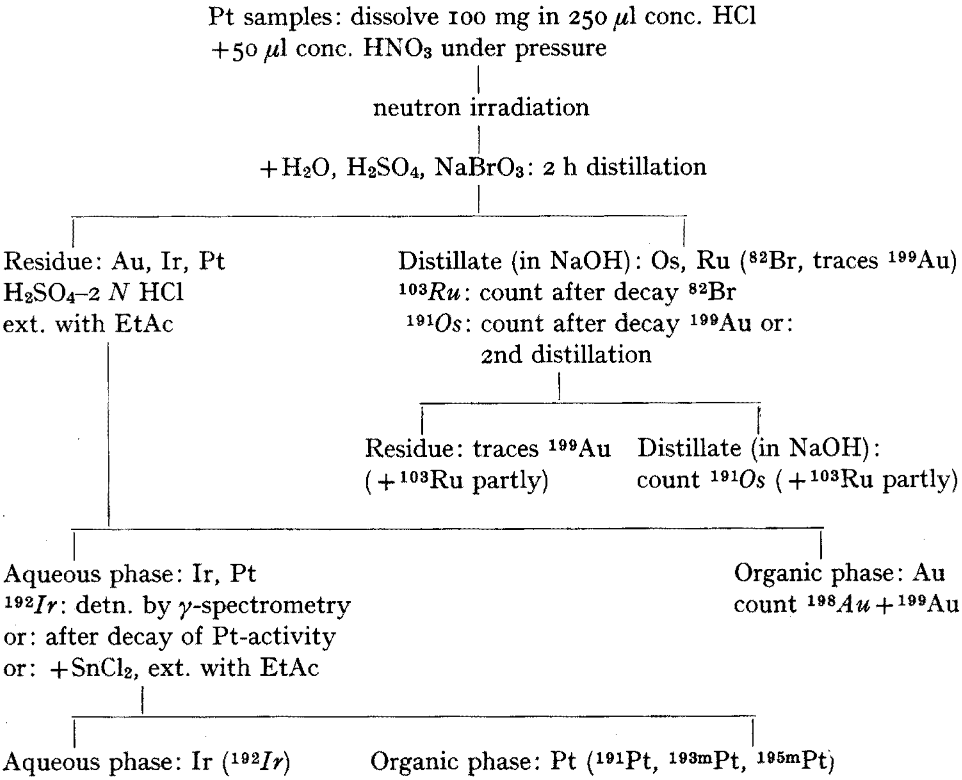
REFERENCES FOR THE DETERMINATION OF IMPURITIES IN PLATINUM BY NEUTRON ACTIVATION ANALYSIS

Ir	*Rh*	*Pd*	*Os*	*Ir*	*Au*	*Ag*
13	14	15	16	17–24	25	26

MORRIS AND KILLICK observed impurity concentrations (p.p.m.) down to 0.6 (Au), 0.85 (Ru), 0.1 (Ir), 0.03 (Os), 0.35 (Pd), 0.25 (Ag), 0.55 (As), 0.14 (Sb), 0.71 (Se), 0.76 (Te), 0.012 (Co) and 2.5 (Fe)[13,15,16,22,25–30]. Only osmium, ruthenium, iridium and gold will be considered here. Because of the small amounts of samples available (a few hundred mg) it was desirable to determine these 4 elements simultaneously; the separation methods were practically quantitative, and in the case of gold an "internal standard method" was followed, thus avoiding the use of isotopic carriers.

TRACER STUDIES OF THE CHEMICAL SEPARATION

Several separation schemes were investigated and finally the following one was adopted.



Pt samples: dissolve 100 mg in 250 μl conc. HCl
+50 μl conc. HNO_3 under pressure

neutron irradiation

+H_2O, H_2SO_4, $NaBrO_3$: 2 h distillation

Residue: Au, Ir, Pt
H_2SO_4–2 *N* HCl
ext. with EtAc

Distillate (in NaOH): Os, Ru (^{82}Br, traces ^{199}Au)
^{103}Ru: count after decay ^{82}Br
^{191}Os: count after decay ^{199}Au or:
2nd distillation

Residue: traces ^{199}Au
(+^{103}Ru partly)

Distillate (in NaOH):
count ^{191}Os (+^{103}Ru partly)

Aqueous phase: Ir, Pt
^{192}Ir: detn. by γ-spectrometry
or: after decay of Pt-activity
or: +$SnCl_2$, ext. with EtAc

Organic phase: Au
count ^{198}Au+^{199}Au

Aqueous phase: Ir (^{192}Ir)

Organic phase: Pt (^{191}Pt, ^{193m}Pt, ^{195m}Pt)

Preparation of tracers

^{191}Os, ^{103}Ru, ^{192}Ir, ^{198}Au: see earlier[31–33].

It has been shown earlier[33] that osmium and ruthenium can be distilled almost quantitatively (>99.5%) in 2–3 h from a boiling sulfuric acid–sodium bromate solution after dissolution in pressure tubes, as described by WICHERS *et al.*[34]. The distillates can be absorbed quantitatively in 9 *N* sodium hydroxide (or in ice-cold 66% hydrobromic acid; when the ^{191}Os activity (129-keV γ-ray, 65-keV X-ray and escape peak) is measured directly in concentrated hydrobromic acid, strong absorption of the X-ray occurs, hence dilution is necessary). From the nuclear data of ^{191}Os and ^{103}Ru it is apparent that both radionuclides can be determined simultaneously by γ-spectrometry[32]. It has also been shown that gold and iridium do not distil under the above conditions[32,33].

After removal of the excess of bromate and acidifying to 2 *N* hydrochloric acid, at least 95% of the gold can be extracted[33]. As will be shown further, a quantitative extraction is not required, as an addition method of analysis was followed, using ^{199}Au (^{199}Pt daughter) as an internal standard: the ratio ^{198}Au/^{199}Au is directly proportional to the gold content. Iridium is practically not extracted (<0.2%)[33]. In the presence of 10–200 mg of platinum, *ca.* 2.5% of iridium is found in the organic phase, after two washings. This contamination can be decreased by repeated washings thus obtaining a gold fraction essentially free from interfering activities (Pt, Ir), see Fig. 1.

The aqueous phase contains platinum and iridium. By adding a solution of tin(II) chloride, a deep red complex is formed, which can be extracted with ethyl acetate. The extraction can be followed visually. After separation of the organic phase, tin(II) chloride is again added to the aqueous phase, followed by a second extraction. After three extractions, >99% of the platinum activity is recovered; *ca.* 1.5–2% of the iridium activity is extracted in the presence of 10–200 mg of platinum. From the above considerations, it follows that >95% of the iridium activity is recovered in the final aqueous phase and that this fraction can be made practically free from interfering platinum activity. Typical γ-spectra of the iridium and platinum fractions are represented in Figs. 2 and 3.

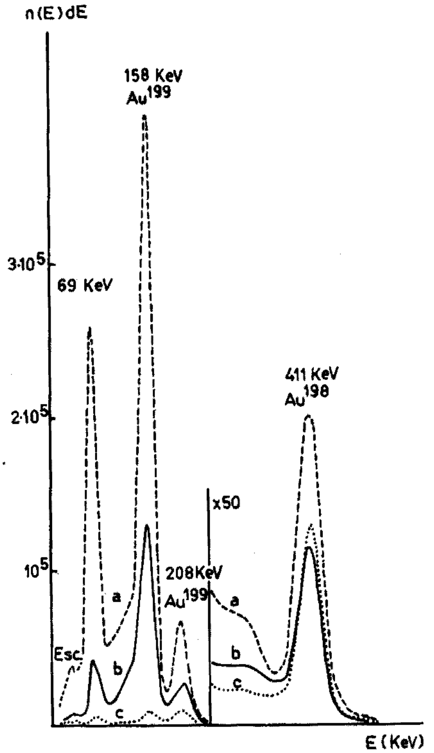


Fig. 1. γ-Spectrum of ethyl acetate extract, 2 weeks after the end of irradiation (100 mg Pt JM 2, containing 30 p.p.m. Au) (7 min—background). a = plexiglass absorber, dead time 26%; b = Al–Cu absorber, dead time 11%; c = Pb absorber, dead time 2%.

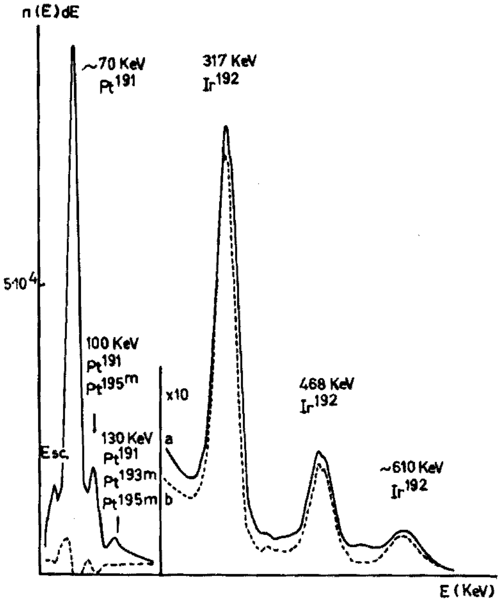
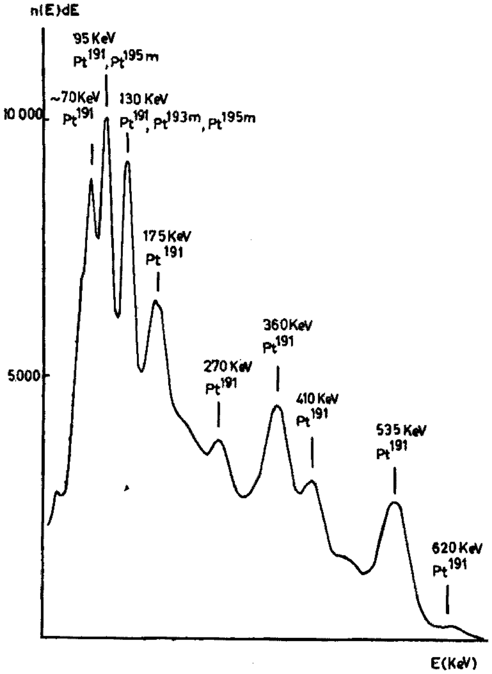


Fig. 2. (a) γ-Spectrum of aqueous phase after extraction of gold, 25 days after the end of irradiation (55 mg Pt Md, containing 1.3 p.p.m. Ir) (5 min—background; no absorber). (b) idem minus ^{191}Pt, ^{193m}Pt, ^{195m}Pt.

In actual analyses, the distillates were found to contain ^{82}Br (from the reagents used to dissolve the samples before activation) and traces of ^{199}Au (< 0.005% of the total ^{199}Au activity). After decay of ^{82}Br ($T_{½}$ = 35.9 h; γ-peaks at 550, 630, 700, 780 keV + others) ^{103}Ru can be determined from its 498-keV photo-peak. The ^{199}Au contamination ($T_{½}$ = 3.15 d; γ-peaks at 208, 158 + 150 keV, and intense X-ray at 67 keV) however, strongly interferes with the ^{191}Os activity ($T_{\frac{1}{2}}$=16 d, γ-peak at 129 keV, X-ray at 65 keV). Consequently, a second distillation is required. By adding concentrated nitric acid to the sodium hydroxide solution, *ca.* 99.5% of the osmium activity can be distilled. (The distillate is free from ^{199}Au interference and ^{191}Os can be counted although, in practice, its activity is very low.) The behaviour of ruthenium is, however, not quite reproducible, so that it was always determined before the second distillation.



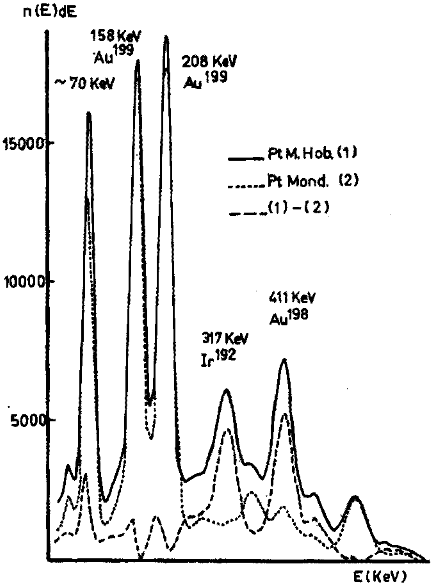


Fig. 3. γ-Spectrum of platinum extract, 7 days after the end of irradiation. Absorber 6 mm Al + 6 mm Cu.

Fig. 4. γ-Spectrum of irradiated platinum, 5 days after the end of irradiation (with lead absorber 2.2 g·cm^{-2}).

PRACTICAL PROCEDURE FOR NEUTRON ACTIVATION ANALYSIS

Samples of 100 or 20 mg of platinum sponge are accurately weighed (within ±1%) in silica tubes (internal diameter 4 mm; length 5 cm; wall thickness 1 mm). After sealing, the samples are dissolved in 250 μl of concentrated hydrochloric acid +50 μl of concentrated nitric acid by heating for 10 h at 150°. To some samples 100 μl of standard solutions of ruthenium, iridium, gold and osmium (+iron(II))[31] are added and evaporated to dryness before addition of the reagents. The preparation of the standard solutions was described earlier[32]. A typical addition scheme is given in Table II.

Determination of ruthenium

After irradiation for 11 days at a flux of 4·10^{11} n·cm^{-2}·sec^{-1}, the silica ampoules are opened. Previous solidification of the contents by immersion in liquid nitrogen is required to reduce the internal pressure. Both halves of the ampoule are then quickly placed in the distillation flask[31] and 20 ml of water, 10 ml of 18 *N* sulfuric acid and 15 ml of 20% sodium bromate are added. During the distillation (2–3 h at *ca.* 100°), 15 ml of 20% sodium bromate is added per hour. The distillates are absorbed in ice-cold 9 *N* sodium hydroxide, transferred to 100-ml measuring flasks and diluted to the same volume. After the decay of ^{82}Br (1–2 weeks) the distillates are counted for 1–10 h on a flat 3″ × 3″ NaI(Tl) detector, coupled to a 400-channel pulse-height analyzer and the ^{103}Ru activity is determined from the 498-keV photo-peak.

TABLE II

ADDITION SCHEME FOR THE DETERMINATION OF OSMIUM, RUTHENIUM, IRIDIUM AND GOLD IN PLATINUM

Pt samples (100 mg)	*JM 1*[a]	*JM 1*	*JM 1*	*JM 1*	*JM 1*	*MH*	*MH*	*JM 2*	*JM 2*
+Ru (μg)	—	—	0.2	0.2	0.5	0.5	—	—	—
+Ir (μg)	—	—	0.2	0.2	0.4	0.4	—	—	—
+Au (μg)	—	—	—	0.4	0.4	0.4	—	—	—
+Os (μg)	—	—	—	0.4	0.4	0.4	—	—	—

[a] Sample number.

Determination of osmium

The alkaline solutions are transferred to the distillation flask. An air current is drawn through the apparatus and 20 ml of concentrated nitric acid is added. During the distillation (1 h at *ca.* 100°) a further 10 ml of concentrated nitric acid is added. The distillates are again absorbed in cold 9 *N* sodium hydroxide and counted for 1–10 h as described above. The ^{191}Os activity can be determined from the 65-keV X-ray or from the 129-keV photo-peak.

Determination of gold

The residue of the first distillation is evaporated whilst concentrated hydrochloric acid is added dropwise to decompose the excess of the bromate. When the development of chlorine ceases, evaporation is continued to reduce the volume to *ca.* 30 ml and 9 ml of concentrated hydrochloric acid is added. A possible precipitate of sodium chloride dissolves later. The solution is transferred to a separatory funnel, and the distillation flask (+ the quartz ampoule) is rinsed with small portions of water, to obtain a volume of *ca.* 50 ml in the funnel (concentration of hydrochloric acid ~2 *N*). After extraction with 50 ml of preequilibrated ethyl acetate, the yellow aqueous phase (H_2PtCl_6) is collected in a 200-ml beaker. The organic phase is washed several times, first with two or three 5-ml portions of preequilibrated 2 *N* hydrochloric acid until completely colourless, then twice with 5 ml of preequilibrated 2 *N* hydrochloric acid containing 0.1 mg of iridium carrier and finally once with 5 ml of preequilibrated 2 *N* hydrochloric acid containing 1 mg of platinum carrier. In this way a radiochemically pure ^{199}Au + ^{198}Au fraction is obtained (Fig. 1); the yield is practically quantitative (>95%). The organic phase is transferred to a 100-ml measuring flask, diluted with ethanol and counted on a 3″ × 3″ NaI(Tl) detector for 3–30 min, using a lead absorber, to reduce the high ^{199}Au activity, which causes too high a dead time on the multichannel analyzer (see Fig. 1).

The net ^{198}Au activity can be determined from the 411-keV photo-peak. The 69, 158 or 208-keV peak can be used as a measure for the ^{199}Au activity, this being the "internal standard". In the case of "high" gold contents (>10 p.p.m.), a correction must be made for the Compton contribution of the 411-keV γ-ray in the energy regions due to ^{199}Au. The ratio net ^{198}Au/net ^{199}Au activity is a direct measure for the gold content in platinum, independent of the weight of the irradiated platinum, of the yield of the extraction and of the counting time. Because of the approximately equal half-lives of ^{198}Au and of ^{199}Au (2.69 and 3.15 d respectively), no corrections are required in practice for the decay during a whole series of measurements.

TABLE III

DETERMINATION OF GOLD IN PLATINUM FROM THE RATIO NET ^{198}Au/NET ^{199}Au ACTIVITY

Sample	*411/net 69*	*411/net 158*	*411/net 208*	*Calc. content (p.p.m.)*
JM 2 (1)	0.8719	0.4723	0.4238	411/69: 31.2
(2)	0.8534	0.4696	0.4147	411/158: 32.7
(3)	0.8849	0.4885	0.4332	411/208: 32.9
(4)	0.8784	0.4805	0.4230	Average: 32.3
MH (5)	0.7385	0.4481	0.3560	411/69: 27.8
(6)	0.7431	0.4003	0.3537	411/158: 27.3
(7)	0.7470	0.3990	0.3617	411/208: 27.7
(8)	0.7412	0.3914	0.3538	Average: 27.6
Md (9)	0.02633	0.01345	0.01123	411/69: 0.93
(10)	0.02568	0.01311	0.01179	411/158: 0.91
(11)[a]	0.05791	0.02988	0.02621	411/208: 0.90
				Average: 0.91
1 p.p.m. Au	0.02794	0.01454	0.01287	

[a] To sample (11) 1.14 p.p.m. Au was added.

As an example, the calculations are given in detail (see Table III); measurements are made using a 2.2-g·cm^{-2} lead absorber, 13 days after the end of irradiation, during 3–30 min. The ratio net ^{198}Au/net ^{199}Au activity, corresponding to 1 p.p.m. of gold is deduced from samples (9), (10) and (11). This allows the calculation of the gold content in the other samples.

Determination of iridium

The remaining aqueous phase (+washing liquid) is transferred to a 100-ml measuring flask and counted on a 3″ × 3″ NaI(Tl) detector for 1–5 min (*ca.* 3 weeks after the end of irradiation). To correct for the platinum activity (^{191}Pt, ^{193m}Pt, ^{195m}Pt), which is still present, a 100-ml platinum extract from 100 mg of simultaneously irradiated platinum is used as background (see Fig. 2). In the case of small iridium contents this correction is necessary: on the 27th day after the irradiation a positive error of 7–8% is made by measuring directly the 317-keV photo-peak of

^{192}Ir in the case of a platinum sample containing 1 p.p.m. of iridium. The platinum activity can, of course, also be separated chemically from ^{192}Ir for all the samples. (An alternative procedure is to wait at least 2 months, to obtain a pure ^{192}Ir spectrum. This can obviously also be done for unprocessed irradiated platinum.)

Preparation of the ^{191}Pt, ^{193m}Pt, ^{195m}Pt extract (Fig. 3)

After the bromate distillation and extraction of gold, the remaining yellow aqueous phase (H_2PtCl_6) is transferred to a 250-ml beaker, 6.5% tin(II) chloride solution is added to obtain a red colour of maximal intensity and the concentration of hydrochloric acid adjusted to *ca.* 3 *N*. This solution is extracted with an equal volume of preequilibrated ethyl acetate.

The aqueous phase is transferred to the 250-ml beaker, the organic phase washed twice with preequilibrated 3 *N* hydrochloric acid and the washings also transferred to the beaker. The organic phase, which is then practically free from ^{192}Ir but does not yet contain all the platinum, is transferred to a 100-ml measuring flask. Tin(II) chloride solution is again added to the combined aqueous phase and the latter extracted again. The second extract is washed and also added to the measuring flask. This is repeated again. The final organic phase contains >99% of the platinum activity, whereas the remaining aqueous phase contains >97% of the iridium activity.

TABLE IV

ANALYTICAL RESULTS FOR Ru, Os, Au AND Ir IN PLATINUM (IN p.p.m.)

Sample	*Series*	*Ru*	*Os*	*Au*[b]	*Ir*
Pt JM 1	A	<1	—	0.74 ± 0.16	0.87 ± 0.16
	B	0.75 ± 0.16	0.67 ± 0.15	0.73 ± 0.3	1.1 ± 0.2
	E	—	—	—	0.84
	Average	0.7^5	0.7	0.73	0.9^5
Pt JM 2	A	<1	—	35	0.3–2.2
	B	<0.8	?	34	0.45–0.49
	C	—	0.24–0.27	—	—
	D	0.31 ± 0.08	0.34 ± 0.04	30.5 ± 0.7	0.9–2.2
	E	—	—	—	3.55
	F	—	—	36	(0.7–1.7)
	Average	0.3	0.3	33	0.5–3.5[a]
Pt MH	B	<0.6	0.22	(50)	18.9 ± 1.4
	D	?	0.29 ± 0.02	27.1 ± 0.6	22.5 ± 0.8
	E	—	—	—	24.7
	F	—	—	26.3	19.5
	Average	?	0.28	26.8	21
Pt Md	D	0.41 ± 0.1	0.19–0.35	0.84 ± 0.03	1.22 ± 0.2
	E	—	—	—	1.39
	Average	0.41	0.19–0.35	0.84	1.3
	Ref. 25	1.0	0.85	0.78	0.31
	Ref. 35	0.1[c]	<0.2[c]	<0.03[c]	<0.08[c]

[a] The distribution of iridium in sample Pt JM 2 seems to be quite heterogeneous.

[b] As will be pointed out further, correction for the second-order reaction $^{196}\text{Pt}(n,\gamma)^{197}\text{Pt} \xrightarrow{\beta^-} {}^{197}\text{Au}(n,\gamma)^{198}\text{Au}$ is necessary and was *ca.* 0.07 p.p.m. in the described experimental conditions. This correction was taken into account.

[c] Results of mass spectrographic analysis[35]. Some differences in the results of Pt Md can be observed. This might be due to sampling, as the batch in question was a particularly large one.

RESULTS

A number of results for ruthenium, osmium, gold and iridium are given in Table IV. Several series of analyses were carried out, A, B, C and D. Moreover, iridium was determined without chemical separation, by waiting *ca.* 10 weeks after the irradiation (series E). In some favourable cases, gold (and iridium) can be determined simultaneously without chemical separations, a few days after the end of irradiation, if correction is made for the platinum activity (^{191}Pt, ^{193m}Pt, ^{195m}Pt and particularly the ^{199}Au daughter of ^{199}Pt), using a high-purity platinum sample such as Pt Md, which contains *ca.* 1 p.p.m. of both gold and iridium (series F). This can be seen from Fig. 4. The latter sample (Pt Md) has also been analyzed by KILLICK AND MORRIS[13,16,25] and by The Mond Nickel Company[35].

DISCUSSION

The importance of some interfering reactions is discussed below.

Determination of osmium (^{191}Os measured)

The reaction $^{194}\text{Pt}(\text{n},\alpha)^{191}\text{Os}$ and ^{191m}Os could possibly interfere with the determination of osmium. The cross section $\bar{\sigma}(\text{n},\alpha)$ for this reaction has been estimated to be < 0.0001 mb[36]. In the irradiation position used, the fast flux was *ca.* $2.17 \cdot 10^{10}$ $\text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ [37], whereas the thermal flux was $4 \cdot 10^{11}$ $\text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$. Hence the apparent osmium content, caused by the above reaction, can be calculated. It appears to be negligible (< 1 p.p.b.).

Determination of iridium (^{192}Ir measured)

The reaction $^{192}\text{Pt}(\text{n,p})^{192}\text{Ir}$ and ^{192m}Ir has a cross section of *ca.* 0.02 mb in a fission flux[36]. Under the described conditions, the apparent iridium concentration can be shown to be *ca.* 0.02 p.p.b. The second-order reaction $^{190}\text{Pt}(\text{n},\gamma)^{191}\text{Pt} \xrightarrow{\text{E.C.}} {}^{191}\text{Ir}(\text{n},\gamma)^{192}\text{Ir}$ need not be considered either, as the apparent iridium concentration is 0.22 p.p.b. only for an irradiation period of 11 days at a thermal flux of $4 \cdot 10^{11}$ $\text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$.

Determination of gold (^{198}Au measured)

Under the present experimental conditions, the interference by the second-order reaction $^{196}\text{Pt}(\text{n},\gamma)^{197}\text{Pt} \xrightarrow{\beta^-} {}^{197}\text{Au}(\text{n},\gamma)^{198}\text{Au}$ is not negligible for high-purity samples. At a thermal flux of $4 \cdot 10^{11}$ $\text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$, the apparent gold concentration

TABLE V

CALCULATED SECOND-ORDER INTERFERENCE (IN p.p.m.) FOR THE DETERMINATION OF GOLD IN PLATINUM (^{198}Au MEASURED)

t (sec)	10^4	$5 \cdot 10^4$	10^5	$5 \cdot 10^5$	10^6	$5 \cdot 10^6$
t (days)	0.116	0.58	1.16	5.79	11.57	57.87
p.p.m. Au ($\varnothing = 10^{12}$)	0.00005	0.00114	0.0042	0.063	0.175	1.270
($\varnothing = 10^{11}$)	0.000005	0.000114	0.00042	0.0063	0.0175	0.127

is *ca.* 0.07 p.p.m., so that a correction is necessary for high-purity platinum samples (Pt JM 1, Pt Md). In Table V some calculated data are given (*cf.* ref. 38).

From Table V it appears that short irradiation times are preferable to avoid second-order interference. Because of the small size of the samples available (a few hundred mg), gold, iridium, ruthenium and osmium had to be determined simultaneously; the latter elements required a longer irradiation time, as they are less sensitive.

Sensitivity

With the described experimental conditions (100-mg samples, irradiated for 11 days at a thermal flux of $4 \cdot 10^{11}$ n·cm^{-2}·sec^{-1}) the lower limit of determination is *ca.* 0.5 p.p.m. for ruthenium (^{103}Ru, 498 keV), *ca.* 0.2 p.p.m. for osmium (^{191}Os, 65-keV X-ray), *ca.* 0.1 p.p.m. for gold (^{198}Au, 411 keV) and *ca.* 0.1 p.p.m. for iridium (^{192}Ir, 317 keV). The limiting factor for the determination of ruthenium is the background activity; for osmium the ^{199}Au contamination of the distillate or the background activity (Pb K X-ray in the lead castle); for gold the accompanying ^{199}Au activity and for iridium the accompanying platinum activity, if no chemical separation of Pt/Ir is carried out; if platinum is extracted, the sensitivity for Ir can easily be improved to *ca.* 1–10 p.p.b.

This work is sponsored by the "Interuniversitair Instituut voor Kernwetenschappen" whose financial support is gratefully acknowledged. We are also grateful to Mr. TOMBU of the "Metallurgie Hoboken" and to Mr. BETTERIDGE of the "Mond Nickel Company" for the loan of samples of platinum.

SUMMARY

Osmium, ruthenium, iridium and gold can be determined simultaneously in 100-mg platinum samples after irradiation for 11 days at a thermal neutron flux of $4 \cdot 10^{11}$ n·cm^{-2}·sec^{-1}. An addition method of analysis is used; samples are dissolved in small sealed silica tubes before activation. After irradiation, Os and Ru are distilled from sulfuric acid–sodium bromate, Ru being determined by counting the 498-keV peak of ^{103}Ru; Os is determined after a second distillation. Gold is extracted with ethyl acetate from the residue of the first distillation; the ratio ^{198}Au/^{199}Au is a direct measure for the gold content, with appropriate correction for the second-order reaction $^{196}\mathrm{Pt}(n,\gamma)^{197}\mathrm{Pt} \rightarrow {}^{197}\mathrm{Au}(n,\gamma)^{198}\mathrm{Au}$. Ir is determined in the residual aqueous phase using the 317-keV peak of ^{192}Ir; a correction for the platinum activity (^{191}Pt) is made. The lower limit of determination is *ca.* 0.5 p.p.m. for ruthenium, *ca.* 0.2 p.p.m. for osmium, *ca.* 0.1 p.p.m. for gold and *ca.* 0.1 p.p.m. for iridium. After a separation of Pt from Ir, the sensitivity for Ir can easily be improved to < 10 p.p.b.

RÉSUMÉ

L'osmium, le ruthénium, l'iridium et l'or peuvent être dosés simultanément dans des échantillons de 100 mg de platine après irradiation de 11 jours avec un flux de neutrons thermiques de $4 \cdot 10^{11}$ n cm^{-2} sec^{-1}. Les échantillons sont dissous dans des tubes de silice scellés avant activation. Après irradiation Os et Ru sont distillés en milieu acide sulfurique–bromate de sodium. Ru est dosé par comptage du pic 498-keV de ^{103}Ru; Os est déterminé après une seconde distillation. L'or est extrait avec l'acétate d'éthyle du résidu de la première distillation. Le rapport ^{198}Au/^{199}Au est une mesure directe de la teneur en or, avec correction appropriée pour la réaction de second ordre $^{196}\mathrm{Pt}(n,\gamma)^{197}\mathrm{Pt} \rightarrow {}^{197}\mathrm{Au}(n,\gamma)^{198}\mathrm{Au}$. Ir est dosé dans la phase aqueuse résiduelle en utilisant le pic 317-keV de ^{192}Ir; on effectue une correction pour l'activité du platine (^{191}Pt). La limite inférieure pour le dosage est environ de 0.5 p.p.m. pour le ruthénium, 0.2 p.p.m. pour l'osmium, 0.1 p.p.m. pour l'or et 0.1 p.p.m. pour l'iridium. Après séparation de Pt d'avec Ir, la sensibilité pour Ir peut facilement être portée à $<$ 10 p.p.b.

ZUSAMMENFASSUNG

Mit der Neutronenaktivierungsanalyse können in Platinproben von 100 mg gleichzeitig Osmium, Ruthenium, Iridium und Gold bestimmt werden. Es wurde die Additionsmethode verwendet und die Proben von der Aktivierung gelöst und in kleine Quarzröhren eingeschmolzen. Die Bestrahlung dauerte 11 Tage bei einem thermischen Neutronenfluss von 4×10^{11} n cm^{-2} sec^{-1}. Nach der Bestrahlung wurden Os und Ru aus einer schwefelsauren Natriumbromatlösung abdestilliert und Ru durch Zählen des 498-keV-Peaks von ^{103}Ru bestimmt, während Os erneut destilliert wurde. Gold wird aus dem Rückstand der ersten Destillation mit Äthylacetat extrahiert; das Verhältnis ^{198}Au/^{199}Au ist ein Mass für den Goldgehalt unter Berücksichtigung der Reaktion $^{196}\mathrm{Pt}(n,\gamma)^{197}\mathrm{Pt} \rightarrow {}^{197}\mathrm{Au}(n,\gamma)^{198}\mathrm{Au}$. Im Rückstand der wässrigen Phase wird ^{192}Ir unter Verwendung des 317 keV-Peaks bestimmt; dabei muss die Platinaktivität (^{191}Pt) berücksichtigt werden. Die Nachweisgrenzen betragen etwa: 0.5 p.p.m. Ru, 0.2 p.p.m. Os, 0.1 p.p.m. Au und 0.1 p.p.m. Ir. Nach der Abtrennung des Pt vom Ir kann die Empfindlichkeit für Ir auf $<$ 10 p.p.b. verbessert werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DETERMINATION OF IMPURITIES IN SINGLE CRYSTALS OF MAGNESIUM OXIDE BY NEUTRON ACTIVATION ANALYSIS

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(Received August 27th, 1967)

Single crystals of magnesium oxide, grown from its melts, can accommodate small amounts of impurities in either substitutional or interstitial positions of the crystal lattice. Many transition metal ions have radii near enough to that of magnesium(II) to be easily accommodated in the lattice. However, the presence of these impurities has a strong influence on many of the physical properties of single crystal[1], such as ionic conductivity, optical absorption, dielectric loss etc. If the impurity has a valence different from the valence of the main constituent of the crystal the effect is particularly strong[2].

The determination of these impurities at the trace level is therefore very important for the understanding of the properties of magnesium oxide crystals. Although many of these impurities can be determined by currently available analytical methods, neutron activation analysis is particularly attractive because of its excellent sensitivity for most trace impurities. Furthermore, the combined techniques of activation and γ-spectrometry have become frequently employed for the determination of micro or submicro amounts of most elements in very pure materials[3].

As part of a programme of research designed to investigate the defect structure of magnesium oxide crystals, the determination of transition metal impurities in single crystals of magnesium oxide was studied by neutron activation analysis. The materials employed were high-purity single crystals, and the basic approach was to compare the amount of impurity separated from an irradiated sample with those from the comparator standard.

Nuclear data

Irradiation of single crystals of magnesium oxide with thermal neutron gives rise to a series of long-lived radionuclides from the impurities contained, the characteristics of which are shown in Table I. The spectra of these γ-emitting radionuclides, measured by using a $3 \times 3''$ NaI(Tl) detector are shown in Figs. 1 and 2. It is apparent that magnesium oxide is a favourable matrix for activation analysis because the oxygen is virtually inert to thermal neutrons and the magnesium produces only short-lived isotopes.

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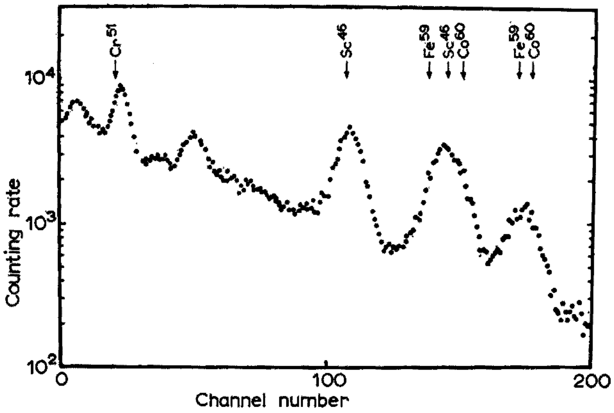

Fig. 1. γ-Spectra of MgO crystal activated with neutrons for one week, after 3 days' decay. Peaks are due to ^{46}Sc, ^{51}Cr, ^{59}Fe and ^{60}Co.

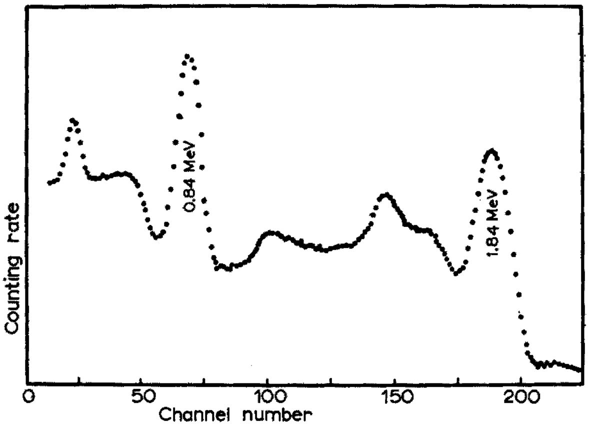

Fig. 2. γ-Spectrum of MgO crystal activated with neutrons for 30 min, after decay for 1 h. The spectrum is that of ^{56}Mn.

TABLE I

NUCLEAR CHARACTERISTICS OF MAGNESIUM, OXYGEN AND IMPURITIES STUDIED

Element	*Isotope*	*Abundance (%)*	*Reaction*	*Product reaction*	*Cross-section (barns)*	$T_{\frac{1}{2}}$	*γ-ray (eV)*
Magnesium	^{26}Mg	11.1	(n,γ)	^{27}Mg	0.03	9.5m	1.02
Oxygen	^{18}O	0.204	(n,γ)	^{19}O	$0.2 \cdot 10^{-3}$	29s	0.197
Scandium	^{45}Sc	100	(n,γ)	^{46}Sc	12	85d	0.89, 1.12
Chromium	^{50}Cr	4.4	(n,γ)	^{51}Cr	13.5	27.8d	0.32
	^{54}Cr	2.4	(n,γ)	^{55}Cr	0.37	3.6m	
Manganese	^{55}Mn	100	(n,γ)	^{56}Mn	13.3	2.58h	0.84
Iron	^{58}Fe	0.98	(n,γ)	^{59}Fe	0.98	45.1d	1.10, 1.29
Cobalt	^{59}Co	100	(n,γ)	^{60}Co	20	5.3y	1.17, 1.33
				^{60m}Co		10.5m	0.059

EXPERIMENTAL

Samples

Optical-grade, single crystals of magnesium oxide, grown from its melts, were obtained from two sources, Norton Co. Ltd., U.S.A. and Bristol University. The samplings were made by selecting randomly from the various part of an ingot, and in order to minimize the effect of self-shielding, the samples were crushed to a small mesh size and sealed in a silica vial for irradiation.

Comparison standards and reagents

In all determinations, comparative methods of analysis were used. The chemical and physical forms of the standards were chosen to have low absorption cross-sections for thermal neutrons.

For scandium, chromium and manganese, the standards were prepared from Specpure Sc_2O_3, MnO_2 and chromium metal (Johnson, Matthey Co. Ltd.). An appropriate amount of the standards was dissolved in a minimum amount of hydrochloric acid, evaporated almost to dryness and finally taken up in 100 ml of dilute hydrochloric acid; these solutions served as comparison standards after appropriate dilution.

Cobalt nitride and iron(III) sulfate (A.R.) were dissolved in 100 ml of water and the standard solutions were prepared by appropriate dilution before irradiation.

Ion-exchange column

A strong base-type anion exchanger, Dowex-1, 100–200 mesh, sulfate form, was used in conventional 20-cm glass columns of 1-cm internal diameter, packed at the bottom with glass wool. The columns were filled with a slurry of about 10 g of the dried resin and the resulting bed was usually 15–20 cm in length.

Irradiation

The samples and the standards were sealed in polythene or thin silica vials. The vials were packed as closely as possible in an aluminum capsule to minimize the flux inhomogeneity and irradiated at the U.K.B.E.P.O. reactor at Harwell. The thermal flux used[4] was approximately $2 \cdot 10^{12}$ neutron/cm^2/sec. The irradiation times varied from several days to two weeks depending on the nature or the concentration of the impurity of interest.

For the determination of manganese, the irradiations were carried out using the E 1/5 rabbit irradiation facility in the reactor. In this position[5], the thermal flux was about $1.2 \cdot 10^{12}$ neutron/cm^2/sec and fast flux was about $2 \cdot 10^{11}$ neutron/cm^2/sec.

Activity measurements

The method of analysis was based on the detection of the γ-ray emission accompanying the decay of the radionuclides produced by capture of thermal neutrons. A 3 × 3″ NaI(Tl) crystal in conjunction with a 512-multichannel analyser (Laben Model A.51) was used. The digital output of a spectrometer was connected to a H.P. 561 digital printer, which relayed the number of counts registered for each channel during the time of the measurement. The crystal and the photomultiplier were placed in a large lead shield, with an inside lining of 1/32 in of copper and 1/32 in of cadmium sheet, to minimize the effect of X-rays at 0.072 MeV, which are produced by photoelectric absorption of the lead shield as described by HEATH[6]. For absorption of β-particles, 0.5-in thick polystyrene was placed directly on the crystal, and the sample trays were placed in the centre of the crystal.

The radionuclides with significant emission of cascade γ-rays or annihilation γ-rays may be selectively measured by employing a coincidence-counting device. The technique was used to resolve the activity of separated ^{60}Co from the prevailing ^{59}Fe activity.

Photopeak area measurements

In a γ-ray spectrum, the photopeak stands on the Compton continuum as well as the background. Although all parts of the spectrum are characteristic of a particular energy of γ-ray, only the photopeak areas are normally used to identify and measure a particular nuclide. However, the spectra were constructed from the digital output as shown in Fig. 3. The base line of the photopeak was constructed using a straight line edge to the feet of the peak. Then, the area above the base line may be expressed by the formula

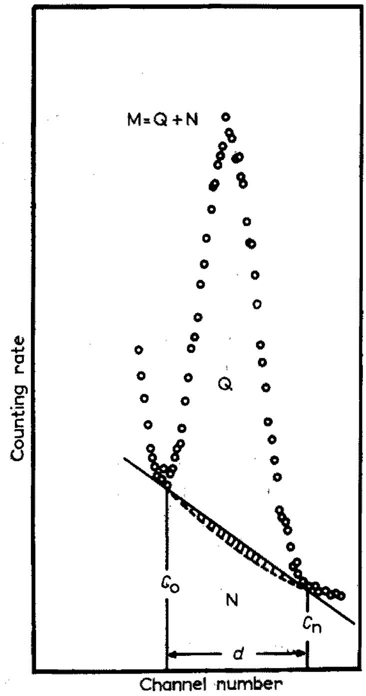

Fig. 3. Measurement of a photopeak on a multichannel analyser.

$$Q = \sum_{k=0}^{n} C_k - \tfrac{1}{2}d(C_0+C_n) = M-N \qquad (1)$$

where M is the total area under the peak, N the background and d the number of channels between the beginning and the end of the peak. The area so derived is proportional to the amount of the corresponding radionuclide present in the sample.

The small systematic error resulting from this method (shaded area in Fig. 3) is approximately equal for each sample and is cancelled out in the calculation.

The specific activity of impurities in a sample is then given by

$$Q=(M-N)\exp(\lambda t)/G\cdot T \text{ (counts/min/mg)} \qquad (2)$$

where G is the weight of a sample, T the period of measurement, $\lambda = 0.693/T_{\frac{1}{2}}$, and t the time interval between the end of irradiation and γ-ray measurement.

Determination of manganese in magnesium oxide

The determination of manganese is based on the non-destructive method of analysis because of its relatively short life. The samples were sealed in polythene vials and irradiated for 30 min. After irradiation, the samples were left for 1 h for the decay of short-lived isotopes. Then, the irradiated samples were etched in dilute hydrofluoric acid solution to remove surface contamination, weighed and counted in a thin aluminum source tray placed on the crystal. The γ-spectrometer was adjusted to cover the range of 0.1 MeV to 2 MeV, and the content of manganese was calculated from the photopeak at 0.84 MeV.

Determinations of scandium, chromium, iron and cobalt

For determinations of scandium, chromium, iron and cobalt, destructive methods were employed because of their long half-lives.

After irradiation, the samples were placed in a lead shield for at least 2 weeks to allow decay of short-lived isotopes; this period was found adequate before the radiochemical separation was started[7]. The samples were then removed from the irradiation capsule and placed in a platinum dish, and the surfaces were completely etched with hydrofluoric–nitric acid solution to remove any surface contamination which might have been present. The samples were then dried and weighed on a semimicro balance.

The separation procedures are outlined below (see Fig. 4). After being weighed, the irradiated samples were ground to a fine powder and treated with small amounts

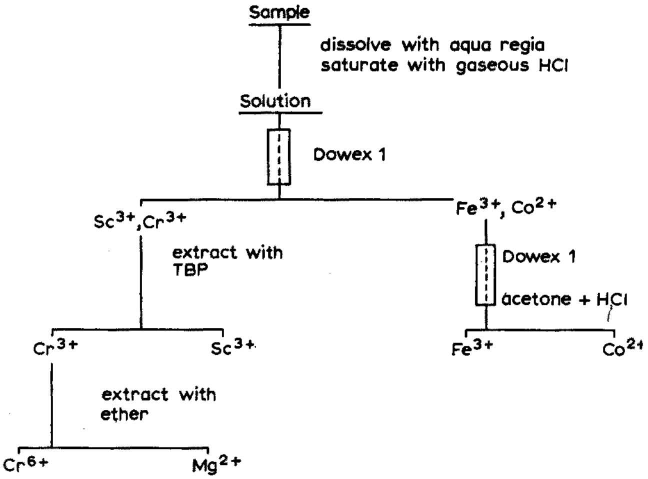

Fig. 4. Separation scheme for the determination of long-lived γ-emitting impurities in magnesium oxide.

of aqua regia until completely dissolved; the solutions were then evaporated almost to dryness and added to each carrier. The solutions were saturated with gaseous hydrogen chloride to make 12 N hydrochloric acid, filtered on a Waterman filter and washed 3 times with 1-ml portions of 12 N hydrochloric acid solution.

The filtrate and washings were passed through an ion-exchange column equilibrated with 12 N hydrochloric acid solution. Iron(III) and cobalt(II) were retained in the column. The elution rates were 0.2–0.3 ml/min. Elution was completed with 8 ml of 12 N hydrochloric acid solution, the unadsorbed chromium(III) and scandium(III) remaining in the effluent.

Iron(III) was then eluted with 10 ml of 90% acetone:10% hydrochloric acid solution, and the same eluant was then used to remove iron(III) completely from the resin. A fraction from the column was collected in a polythene bottle and analysed by γ-spectrometry to confirm the separation. After the acetone in the effluent had been evaporated, the iron(III) was precipitated with 5 N sodium hydroxide and the precipitate was centrifuged and dissolved in dilute hydrochloric acid solution. This solution was then extracted with ether and stripped with distilled water, and iron(III) was reprecipitated with sodium hydroxide solution and ignited to the oxide. After the oxide had been weighed to determine the chemical yield, the γ-activity was measured and the 1.29-MeV peak was used for the calculation.

After the removal of iron(III), 10 ml of 1 N hydrochloric acid solution was added to elute the cobalt(II) remaining in the resin, and this elution was completed with a further 10 ml of the solution. Cobalt(II) in the eluant was precipitated with hydrogen sulphide, and the cobalt sulphide was then dissolved with nitric acid solution containing some bromine. The solution was evaporated several times to fumes with hydrochloric acid and cobalt(II) was precipitated by adding potassium nitrite. The precipitated potassium cobaltinitrite was then dissolved, reprecipitated, dried at 110° and weighed as such. The γ-activity was measured and the 1.33-MeV peak was used to calculate the amount of cobalt(II) present. After the measurement, the precipitate was again dissolved and precipitated with nitroso-R salt to confirm the isolation of cobalt(II). However, the iron(III) which may be present in the sample may interfere in the measurement of the cobalt-60 activity because of the close similarity of the two γ-ray spectra. This was checked by measuring the coincidence peak of ^{60}Co at 2.50 MeV.

The effluent obtained in the step involving adsorption of iron(III) and cobalt(II) was evaporated to a definite volume and made 8 N in hydrochloric acid. This solution was then extracted with an equal amount of tributyl phosphate. The organic layer containing scandium(III) was stripped with distilled water and washed 3 times with water. The solution was then evaporated to a small volume and ammonia solution was added to precipitate scandium hydroxide. The precipitate was centrifuged and the supernate discarded. The precipitate was then dissolved with 5 ml of 6 N hydrochloric acid, the solution neutralized with ammonia solution and a few drops of hydrochloric acid were added to clear the solution. Sodium sulphinate solution was then added, and the precipitate was centrifuged and washed 3 times with distilled water and dried. The γ-ray activity was then measured, after which the precipitate was dissolved and titrated with 0.01 M EDTA solution in presence of xylenol orange as indicator to determine the chemical yield.

The aqueous phase from the above extraction contained chromium(III) as well as magnesium(II). The solution was evaporated to fumes with 5 ml of 60%

perchloric acid solution, cooled and transferred to a separation funnel. Then, 10 ml of ice-cold distilled water was added, followed by dropwise addition of 30% hydrogen peroxide until a deep blue colour appeared. This solution was extracted with 20 ml of ice-cold ether until the ether layer became blue. A few more drops of hydrogen peroxide were added to complete the oxidation. Then, the ether layer was stripped with 10 ml of cold water containing one drop of concentrated hydrochloric acid. The solution was adjusted with acetic acid to neutral or weakly acidic. A 10% solution of barium acetate was added dropwise to the boiling solution with constant stirring, and the precipitate was filtered, washed, dried and weighed as barium chromate to determine the chemical yield, before the activity was measured.

After irradiation, the comparison standards were dissolved or diluted in suitable solvents to appropriate volumes; suitable aliquots were taken and precipitated for determination of the γ-activity as described above, the samples and standards being counted consecutively.

RESULTS AND DISCUSSION

By means of the technique described, non-destructive and destructive activation methods were applied to the available single crystals of magnesium oxide (Table II). It can be seen that the distribution of impurities in magnesium oxide differs widely; this may be explained by the fact that the raw materials employed for the growth of single crystals were obtained from different origins.

TABLE II

RESULTS OBTAINED FOR IMPURITIES IN DIFFERENT SAMPLES OF SINGLE CRYSTALS OF MAGNESIUM OXIDE

	MgO[a]		*MgO*[b]	
	p.p.m.	*Error (average)*	*p.p.m.*	*Error (average)*
Sc	0.54	± 0.03	1.16	± 0.08
Cr	5.90	± 0.39	3.55	± 0.18
Mn	3.31	± 0.17	118.1	± 5.98
Fe	343.1	±18.9	217.5	±12.5
Co	3.46	± 0.18	0.14	± 0.02

[a] Norton Co., Ltd.
[b] Bristol University.

It should be noted that the concentration of iron (or manganese) impurity which is most susceptible to valence changes, is extremely high in single crystals of magnesium oxide. From other fields of study it is known that the physical properties of magnesium oxide crystals are markedly affected or even controlled by impurities such as Fe, Mn or Cr ions.

The systematic study of the sources of error in this analysis and their elimination or minimization may be conveniently divided into 3 categories: the irradiation process, chemical separation and the measurement of activity. One of the most obvious sources of error is due to the flux variation and exposure time in the irradiation. However, according to PLUMB AND LEWIS[8], self-shielding of thermal neutrons in solid samples can be computed with reasonable accuracy.

A sample of magnesium oxide crystal can be treated in terms of an equivalent sphere.

$$f = \tfrac{3}{4} N \cdot \sigma \cdot a \tag{3}$$

where f = the fractional flux depression, N = atom density (atom/cm^2), σ = thermal neutron absorption cross-section, a = radius (cm).

The approximate density is a maximum of 3.58/g/cm^3. In the case of cobalt, which has the largest absorption cross-section, if $f = 0.9$, the radius of magnesium oxide particle required to produce a reduction in thermal neutron-induced specific activity of 10% is a minimum of 0.5 cm. For the comparison standards, the probability of self-shielding during the irradiation is considered negligible because of the dilute solution of the standards employed.

Another potential source of error is that, in addition to the (n,γ) reaction which occurs with the impurities being determined, secondary reactions may occur because of the fast neutron flux; further interference may arise from the formation of radioactive isotopes other than the one being used for the determination. Examination of all the possible reactions with the impurities being determined in magnesium oxide crystals reveals that the reactions shown in Table III are possible.

TABLE III

SUMMARY OF POSSIBLE INTERFERENCE REACTIONS WITH THERMAL OR FAST NEUTRONS

Element sought	*Competition reaction*	*Absorption cross-section (mb)*
Scandium	^{46}Ti (n,p) ^{46}Sc	4.1
Chromium	^{54}Fe (n,α) ^{51}Cr	0.37
Manganese	^{56}Fe (n,p) ^{56}Mn	0.44
	^{59}Co (n,p) ^{56}Mn	35
Iron	^{59}Co (n,p) ^{59}Fe	22
	^{60}Ni (n,α) ^{59}Fe	...
Cobalt	^{63}Cu (n,α) ^{60}Co	...
	^{60}Ni (n,p) ^{60}Co	5

In the case of scandium determination, the reactions occurring in the pile are in fact more complicated. A series of scandium radioisotopes is produced by the action of fast neutrons on titanium present as an impurity in the crystals.

But the cross-sections involved are only of the order of a few millibarns or less, so that the error introduced by these reactions is negligible. On the other hand, calcium is one of the commonest impurities in the crystals (about 0.15%). In the pile, in addition to the desired ^{45}Sc (n,γ) ^{46}Sc reaction, other scandium radioisotopes were also produced by β-decay of ^{47}Ca and ^{49}Ca isotopes which were in turn produced by thermal neutrons on natural calcium present in the crystal:

$$^{46}\text{Ca}\,(\text{n},\gamma)\ ^{47}\text{Ca} \xrightarrow[T_{\frac{1}{2}}=4.7\text{d}]{} {}^{47}\text{Sc};\quad ^{48}\text{Ca}\,(\text{n},\gamma)\ ^{49}\text{Ca} \xrightarrow[T_{\frac{1}{2}}=8.8\text{m}]{} {}^{49}\text{Sc}$$

Of these two isotopes, the interference of ^{47}Sc isotope may not be so serious because of its extremely low abundance (0.0032%) and its relatively low absorption cross-section.

The interference of ^{60}Co can occur by a (n,p) reaction on ^{63}Cu or by a (n,γ) reaction on ^{68}Zn. For the magnesium oxide crystals under consideration, the cobalt content is considered to be of the same order as the nickel and copper which are expected to be of the order of a few p.p.m. These conflicting reactions are therefore most unlikely to be serious.

Of all the reactions considered, perhaps the most important interference may be introduced by reactions such as ^{56}Fe (n, p) ^{56}Mn or ^{54}Fe (n,α) ^{51}Cr. The interference of these reactions is serious because the concentration of iron impurity in the crystal is very high and because the iron-56 isotope is almost 300 times as abundant as the iron-58 isotope. Therefore, the ^{56}Fe (n, p) ^{56}Mn reaction would be almost as sensitive as the ^{58}Fe (n,γ) ^{59}Fe reaction in this particular system.

Other types of interference must also be considered in the non-destructive analysis of manganese in magnesium oxide crystals. The fast flux at the E 1/5 position is quite high, so that other secondary reactions, such as ^{24}Mg (n, p) ^{24}Na or ^{27}Al (n,α) ^{27}Na may occur. Thus, the activity of ^{56}Mn is subject to very strong background interference from the ^{24}Na activity, which causes large statistical errors when the photopeak area is measured; this is considered below.

In the application of γ-spectrometry directly to an irradiated sample, the major sources are, apart from the statistical fluctuation of counting, the method of photopeak measurement. To measure the area accurately, various methods[6,9,10] have been devised, these are often based on an inspection of the graphical representation of the spectral data; and require a measurement of either the whole area in the spectrum, or some easily recognizable fraction of the spectrum, such as the area above the Compton continuum. As such data are in digital form, accuracy and precision can be sacrificed in transposing to the graphical form and no direct basis is provided for estimating the errors involved in the measurement of a photopeak. However, the method used for interpretation of the photopeaks takes advantage of the digital nature of the data and permits direct quantitative evaluation.

In the activity measurements, the total error in the count rate consists of the uncertainty in the individual measurements that comprise the rate equation, and can be calculated by the usual approximation for combining errors. It can be shown[11,12] that the percentage error is

$$\mathrm{PE}(\%) = \pm 100 \cdot \frac{SD(Q)}{Q} = \pm 100 \cdot \frac{(1+a)}{\sqrt{M}} \tag{4}$$

where $SD(Q) = \pm Q/(\sqrt{M}(1-a))$, Q is specific counting rate ($=\mathrm{f}(MNGT)$) and $a = N/M$, the fraction of the Compton background in the spectrum and varied randomly from 0.2 to 0.48. This is the basic equation used to determine the percentage error of the countrates obtained from the digital output.

The total error consists of three terms: (*a*) error from weighing of a comparison standard (PE (1)); (*b*) error from the activity measurement of the impurities present in a sample PE (2); and (*c*) error from the activity measurement of a comparison standard PE (3). According to the propagation of errors, the total percentage error is therefore given by

$$\mathrm{PE(T)} = \pm(\mathrm{PE}(1)^2 + \mathrm{PE}(2)^2 + \mathrm{PE}(3)^2)^{\frac{1}{2}} \tag{5}$$

where PE (1) is estimated to be less than 3%, and PE (2) and PE (3) can be calculated from eqn. (4).

It is, however, generally assumed that in the application of γ-spectrometry, the major source of error is the statistical fluctuation of total countrates under a photopeak. The results of the calculation show that the contribution from the

Compton background must also be taken into consideration. If a sufficient number of counts is taken and the background is subtracted, it is possible to minimize the error greatly.

This work was done under a contract from the Atomic Energy Research Establishment, Harwell. The author is indebted to the Isotope Research Division, for providing the irradiation facilities and Mr. J. G. CUNNINGHAME, Rutherford High Energy Laboratory, NIRNS, for laboratory facilities. The advice of Prof. F. C. CHAMPION is gratefully acknowledged.

SUMMARY

The determination of some trace impurities in single-crystal magnesium oxide is described. Radiochemical separations of iron, cobalt, scandium, manganese and chromium by ion exchange and solvent extraction are applied in conjunction with γ-spectrometry. The impurities that give rise to long-lived γ-emitting isotopes are considered.

RÉSUMÉ

On décrit une analyse de quelques impuretés à l'état de traces dans un cristal d'oxyde de magnésium. On utilise des séparations radiochimiques de fer, cobalt, scandium, manganèse et chrome par échangeur d'ions et extraction dans un solvant ainsi que la spectrométrie-γ. Ces impuretés donnent naissance à des isotopes de longue vie, avec émission-γ.

ZUSAMMENFASSUNG

Die Bestimmung von Spuren Verunreinigungen in Einkristallen von Magnesiumoxid mit der Neutronenaktivierungsanalyse wird beschrieben. Eisen, Kobalt, Scandium, Mangan und Chrom werden mit einem Ionenaustauscher und durch Flüssigextraktion abgetrennt und langlebige γ-emittierende Isotope gemessen.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DETERMINATION OF GOLD BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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(Received November 21st, 1967)

NASOURI, SHAHINE AND MAGEE[1] have indicated the usefulness of ferroin[2] in the separation of gold from many other metals (Co, Ni, Cu, Mn, Fe, Zn and Cr). In attempting to extend their procedure to small amounts of gold, the fact that the spectral densities for ferroin and the iron(II) 1,10-phenanthroline tetrabromoaurate complex, $[AuBr_4]_2[Fe(1,10\text{-phen})_3]$, are similar for the peak at 513 nm becomes a serious limitation, since any carry-over of ferroin will result in high and probably variable blanks.

One of the experiments in an attempt to improve the sensitivity of the colorimetric procedure was the use of bathophenanthroline in the chloroform extraction phase of the $[AuBr_4]_2[Fe(1,10\text{-phen})_3]$ to see if this would result in the formation of the iron(II) bathophenanthroline complex. The stoichiometric relationship of gold to iron is 7:1 by weight. The factor for iron(II) bathophenanthroline in 5-cm cells is 12.1 μg per 1.000 absorbance at 536 nm. On this basis the factor for gold should be 85 μg and the experimental data confirmed this. The precision in the range 25–75 μg of gold was $\pm 5\%$. However, when aliquots containing 0.5 g of copper were analyzed for gold, the precision was significantly poorer. The blanks showed poor precision and were unreasonably high, indicating over 60 p.p.m. gold in the high-purity copper. This implied that extraneous ferroin was being extracted into the chloroform layer. For the determination of small amounts of gold in matrices such as copper, the ferroin separation technique, while adequate in isolating the gold, requires a final determination in which iron itself does not interfere. The use of atomic absorption spectrophotometry[3] seemed an obvious solution.

EXPERIMENTAL

Reagents

Ferroin solution (0.0025 M).* Made by dilution of ferroin (0.025 *M*).

Bathophenanthroline (0.05%).* Made by dissolution of 0.10 g of the reagent in 200 ml of absolute ethanol.

Gold standard solutions. 5 μg/ml and 1 μg/ml in 5% hydrochloric acid.

Copper (high purity) solution. 0.100 g/ml in 5% hydrochloric acid.

Apparatus

Spectrophotometer (Bausch and Lomb, Precision) with 5-cm cells.

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* Obtained from G. Frederick Smith Chemical Co.

Atomic absorption spectrophotometer, Perkin-Elmer, Model 303, with Boling burner and digital concentration readout, and a gold hollow-cathode lamp.

Procedures

Method A. A standard curve with ferroin is prepared as follows. Add aliquots of the appropriate standard gold solution to small beakers. Adjust the volume to 20–25 ml with water. Then add 3 ml of 0.1 *M* sodium bromide and 2 ml of the 0.0025 *M* ferroin solution. Adjust the pH to 1±0.5 with hydrochloric acid or 3 *M* sodium acetate solution as needed. Then transfer these solutions to separatory funnels and extract with 10 ml of chloroform for 1 min. Reserve the chloroform layer in a dry 25-ml volumetric flask. Repeat the extraction with a second 10 ml of chloroform and combine in the volumetric flask. Add 5 ml of absolute ethanol and make to volume with chloroform.

For the colorimetric determinations, read the absorbance at 513 nm in 5-cm cells. For the atomic absorption analysis, the apparatus and the gold hollow-cathode lamp were used in conformity with the manufacturer's recommendations. The wavelength used was 2433 Å. The digital concentration readout was used up to full-scale expansion when necessary.

Method B. The standard curve for the colorimetric determination using bathophenanthroline can be prepared by modifying the preceding method as follows. To the dry 25-ml volumetric flask add 5 ml of bathophenanthroline solution and 5 drops of aqueous 20% hydroxylamine hydrochloride solution. Add the chloroform extracts, prepared as described above, to the flasks and make to volume with chloroform. Measure the colorimetric absorbance in 5-cm cells at a wavelength of 536 nm after 1 h. The solutions can also be used for atomic absorption determinations.

Samples can be dissolved in 1:1 nitric acid or in aqua regia; hydrochloric acid is then added and the samples are evaporated to a syrup. The samples are made to a volume such that aliquots of 20 ml or less can be used.

Method C. For samples containing less than 10 p.p.m. gold, a single 8-ml extraction with chloroform is sufficient. This extract is reserved in a 10-ml volumetric flask containing 2 ml of absolute ethanol, the solution is diluted to volume with chloroform and compared by atomic absorption with standards prepared similarly.

RESULTS AND DISCUSSION

The results obtained for the calibration curves by the spectrophotometric ferroin method are shown in Table I. Results for the spectrophotometric procedure with bathophenanthroline in the absence and presence of copper are shown in Table II; the undesirable effect of large amounts of copper is obvious from this Table. The results shown in Table III indicate the feasibility of the atomic absorption method for the final determination of gold in samples containing up to 1 g of copper and 10–50 μg of gold.

For the determination of gold in high-purity copper, the sensitivity of the atomic absorption procedure must be maximized; the results shown in Table IV indicate the applicability of the method when the maximum scale expansion of the digital concentration readout is utilized. The maximum increase in sensitivity is achieved when scale expansion is used in conjunction with a chloroform extraction

TABLE I

STANDARD CURVE FOR COLORIMETRIC DETERMINATION OF GOLD WITH FERROIN (METHOD A)

Au (μg)	*Abs. 513 nm/5-cm cells*		*Corr. abs.*	*Abs./1 μg Au*
0	0.017	Av. 0.022		
	0.027			
25	0.127		0.105	0.00420
	0.131		0.109	0.00436
50	0.270		0.248	0.00496
	0.269		0.247	0.00494
75	0.396		0.374	0.00499
	0.387		0.365	0.00487

TABLE II

STANDARD CURVE FOR COLORIMETRIC DETERMINATION OF GOLD WITH BATHOPHENANTHROLINE (METHOD B)

Au (μg)	*Cu (g)*	*Abs. 536 nm/5 cm*		*Corr. abs.*	*Abs./1 μg Au*
0	0.0	0.056	Av. 0.054		
		0.052			
25	0.0	0.342		0.288	0.0115
		0.350		0.296	0.0118
50	0.0	0.594		0.540	0.0108
		0.588		0.534	0.0107
75	0.0	0.884		0.830	0.0111
		0.906		0.852	0.0114
0	0.1	0.062	Av. 0.067		
		0.072			
10	0.1	0.168		0.101	0.0101
		0.176		0.109	0.0109
25	0.1	0.348		0.281	0.0112
		0.362		0.295	0.0118
50	0.1	0.696		0.529	0.0106
		0.722		0.555	0.0111
0	0.5	0.511	Av. 0.467		
		0.423			
50	0.5	0.976		0.509	0.0102
		1.091		0.624	0.0125

volume of 8 ml (Table V). When scale expansion is not available, the method is still useful for larger amounts of gold, as shown in Table VI. Table VII shows a comparison of results by atomic absorption spectrophotometry and the classical fire-assay method.

Although the spectrophotometric determination of gold with ferroin lacks sensitivity, the procedure allows an adequate separation of small amounts of gold from copper and many other elements. The use of bathophenanthroline doubles the sensitivity of the spectrophotometric method: however, a high value was obtained for gold when a 0.5-g sample of high-purity copper was analyzed, whereas the same solution analyzed by atomic absorption spectrophotometry gave satisfactory results, which indicates a carry-over of excess iron from the ferroin reagent.

The use of atomic absorption spectroscopy for the final determination of gold

TABLE III

ATOMIC ABSORPTION ANALYSIS FOR GOLD (METHOD A)

Au (μg)	*Cu (g)*	*Abs.*[a]		*Ave. abs.*	*Corr. abs.*	*Abs./1 μg Au*
0	0	0.118	0.126	>0.111		
		0.097	0.104			
10	0	0.502	0.500	0.501	0.390	0.0390
		0.532	0.520	0.526	0.415	0.0415
20	0	0.843	0.865	0.854	0.743	0.0372
		0.830	0.826	0.828	0.717	0.0359
30	0	1.071	1.073	1.072	0.961	0.0320
		1.057	1.055	1.056	0.945	0.0315
50	0	1.612	1.598	1.605	1.494	0.0299
		1.534	1.527	1.531	1.420	0.0284
0	1.0	0.127	0.131	>0.114		
		0.099	0.100			
10	1.0	0.504	0.505	0.505	0.396	0.0396
50	1.0	1.553	1.555	1.554	1.443	0.0289
		1.602	1.578	1.590	1.479	0.0296

[a] Expanded full scale on digital concentration readout.

TABLE IV

ATOMIC ABSORPTION ANALYSIS FOR GOLD (METHOD A)

Au (μg)	*Cu (g)*	*Abs.*[a]		*Ave. abs.*	*Corr. abs.*	*Abs./1 μg Au*
0	1.0	0.131	0.127	>0.116		
		0.100	0.106			
4	1.0	0.281	0.270	0.275	0.159	0.0398
		0.261	0.259	0.260	0.144	0.0360
7	1.0	0.369	0.356	0.363	0.247	0.0353
		0.373	0.374	0.374	0.258	0.0369
10	1.0	0.482	0.484	0.483	0.367	0.0367
		0.485	0.490	0.488	0.372	0.0372

[a] Expanded full scale on digital concentration readout.

TABLE V

ATOMIC ABSORPTION ANALYSIS FOR GOLD (METHOD C)

Au (μg)	*Cu (g)*	*Abs.*[a]		*Ave. abs.*	*Corr. abs.*	*Abs./1 μg Au*
0	0.0	0.092	0.086	>0.094		
		0.099	0.100			
1	0.0	0.177	0.165	0.171	0.077	0.077
2	0.0	0.267	0.274	0.270	0.176	0.088
		0.277	0.284	0.280	0.186	0.093
4	0.0	0.427	0.441	0.434	0.340	0.085
		0.455	0.440	0.448	0.354	0.089

[a] Expanded full scale on digital concentration readout.

also eliminates the interference of the platinum metals, which are also extractable as ferroin complexes. The use of an organic solution and the full scale expansion of the digital concentration readout permits the determination of as little as 1 p.p.m. of gold in copper with a precision of *ca.* ±0.25 p.p.m. The data on a series of emission

TABLE VI

ATOMIC ABSORPTION ANALYSIS FOR GOLD (METHOD A)

Au (μg)	*Abs.*		*Ave. abs.*	*Corr. abs.*	*Abs./1* μg *Au*
0	0.001	0.003	>0.003		
	0.003	0.003			
50	0.097	0.098	0.098	0.095	0.00190
	0.100	0.102	0.101	0.098	0.00196
100	0.173	0.173	0.173	0.170	0.00170
	0.172	0.172	0.172	0.169	0.00169
150	0.270	0.268	0.269	0.266	0.00177
	0.259	0.260	0.260	0.257	0.00171
200	0.325	0.328	0.327	0.324	0.00162
	0.337	0.338	0.338	0.335	0.00168

TABLE VII

ANALYSIS OF COPPER STANDARDS FOR GOLD BY ATOMIC ABSORPTION

Sample	*Fire assay value (p.p.m. Au)*	*At. abs. value (p.p.m. Au)*
A	0.2	0.3
		0.6
B	1.4	5.0
		5.0
C	53	49.2
		47.0
D	19	21.0
		20.2

spectrographic copper standards checked well in 3 of the 4 standards analyzed originally by classical fire assay. The high-purity copper was found to have a content of less than 0.25 p.p.m. of gold, which is reasonable.

The use of atomic absorption for the final determination of gold in samples containing less than 100 p.p.m. seems preferable to either of the colorimetric procedures. However, for larger concentrations of gold either of the colorimetric procedures or the determination by atomic absorption without prior separation may be preferable, especially as the concentrations increase.

SUMMARY

Gold can be isolated from most other elements other than the platinum metals by the extraction of iron(II) 1,10-phenanthroline tetrabromoaurate in chloroform. After isolation gold can be determined in the organic solvent by atomic absorption spectroscopy or colorimetrically by decomposition of the complex and determination of the iron by bathophenanthroline.

RÉSUMÉ

L'or peut être isolé de la plupart des éléments, autres que les métaux du platine, par extraction du fer(II)1,10-phénanthrolinetétrabromoaurate dans le chloroforme. Après séparation, l'or peut être dosé dans le solvant organique par spectroscopie par absorption atomique, ou colorimétriquement par décomposition du complexe et dosage du fer par la bathophénanthroline.

ZUSAMMENFASSUNG

Gold kann von den meisten anderen Elementen, ausser den Platinmetallen, durch Extraktion des Eisen(II)-1,10-phenanthrolintetrabromaurats mit Chloroform getrennt werden. Anschliessend wird das Gold in der organischen Lösung mittels der Flammenabsorptionsspektroskopie oder colorimetrisch durch Zersetzung des Komplexes und Bestimmung des Eisens mit Phenanthrolin bestimmt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE DETERMINATION OF MINOR AMOUNTS OF TELLURIUM IN IRON AND STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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(Received November 27th, 1967)

Minor amounts of tellurium in iron and steel have a significant effect on the properties of the product[1]; quantities as low as 0.01% will stabilise much of the iron carbide in cast iron[2]. Gravimetric[3] and titrimetric[4] methods for the determination of minor amounts of tellurium are relatively insensitive and presuppose the absence of interfering elements.

The colorimetric determination of tellurium has been effected through the complexes with thiourea[5-7], iodide[4], sodium diethyldithiocarbamate (Na-DDC)[8] and sols of metallic tellurium[9]. BURKE *et al.*[10] made X-ray spectrometric determinations of tellurium following separation of silica and selenium; MAIENTHAL AND TAYLOR[11] applied cathode-ray polarography to the determination of tellurium in white cast iron and results were presented for the range 0.002–0.075% tellurium. The above procedures require a preliminary separation of tellurium in order to remove interfering elements. Tellurium may be separated: by reduction to metallic tellurium[4,6,8,10,11], by solvent extraction[6,7], through acid-insoluble tellurium-containing phases[4] or by a combination of these techniques[4,6].

The use of atomic absorption spectrophotometry for the determination of tellurium in iron and steel has not been reported and the present study covers the determination of tellurium in the range 0.0005–0.030%. The sensitivity (1% absorption, Te 2142.75) observed for tellurium was 1.3 p.p.m. in aqueous solution; however, a sensitivity of 0.3 p.p.m. was obtained in amyl acetate, which is adequate for this determination. The selectivity of atomic absorption spectrophotometry is attractive because a complete separation from other elements is not required.

EXPERIMENTAL

Apparatus

Atomic Absorption Spectrophotometer, Techtron (Melbourne).

Reagents

Tin(II) chloride solution. Dissolve 100 g of $SnCl_2 \cdot 2H_2O$ in 100 ml of hydrochloric acid (s.g. 1.18).

Sodium diethyldithiocarbamate (Na-DDC) solution (0.7% w/v). Dissolve 0.7 g of Na-DDC in 100 ml of water and filter.

Iron. Johnson and Matthey, spectrographically standardised sponge.

Tellurium stock solution. Dissolve 0.100 g of tellurium metal in 15 ml of 50% (v/v) nitric acid. Add 10 ml of 50% (v/v) sulphuric acid and evaporate to fumes. Add water, warm to dissolve and dilute to 100 ml. Store in a low-actinic glass bottle; 1 ml of this solution contains 1.00 mg of tellurium(IV). Prepare a solution containing 20 µg of tellurium(IV) per ml.

Recommended procedure

Weigh a 0.5-g sample into a 125-ml conical beaker (a half-weight sample is used to establish the blank level). Prepare a calibration series for the range 0–0.030% tellurium by making additions of 20 µg/ml tellurium(IV) solution to 0.5-g portions of iron sponge. Add 60 ml of 25% (v/v) sulphuric acid and simmer to dissolve (in the presence of W, Nb or Ta, add 5 ml of hydrofluoric acid). Oxidize carbides with the minimum quantity of 50% (v/v) nitric acid, dilute to 80 ml with water, heat to 90°, add 10 ml of tin(II) chloride solution, mix, cool to room temperature, and stand for 1 h. Filter the precipitate on a Whatman 542 paper, wash 6 times with 50% (v/v) hydrochloric acid and 10 times with water. Return the filter paper to the original beaker, add 10 ml of 50% (v/v) nitric acid and 3 ml of 50% (v/v) sulphuric acid, cover the beaker and heat gently for 30 min to dissolve tellurium. Filter through a Whatman 542 paper into a 125-ml conical beaker, wash 5 times with warm 2% (v/v) sulphuric–2% (v/v) nitric acid and evaporate the filtrate to fumes. If the solution darkens add a few drops of nitric acid and again evaporate to fumes. Add 10 ml of water, cool and transfer to a 100-ml separating funnel, adding water to bring the total volume to 30 ml. Add 5.0 ml of amyl acetate, shake for 5 sec, add 4 ml of 0.7% (w/v) Na-DDC solution and shake the mixture vigorously for 60 sec. Allow the phases to separate and transfer the amyl acetate extract into a capped 10-ml polyethylene bottle. Make a second extraction with a further 4 ml of 0.7% (w/v) Na-DDC solution and store the extract separately. Measure the absorbance at Te 2142.75 Å, atomising the extracts in a 10-cm slot burner using a lean air–acetylene flame and operating the hollow-cathode lamp at 12 mA. Determine the tellurium content of the sample from the concurrently prepared calibration graph.

RESULTS AND DISCUSSION

In aqueous media the following elements can be reduced to the metallic state by tin(II) chloride: arsenic, bismuth, copper, gold, mercury, selenium, silver and tellurium; the precipitation of metallic tellurium is quantitative when the acidity is not less than 1.5 *M* of sulphuric acid[8]. Initially, several separations were made with tin(II) chloride in crystalline form; however, a white turbidity of basic tin(II) compounds was observed in the sulphuric acid solution and the precipitated metallic tellurium could not be washed free of tin(II) salts. A study was made of the effect of tin salts on the extraction of Te(IV)–DDC with amyl acetate; as much as 5 mg of tin(IV) could be present without influencing the extraction but tin(II) was found to be a source of serious interference. The results of this series of tests are presented in Table I. The presence of more than 0.1 mg of tin(II) compounds in the precipitated tellurium was avoided by using a clear, freshly prepared tin(II) chloride–hydrochloric acid solution in subsequent work.

Sodium diethyldithiocarbamate forms extractable chelates with all the elements that are reduced to the metallic state by tin(II) chloride[12]. These elements when present in a sample will accompany tellurium into the organic phase and therefore it was necessary to assess the effect of these elements upon the determination. The recommended procedure was applied to 20 and 100 µg of tellurium(IV) with 1000 µg additions of arsenic, bismuth, copper and selenium; the results are presented in Table II. The results demonstrate that these elements do not influence the determination of tellurium by atomic absorption spectrophotometry, although serious interference could be caused in colorimetric determinations.

TABLE I

THE INFLUENCE OF TIN(II) ON THE EXTRACTION OF TELLURIUM(IV) DIETHYLDITHIOCARBAMATE WITH AMYL ACETATE

Tin(II) added (µg)	*Tellurium (µg)*				
	Taken	*Found*			
		extr. 1	*extr. 2*	*extr. 3*	*extr. 4*
100	100	100	<1	—	—
200	100	76	26	<1	—
300	100	58	44	<1	—
500	100	40	40	19	—
1000	100	49	33	10	—
2000	100	34	35	17	7

TABLE II

A STUDY OF THE POTENTIAL INTERFERENCE OF OTHER ELEMENTS ON THE DETERMINATION OF TELLURIUM

Element (Each addition 1000 µg)	*Tellurium*			
	Taken (µg)	*Found (µg)*	*Taken (µg)*	*Found (µg)*
As	20	20	100	98
Bi	20	21	100	100
Cu	20	20	100	103
Se	20	19	100	99
As + Bi + Cu + Se	20	20	100	101

Tellurium(IV) diethyldithiocarbamate is extracted quantitatively from $2.5 \cdot 10^{-4}$–$2.5\ M$ sulphuric acid solution[8]. Although sodium diethyldithiocarbamate is unstable in acid solutions[13,14], $1\ M$–$2\ M$ sulphuric acid was used in the recommended procedure; no difficulties were encountered because amyl acetate was added to the separating funnel before the addition of diethyldithiocarbamate, thus allowing rapid extraction of the chelate[10]. By using a 0.7% (w/v) diethyldithiocarbamate solution rather than a 0.1% (w/v) solution, the problems of reagent consumption by other elements were eliminated. Within a few minutes the yellow extract of tellurium(IV)–diethyldithiocarbamate became lighter in colour because of photodecomposition of the chelate, and while this effect causes uncertainty in the colorimetric determination of tellurium there is no influence on the determination of tellurium by atomic absorption spectrophotometry.

The proposed procedure was applied to a series of calibration samples (iron and standard tellurium solution) and a statistical evaluation of the method was made; for 20, 40, 60, 100 and 150 μg of tellurium, the standard deviations (1σ, $n=9$) were 1, 2, 2, 3 and 4 μg respectively. Accordingly, the proposed procedure was applied to three standard cast iron samples and the results are presented in Table III.

TABLE III

TELLURIUM CONTENT OF STANDARD CAST IRON SAMPLES

N.B.S. sample no.	*Nominal composition*	*% Tellurium*		
		X-ray spectrometry[10]	*Cathode-ray polarography*[15]	*Recommended procedure*
1176	3%C, 3%Si, 0.8%Cu 0.5%Cr, 0.01%As, 0.01%Bi		0.014	0.014_7 0.013_8
1180	3%C, 3%Si, 0.2%Cu 0.1%Cr, 0.06%As, 0.002%Bi	0.018	0.024	0.021_4 0.021_0
1182	2%C, 0.3%Si, 0.5%Cu 0.03%Cr, 0.2%As, 0.006%Bi	0.007	0.009	0.008_0 0.008_0

The agreement between the results obtained by atomic absorption spectrophotometry and those reported previously by X-ray spectrometry[10] and cathode-ray polarography[15] is satisfactory and provides confirmation of the validity of the proposed procedure.

Appreciation is expressed to the Research Manager, The Broken Hill Proprietary Company Limited for permission to publish this work.

SUMMARY

A study was made of the determination of 0.0005–0.030% tellurium in iron and steel by atomic absorption spectrophotometry. Tellurium is separated by precipitation with tin(II) chloride and concentrated by extraction of the diethyldithiocarbamate complex into amyl acetate. The procedure is free from interference by elements which are reduced by tin(II) chloride or from the diethyldithiocarbamates of these elements. The results obtained on standard samples are in agreement with those reported with X-ray spectrometry and cathode-ray polarography.

RÉSUMÉ

Les auteurs ont effectué une étude sur le dosage du tellure (0.0005–0.030%) dans le fer et l'acier par spectrophotométrie par absorption atomique. Le tellure est séparé par précipitation avec le chlorure d'étain(II) et concentré par extraction du complexe diéthyldithiocarbamate dans l'acétate d'amyle. Les éléments réduits par le chlorure d'étain(II) ou précipités comme diéthyldithiocarbamates ne gênent pas. Les résultats obtenus avec des échantillons standards correspondent bien à ceux de la spectrométrie aux rayons-X et de la polarographie à rayon cathodique.

ZUSAMMENFASSUNG

Es wurden Untersuchungen zur Bestimmung von 0.0005–0.030% Tellur in Eisen und Stählen mittels der Flammenabsorptionsspektralphotometrie durchgeführt. Tellur wird durch Fällung mit Zinn(II)-chlorid abgetrennt und durch Extraktion des Diäthyldithiocarbamat-Komplexes mit Amylacetat angereichert. Das Verfahren ist frei von Störungen durch Elemente, die durch Zinn(II)-chlorid reduziert und durch Diäthyldithiocarbamat extrahiert werden. Ergebnisse, welche mit Eichproben erhalten wurden, stimmen mit denen der Röntgenspektralanalyse und der Kathodenstrahlpolarographie überein.

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X-RAY DETERMINATION OF TRACES OF HAFNIUM IN ZIRCONIUM METAL OR TRACES OF ZIRCONIUM IN HAFNIUM METAL AFTER SEPARATION BY ION EXCHANGE

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(Received December 11th, 1967)

To determine traces of hafnium in zirconium metal or zirconium in hafnium metal, it is necessary to separate the trace metal from the bulk of the matrix metal before the analysis. STRELOW AND BOTHMA[1] have developed an excellent anion-exchange separation of hafnium and zirconium, using a column of Dowex 1 resin in the sulfate form. This method has been used for the separations required in the present investigation.

Once the traces of hafnium or zirconium have been reasonably well isolated, they can be conveniently determined by X-ray fluorescence spectroscopy. Small amounts of hafnium cause no line or absorption interference in the zirconium determination when the Kα line is used. Moreover, the line interference due to zirconium in the hafnium determination is small and can be easily corrected for if the X-ray measurements for hafnium are made with the Lβ line.

After the trace metals have been separated by ion exchange, they can be determined by the coprecipitation–X-ray method[2]. From 0.004 to 2% of hafnium can be determined in zirconium metal or 0.002 to 2% of zirconium in hafnium metal. Confirmatory data on synthetic samples have shown the method to be satisfactory.

EXPERIMENTAL

Apparatus

Ion-exchange column. Fill a 1-in (I.D.) × 10-in glass column with a fused-in, coarse, fritted glass bottom to a height of 2–2.25 in with Dowex 1-X8, 200–400 mesh, chloride form, anion-exchange resin, which is purified and sold by Bio-Rad Laboratories, Richmond, California under the designation AG 1-X8. Cover with a 1.5-in layer of 1/8-in glass beads. Place a filter funnel that reaches down to the glass beads in the top of the column. Pass 10% (v/v) sulfuric acid through the column until the effluent is free of chloride ion as shown by the silver nitrate test. Pass 50 ml of 3% (v/v) sulfuric acid at a flow rate of about 3 ml per min through the column to equilibrate it for use. To regenerate a column after use, elute with 50-ml portions of 10% sulfuric acid until the effluent shows little or no white cloudy precipitate on adding 5 ml of 1% cupferron solution and allowing to stand. Finally, equilibrate again with 50 ml of 3% sulfuric acid.

Reagents

Standard hafnium solution (100 μg Hf per ml). Dissolve 23.6 mg of pure HfO_2 or 20.0 mg of pure hafnium metal in a covered platinum crucible in 2 ml of 48% hydrofluoric acid by warming. Add 0.5 ml of concentrated sulfuric acid and evaporate to copious white fumes to expel all the hydrofluoric acid. Cool and wash into a 200-ml volumetric flask containing about 100 ml of water plus 20 ml of concentrated sulfuric acid. Dilute to 190 ml, cool and then dilute to the mark and mix.

Standard zirconium solution (100 μg Zr per ml). Repeat the above procedure using 27.0 mg of pure ZrO_2 or 20.0 mg of pure zirconium metal.

Procedures

Dissolve 0.500 g of the zirconium or hafnium metal sample in a platinum crucible in dilute hydrofluoric acid solution, add 5 ml of concentrated sulfuric acid, evaporate to fumes to expel hydrofluoric acid, add water, cool and then dilute to 50.0 ml.

Determination of traces of hafnium in zirconium metal. Depending on the expected hafnium content, transfer 0.5 ml or 5.0 ml of the zirconium sample solution to a 100-ml beaker, add 4 or 3 ml respectively of (1+1) sulfuric acid and evaporate to copious white fumes to depolymerize the zirconium and hafnium. Once this depolymerization has been accomplished, carry the sample through the ion-exchange and cupferron separations without delay. Add 10 ml of a 60-ml portion of water, cool, add the remaining 50 ml of water, stir and then pour into the reservoir of the equilibrated ion-exchange column. Allow the solution to drain through the column at a flow rate of about 3 ml per min and discard the 60 ml of effluent. Then remove the hafnium from the column by elution with successive 50-ml portions of 3% sulfuric acid. As each 50-ml aliquot is received in a 150-ml beaker carry it, without delay, through the cupferron precipitation as described below. Continue the elution until the cupferron precipitate obtained in the aliquot has a white cast, indicating that breakthrough of the zirconium has occurred. Usually breakthrough occurs during the elution of the 5th aliquot.

Determination of traces of zirconium in hafnium metal. Transfer 0.5 or 5.0 ml of the hafnium sample solution to a 100-ml beaker and proceed as directed above but after discarding the first 60 ml of effluent, elute with seven successive 50-ml aliquots of 3% sulfuric acid to remove all but traces of the hafnium from the column. Then elute with three successive 50-ml portions of 10% sulfuric acid and make the cupferron precipitation on each portion of the effluent as described below.

Precipitation with cupferron and determination by X-ray analysis. To each 50-ml portion of effluent containing hafnium or zirconium, add 1 ml of a solution containing 50 μg of iron(III) and then 5 ml of a freshly prepared 1% cupferron solution. Filter and determine the hafnium or zirconium on an X-ray spectrograph, taking 100-sec counts at 39.90° when determining hafnium or at 22.55° when determining zirconium[2]. Compare the X-ray count to that of a calibration graph which has been prepared from data obtained by carrying 0–100 μg of hafnium or zirconium through the precipitation and X-ray analysis. The count obtained on the last hafnium-containing disk must be corrected for line interference due to zirconium. To do this, measure the disk at 22.55° to determine how much zirconium is present. Then obtain the count contributed at 39.9° by the zirconium present by referring to a graph prepared by measuring the standard zirconium disks at this wavelength. With the conditions used it was found that each microgram of zirconium present contributes about 0.1 count per sec compared to 10 counts/sec/μg for hafnium at 39.90° or 20 counts/sec/μg for zirconium at 22.55°. All counts for the analyses and the various graphs must be corrected for the scattered background counts obtained on a disk which contains only the iron(III).

DISCUSSION

In preliminary tests of the ion-exchange separation, using a 12-in column, it was found that the elution was very time-consuming and that somewhat low recoveries of hafnium were obtained. This latter suggests that a small amount of the hafnium has become hydrolyzed or polymerized during the slow elution and remains on the column with the zirconium.

In order to speed up the elution, it was necessary to use a 2-in column and a relatively fast flow rate in the ion exchange. Under these conditions, the volume of eluant required is markedly reduced and the recovery of the hafnium is quantitative. However, when the short column is used in the determination of hafnium, the last 50 ml of the hafnium effluent will contain some zirconium and in a determination of zirconium the first 50-ml aliquot of the effluent will contain some hafnium. This makes it necessary to use a specific method for the analyses.

The optimum acid concentration for the separation on a 2-in column appears to be about 3% sulfuric acid. Tests with progressively higher acid concentrations showed that a reasonably good separation of the two metals is still possible with 3.5% sulfuric acid but that the elution of the two metals begins to overlap at higher acidities. At acidities lower than 3%, problems from hydrolysis and polymerization of the two metals may be encountered.

As expected, in the determination of hafnium, the amount of 3% sulfuric acid required for complete elution of the hafnium, and the amount of zirconium that accompanies the hafnium in the elution is controlled by the column length, the rate of elution, the size of the sample taken and the amount of Hf present. From this, it is seen that close control of all parameters is necessary if a good separation is to be achieved. However, in using the method on a wide variety of samples, it may be necessary to vary the parameters slightly. Thus, if tests with a 2-in column show that more than about 0.3 mg of zirconium is accompanying the hafnium in the last 50-ml aliquot of effluent, it will be desirable to increase the columnn length to 2.25 in in order to retard the elution of the zirconium a little.

STRELOW AND BOTHMA[1] have recommended the addition of a small amount of hydrogen peroxide to the eluant in the separation of hafnium and zirconium. However, it is doubtful whether this serves any useful purpose. In fact, it may be slightly detrimental to the separation since the peroxy complex of zirconium is stronger than that of hafnium and this tends to decrease the resolution of the separation. In fact, tests have shown that, in the presence of large amounts of peroxide, the zirconium will accompany or even precede the hafnium through the column.

If the amount of hafnium in a sample is very small or if it is desirable to save time in the X-ray analysis, the first 200 ml of hafnium effluent can be combined in a 600-ml beaker and treated as one sample. To do this, add 1 ml of 72% perchloric acid and boil down to a volume of 2 ml, cool, add 50 ml of water and then proceed to the cupferron precipitation. While the 200 ml of solution is evaporating, complete the elution of the hafnium with 50-ml portions of eluant in the recommended manner. In this way each sample will require at most only three disks for the X-ray analysis. In the same manner the 3 successive 50-ml aliquots of zirconium effluent can be combined and run as one sample, if desired.

If the evaporation technique is preferred, it may be more convenient to add the full 200 ml or 150 ml of eluant to the column rather than successive 50-ml aliquots. If this is done, however, it will be well to use a column which has a rather large reservoir so that the flow rate does not vary too much during elution.

In order to prevent possible errors due to failure to elute zirconium or hafnium completely from the column in preparation for a succeeding analysis, it will be best to reserve one column for the hafnium analysis and another for the zirconium analysis. It will be noted that after a determination of zirconium the column is freed of hafnium and zirconium and only needs to be equilibrated with 3% sulfuric acid for the succeeding separation.

In the anion-exchange separation, part of some of the metals, other than zirconium and hafnium, that may be present in the sample being analyzed will be eluted and discarded with the first 60 ml of effluent. Other metals may accompany the hafnium or the zirconium or both, and still others may remain on the column after the removal of the zirconium.

The cupferron precipitation method of gathering the hafnium or zirconium after the ion-exchange separation has the advantage that it isolates these metals from all but the cupferron group of metals. This should make the proposed method for hafnium applicable to the analysis of most of the common zirconium-base alloys. Of the alloying or contaminating metals usually found in such alloys, the only ones which will accompany the hafnium through the ion-exchange and cupferron separations are iron, titanium and perhaps tin, but small amounts of these metals will cause no interference in the X-ray analysis.

The ion exchange–coprecipitation–X-ray method can probably be used for the analysis of ZrO_2 or HfO_2 rather than Zr or Hf metal provided that these materials can be dissolved completely in hydrofluoric acid. Moreover, if the ratio of Zr to Hf or Hf to Zr is not over 100 to 1, certain ores or oxides containing hafnium and zirconium can probably be analyzed directly by the coprecipitation–X-ray method, without resorting to the use of the ion-exchange separation, provided of course, that correction for line interference of zirconium in the determination of hafnium is made. The use of the proposed technique rather than direct X-ray analysis has the advantage that standards can be readily prepared and that X-ray absorption effects will be much less. The direct coprecipitation–X-ray method should also be applicable to the determination of hafnium and zirconium in ferrous and nonferrous alloys after first separating the metals from the bulk of the matrix metals by suitable chemical separations. Of course, when hafnium and zirconium are present in a sample in comparable amounts, the ion-exchange separation can be included in the analysis, if desired, and the two metals can be eluted in succession and determined.

And finally, it would appear that by suitable adjustment of conditions it should be possible to prepare extremely high-purity oxides or salts of zirconium or hafnium, by means of the ion-exchange separation described. Of course, when large samples of metals or oxides are to be purified, longer ion-exchange columns will have to be used and this will introduce problems of polymerization of the metals. This in turn will probably make it necessary to repeat the ion-exchange purification.

RESULTS

A sample of zirconium metal sponge was analyzed by the method and shown to contain 0.005% of hafnium. Then 10 or 50 mg of the sample was dissolved, various aliquots of standard hafnium solution were added and the mixtures were analyzed. The results obtained, corrected for the hafnium content of the sample, are shown in Tabel I. Similar results obtained in the analysis of 50 mg portions of a sample of pure hafnium metal, which was shown to contain 0.004% of Zr, are shown in Table II.

TABLE I

DETERMINATION OF HAFNIUM IN ZIRCONIUM METAL

Zr taken (mg)	*Hf added (μg)*	*Hf found (μg)*	*Zr taken (mg)*	*Hf added (μg)*	*Hf found (μg)*
10	5.0	5.0	10	50.0	51.0
50	10.0	10.2	50	50.0	50.0
10	25.0	25.3	10	100.0	98.5
50	25.0	25.0	50	100.0	100.4
—	50.0	50.2	10	200.0	196.0
10	50.0	51.0	50	200.0	197.0

TABLE II

DETERMINATION OF ZIRCONIUM IN HAFNIUM METAL

Zr added (μg)	*Zr found (μg)*
12.5	13.0
25.0	24.3
50.0	49.5
100.0	98.0

SUMMARY

A method is proposed for the determination of traces of hafnium in zirconium metal or zirconium in hafnium metal. The trace metals are first separated from the matrix metals on an ion-exchange column and then determined by X-ray analysis.

RÉSUMÉ

Une méthode est proposée pour le dosage de traces d'hafnium dans un zirconium ou de zirconium dans un hafnium métal. Les métaux à l'état de traces sont préalablement séparés des métaux de la matrice sur une colonne échangeuse d'ions et dosés ensuite par analyse aux rayons-X.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Spuren Hafnium in Zirkonium- oder

Zirkonium in Hafniummetall vorgeschlagen. Die Spuren werden zuerst mit einem Ionenaustauscher abgetrennt und dann röntgenspektralanalytisch bestimmt.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

EMISSION INTENSITY OF CESIUM IN FLAMES OF VARIOUS GAS COMPOSITIONS

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(Received September 11th, 1967)

A requirement arose in this laboratory to determine the cesium-137 content of environmental samples. Because of the extremely low levels of this isotope usually found in such samples, radiochemical separation and purification are necessary before counting. Moreover, an accurate and precise method for the determination of the cesium recovery is necessary. This can be accomplished either by adding another cesium isotope (*i.e.*, add cesium-131 and measure this isotope separately from cesium-137) or by measuring an amount of stable cesium carrier remaining in the final product. Because of the difficulty in obtaining radiochemically pure cesium-131, it was decided that the measurement of the stable cesium carrier offered a better means of analysis. However, precipitates useful in gravimetric determinations, where the solid also suffices for low-level β-activity measurements, are usually contaminated with potassium and ammonium ions. Although gravimetric determinations of cesium could be utilized with proper precautions, it was decided that flame photometry offered a more precise, accurate, convenient, and rapid method of analysis.

Various emission properties of cesium have been studied and reported previously[1-5]. However, little detailed work has been reported on the emission properties of cesium in oxy–hydrogen flames, even though the calibration curve for cesium in a pure oxy–hydrogen flame is nonlinear at concentrations greater than 5 p.p.m. Recent investigations by ANDERSEN AND HUME[6,7], have demonstrated wide variations in the emission properties of strontium and barium in hydrogen flames of varying gas compositions between pure air–hydrogen and oxy–hydrogen. It was shown that although the temperatures of these two flames are not greatly different, there exists a critical difference in composition between the two flames at which the emission properties of the two elements are altered. These results also indicate, based on the ionization potential of the elements being considered, that the emission properties of cesium should be even more significantly altered than those of the alkaline earths studied. As a result, investigations were undertaken to ascertain the flame emission properties of cesium in flames whose compositions were intermediate between those of pure air–hydrogen and oxy–hydrogen. Experiments were made by aspirating gas mixtures with oxygen to nitrogen ratios of 4:1, 3:2, and 2:3 for comparison with air–hydrogen and oxy–hydrogen flames.

EXPERIMENTAL

Equipment and reagents

Emission measurements were made employing a Beckman DU-2 Spectrophotometer equipped with a No. 9200 flame attachment, and normal red sensitive phototube.

Cesium and rubidium solutions were prepared from spectrographically pure cesium chloride and rubidium chloride (Johnson, Matthey and Co., Ltd., London, England). Lithium solutions were prepared from a lithium nitrate flame standard solution (Fisher Scientific Co., Silver Spring, Md.). All other reagents were of analytical grade. Water redistilled through a quartz redistiller was used throughout. Oxygen and nitrogen mixtures were obtained in tanks (Matheson and Co., East Rutherford, N.J.) and were guaranteed accurate in composition to within 1% of the stated value.

Procedures

All cesium standard solutions were prepared for atomization in redistilled water. In order to obtain convenient galvanometer deflections, working solutions of 5.50, 11.00, and 16.50 p.p.m. cesium were employed. Atomization of solutions into the flames was achieved using a medium bore, atomizer burner (Beckman No. 4020). All emission intensity measurements were made with a fixed slit width of 0.10 mm, a sensitivity control setting of 3.0, and atomization rates of 2.0–2.5 ml/min. The atomizing gas was one of 5 oxygen–nitrogen mixtures containing the following oxygen percentages: (1) 20%, (2) 40%, (3) 60%, (4) 80%, and (5) 100%. The effect of the oxygen content of the atomizing gas on the emission intensity of cesium was observed both by employing optimum flow rates in a 20% oxygen–hydrogen (*i.e.*, air–hydrogen) flame and increasing the oxygen percentage of the atomizing gas, and by employing optimum flow rates for each gas mixture. Emission intensity measurements were made at the 852.1-nm cesium atomic line.

RESULTS

Figure 1 shows the effect of the oxygen concentration of the atomizing gas on the relative emission intensity of 5.50, and 11.00, and 16.51 p.p.m. cesium solutions. A pronounced maximum was observed when the oxygen content of the atomizing gas was 60%. This marked increase was more pronounced when the optimum flow rates of each gas mixture were used; the oxygen flow used was 2.5 l/min throughout and hydrogen was varied to 3.5, 3.5, 4.1, 4.8, and 4.8 l/min for oxygen compositions of the aspirating gas of 20, 40, 60, 80, and 100% respectively. At similar instrument settings, an 11.00-p.p.m. cesium solution resulted in relative emission intensities of 12.1, 25.9, and 17.2 when the oxygen content of the atomizing gas was 20, 60, and 100%, respectively. Enhancement of the cesium emission in a 60% oxy–hydrogen flame was 114% relative to the air–hydrogen flame, and 51% relative to the oxy–hydrogen flame.

Studies on the influence of selected ions in varying concentrations, on the relative emission intensity of cesium at the 11.00 p.p.m. level are summarized in Table I. Figure 2 shows the effect of the oxygen concentration in the atomizing gas on the relative emission intensity of cesium in cesium–rubidium and cesium–lithium solutions. The data indicate that the order of influence of the ions studied on cesium

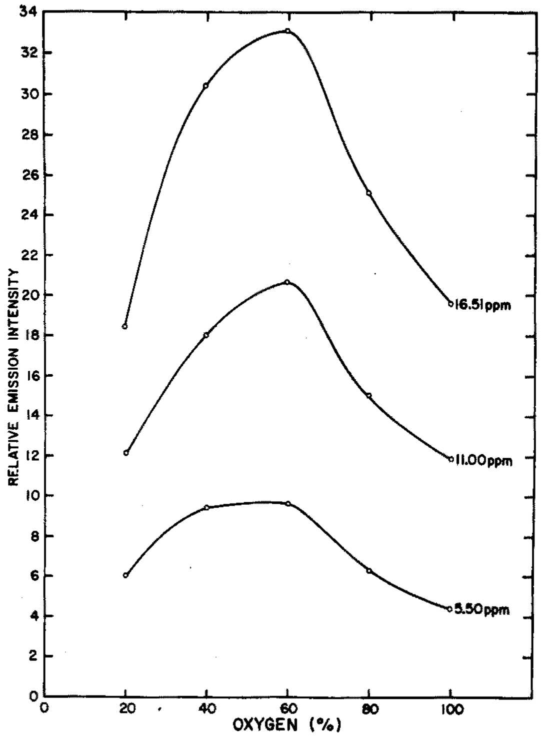

Fig. 1. Cesium emission intensity as a function of oxygen percentage in atomizing gas for various cesium concentrations. H_2, 3.5 l/min; atomizing gas, 2.5 l/min; λ = 852.1 nm.

TABLE I

CHANGE IN RELATIVE EMISSION INTENSITY OF CESIUM IN FLAMES OF VARYING OXYGEN CONTENT (λ 852.1 nm, slit width 0.10 mm, sensitivity control setting 3.0)

Ion	*Concn. (p.p.m.)*	*Cs (11.00 p.p.m.)*		
		20% oxy-hydrogen flame	*60% oxy-hydrogen flame*	*100% oxy-hydrogen flame*
Lithium	4.00	0	+1.5	+1.5
	40.00	0	+1.5	+1.5
Sodium	6.71	−0.1	+0.6	−0.2
	20.12	−0.2	+0.6	0
	33.53	−0.1	+0.6	−0.3
Potassium	5.85	0	+0.6	+2.0
	17.55	+0.4	+1.6	+5.9
	29.25	+0.3	+3.1	+8.3
Rubidium	11.28	0	+1.8	+3.6
	28.19	0	+3.5	+8.4
	56.38	0	+5.1	+11.9
Ammonium	6.30	−0.2	0	0
	15.76	0	0	+0.2
	31.52	+0.2	+0.5	+0.5

emission is $Rb^+ > K^+ > Li^+ > Na^+ > NH_4^+$, the magnitude of their respective effects being dependent on their concentration and the flame composition. Interference from these ions on the cesium emission was shown to be a minimum in the 20% oxy–hydrogen flame (*i.e.* air–hydrogen) and a maximum in the pure oxy–hydrogen flame. The relative emission intensity of an 11.00-p.p.m. cesium solution in redistilled water in the presence of 56.38 p.p.m. of rubidium was enhanced 1, 20, and 70% in the air–hydrogen, 60% oxy–hydrogen, and pure oxy–hydrogen flames, respectively.

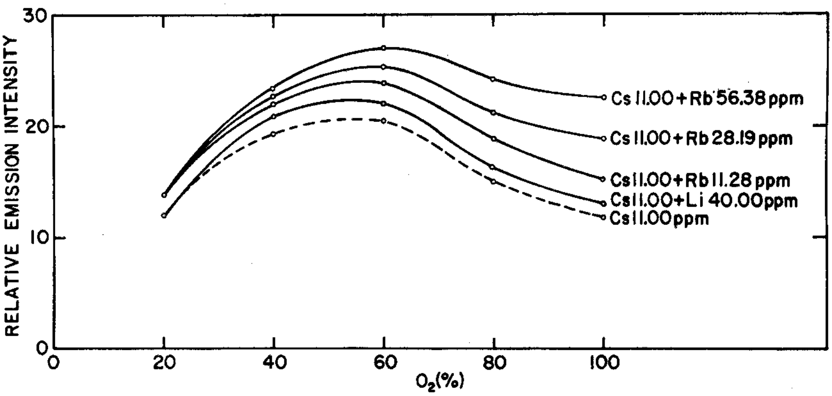

Fig. 2. Cesium emission in cesium, cesium–lithium and cesium–rubidium solutions *vs.* % oxygen in atomizing gas. Flow rates as in Fig. 1.

DISCUSSION

The present studies have indicated that the flame emission intensity of cesium changes markedly when the oxygen percentage of the carrier gas is varied between that of the air–hydrogen flame and the oxy–hydrogen flame. A maximum in emission intensity is observed when the oxygen content of the aspirating gas is 60%. This optimum flame composition not only produces a linear calibration curve in the cesium concentration range of 0–12 p.p.m., but has a slope which is 89% greater than that portion of the calibration curve which is linear (*i.e.*, 0–5 p.p.m.) in the pure oxy–hydrogen flame, and 145% greater than is obtainable in an air–hydrogen flame.

The change in relative emission intensity of cesium at its 852.1-nm atomic line in the presence of Rb^+, K^+, Li^+, Na^+, and NH_4^+ is greatest in the pure oxy–hydrogen flame and least in the 20% oxy–hydrogen flame, with the other flame compositions used causing intermediate variations. This observed effect substantiates previous considerations of ionization interference from diverse ions[8].

The maximum observed in the relative emission intensity of cesium at the 5.50, 11.00, and 16.50 p.p.m. levels (Fig. 1), possibly can be explained by considering the following equilibria:

$$Cs^0 + OH \rightleftharpoons CsOH \qquad (1)$$

$$Cs^0 \rightleftharpoons Cs^+ + e^- \qquad (2)$$

As the oxygen content of the aspirating gas is increased from 20 to 60%, equilibrium (1) is driven to the left (*i.e.*, more energy is available for causing the dissociation of CsOH), making available more cesium atoms for excitation, which results in a net increase of the atomic cesium emission. As the oxygen content of the aspirating gas is increased from 60 to 100%, equilibrium (2), the ionization of atomic cesium, overcomes the enhancing effects due to equilibrium (1) being driven to the left, with the result that the net atomic cesium emission decreases.

Existing data, as summarized in Table II, indicate that equilibria (1) and (2) would affect rubidium and lithium atomic line emission as follows. (*A*) Rubidium having a higher ionization potential and a lower heat of formation of RbOH, would be expected to have a greater dependence on the oxygen content of the aspirating gas, and a maximum relative emission intensity at a higher oxygen percentage than that of cesium. (*B*) Lithium should initially show a smaller effect on increasing oxygen content of the aspirating gas than that of cesium due to a higher value for the heat of formation of lithium hydroxide. Additionally, equilibrium (2) (*i.e.*, ionization) should have less of an effect on the relative emission intensity of lithium than is the case with cesium (or rubidium) as the oxygen content of the aspirating gas is further increased due to the higher ionization potential of lithium. The same conclusions are reached by analogy when employing the values for the percent ionization of the various elements in different flames (Table II). Figure 3, showing the effect of increasing oxygen content of the aspirating gas on the relative emission intensity of cesium, lithium and rubidium, verifies these considerations.

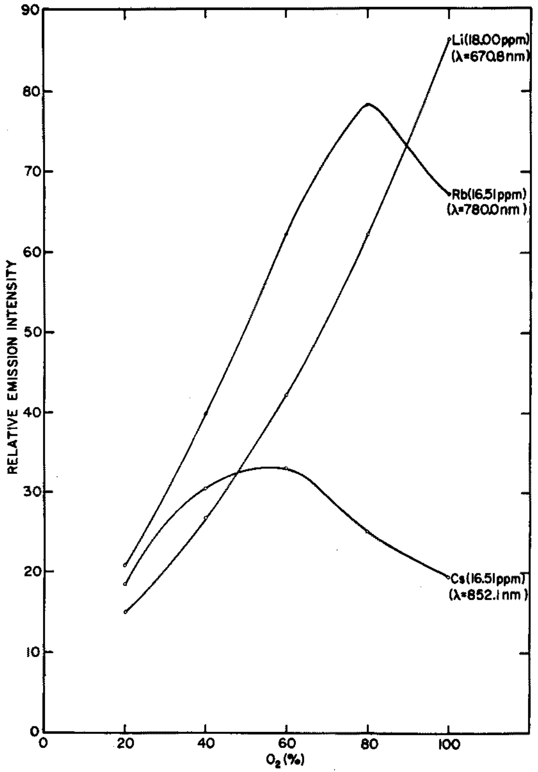

Fig. 3. Cesium, rubidium, and lithium relative emission intensity *vs.* % oxygen in atomizing gas.

TABLE II[4,9,10]

IONIZATION POTENTIAL, EXCITATION ENERGY, PERCENT IONIZATION, AND HEAT OF FORMATION OF THE ALKALI METALS

Element	*Ionization potential (eV)*	*Wavelength of the resonance line (nm)*		*Excitation energy of the resonance line (eV)*	*% Ionization air–propane (2200°K)*	*% Ionization oxy–hydrogen (2450°K)*	*% Ionization oxy–acetylene (2900°K)*	*Heat of formation of gaseous alkali hydroxides (kcal/mole)*
Li	5.390		670.8	1.84	0.01	0.9	16.1	102
Na	5.138	589.0	589.06	2.10	0.03	5.0	26.4	83
K	4.339	766.5	769.9	1.61	2.5	31.9	82.1	86
Rb	4.176	780.0	794.8	1.56	13.5	44.4	89.6	88
Cs	3.893	852.1	894.3	1.39	28.3	69.6	96.4	91

This study was supported at the Naval Oceanographic Office by the Advanced Research Projects Agency under ARPA Order No. 898; this support is gratefully acknowledged.

SUMMARY

The emission intensity of cesium at 852.1 nm has been studied in hydrogen flames burning with various mixtures of oxygen and nitrogen. A significant maximum was observed in the relative emission intensity of cesium at an oxygen to nitrogen ratio of 3:2 in the aspirating gas. The effect of Rb^+, K^+, Li^+, Na^+, and NH_4^+ ions on cesium emission is much less pronounced in this optimum flame than in a pure oxy–hydrogen flame. The optimum flame (60% oxygen) yields a significantly better calibration curve than can be obtained in either the normal air–hydrogen or oxy–hydrogen flame for 0–12 p.p.m. cesium concentrations; the graph is linear over this concentration range.

RÉSUMÉ

L'intensité d'émission du césium à 852.1 nm a été examinée dans des flammes, brûlant avec divers mélanges d'oxygène et d'azote. Un maximum important est observé dans l'intensité d'émission relative du césium pour un rapport oxygène/azote de 3:2 dans le gaz aspiré. L'influence de Rb^+, K^+, Li^+, Na^+ et NH_4^+ sur l'émission du césium est beaucoup moins prononcée dans cette flamme que dans une flamme oxy–hydrogène pure. La flamme optimum (60% oxygène) fournit une courbe de calibrage sensiblement meilleure que celle pouvant être obtenue soit avec la flamme normale air–hydrogène, soit oxyhydrogène pour des concentrations en césium de 0 à 12 p.p.m.; le graphique est linéaire pour cette zone de concentrations.

ZUSAMMENFASSUNG

Die Emissionsintensität von Cäsium bei 852.1 nm in Wasserstoffflammen mit verschiedenen Anteilen von Sauerstoff und Stickstoff wurde untersucht. Für die relative Emissionsintensität wurde ein deutliches Maximum bei einem Sauerstoff: Stickstoff-Verhältnis von 3:2 beobachtet. Der Einfluss von Rb^+, K^+, Li^+, Na^+ und NH_4^+ ist in dieser Flamme weniger deutlich als in der reinen Sauerstoff–Wasserstoff-Flamme. Man erhält auch eine bessere Eichkurve als bei der normalen Luft–Wasserstoff- oder Sauerstoff–Wasserstoff-Flamme für Cäsiumkonzentrationen von 0–12 p.p.m. Die Eichkurve ist über diesen Konzentrationsbereich linear.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SEPARATION RADIOCHIMIQUE RAPIDE DES IONS ARGENT PAR REDUCTION SUR LE MERCURE

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(Reçu le 18 décembre, 1967)

Lors du dosage de traces par spectrométrie-γ d'un radioisotope à courte période, une séparation préalable éventuelle de l'ion à doser doit être extrêmement rapide. A la recherche de telles méthodes de séparations sélectives et quasi spontanées, MEINKE *et al.*[1] ont trouvé qu'une particule activée $^*M^{v+}$ (M = métal) se sépare très rapidement d'un mélange de radioisotopes en solution aqueuse ou organique, si celle-ci est soumise à un contact intime avec l'amalgame liquide, dilué (0.01–2% en poids) du même métal M. Dans un travail récent[2], nous avons appliqué cette méthode à l'échange d'ions mercure avec le mercure même. Lors des essais de sélectivité, nous avons constaté qu'au cours de cet échange, les ions de certains métaux nobles sont entraînés dans la phase mercurique. Ce phénomène s'explique par une simple réduction de ces ions par le mercure même, suivie par leur amalgamation, conformément à l'équation générale suivante:

$$^*MX_j^{v-j} + Hg \rightleftharpoons {}^*M_a + \tfrac{1}{2}v\ Hg_2^{2+} + jX^- \tag{1}$$

(MX_j^{v-j} = ion complexé radioactif d'un métal noble et $^*M_a$ = amalgame radioactif de ce métal)

Lors d'une étude systématique[3] nous avons trouvé que seuls les ions des métaux nobles Ag, Au et Pt ont cette possibilité d'échange avec le mercure pur. Les autres métaux nobles, susceptibles d'être réduits grâce à leurs propriétés électrochimiques, restent en suspension dans la phase aqueuse, du fait de leur faible solubilité dans le mercure.

Ce type d'échange radiochimique permet la séparation et le dosage ultra-rapide de traces d'ions des métaux nobles Ag, Au et Pt d'une solution renfermant un grand nombre d'ions étrangers. Tandis que les ions de l'or et du platine s'amalgament quantitativement dans des conditions chimiques très variées, la réduction des ions argent sur le mercure n'est quantitative que dans un milieu chimique bien défini. La raison de ce comportement particulier de l'argent et les considérations qui nous ont amené à surmonter cette difficulté font l'objet de la partie théorique de ce travail.

CONSIDÉRATIONS ÉLECTROCHIMIQUES DE LA RÉDUCTION DES IONS ARGENT SUR LE MERCURE

La réduction des métaux nobles par le mercure est d'autant plus quantitative que leur potentiel électrochimique est plus élevé par rapport à celui-ci. Or, les potentiels standard d'oxydo-réduction sont les suivants:

$$\mathrm{Ag} \rightleftharpoons \mathrm{Ag^+} + \mathrm{e^-} \qquad E_0 = +0.799\ \mathrm{V} \tag{2}$$

$$2\ \mathrm{Hg} \rightleftharpoons \mathrm{Hg_2^{2+}} + 2\ \mathrm{e^-} \qquad E_0 = +0.798\ \mathrm{V} \tag{3}$$

$$\mathrm{Hg} \rightleftharpoons \mathrm{Hg^{2+}} + 2\ \mathrm{e^-} \qquad E_0 = +0.852\ \mathrm{V} \tag{4}$$

On constate tout d'abord que l'ion mercureux Hg_2^{2+} est la particule formée de préférence lors de la réduction des ions argent. La différence de potentiel $E_0 = E_{0(\mathrm{Ag})} - E_{0(\mathrm{Hg(I)})}$ étant extrêmement faible, une réduction quantitative de l'argent n'est donc pas possible dans les conditions chimiques dans lesquelles ces potentiels ont été déterminés. A l'état d'équilibre électrochimique, on observe une répartition entre les deux phases qui, pour une concentration initiale donnée, se calcule de la manière suivante:

L'équilibre est donné par l'équation de NERNST qui, pour le système ion mercureux/ion argent/amalgame d'argent devient:

$$0.058 \log \frac{(\mathrm{Hg_2^{2+}})(\mathrm{Ag_a})^2}{(\mathrm{Ag_s^+})^2} = 2\ (E_{0(\mathrm{Ag_a})} - E_{0(\mathrm{Hg(I)})}) = 2\ \Delta E_0 \tag{5}$$

(Ag_a) = concentration d'argent amalgamé dans la phase métallique, à l'équilibre.

(Ag_s^+) = concentration des ions Ag^+ dans la phase aqueuse, à l'équilibre.

$E_{0(Ag_a)}$ = potentiel standard du système ion argent/amalgame d'argent. (D'après KIRCHMAYR[4] le potentiel d'un amalgame dilué varie non seulement avec la concentration des ions M^{v+} de la phase aqueuse, mais aussi dans un sens inverse, avec celle des atomes M amalgamés. Pour cette raison, on a défini[5] un potentiel standard d'amalgame, caractérisé par l'égalité des deux concentrations volumétriques de M^{v+} et de M_a dans les deux phases.)

$E_{0(Hg(I))}$ = potentiel standard du système ion mercureux/mercure.

Or, nous définissons le rendement de l'extraction des ions argent par le pourcentage Q de la radioactivité initiale en solution ayant passé dans le mercure

$$Q = \frac{A_a}{A_0} \cdot 100\% = \left(\frac{A_0 - A_s}{A_0}\right) \cdot 100\% = \left(1 - \frac{A_s}{A_0}\right) \cdot 100\% \tag{6}$$

A_0 = radioactivité mesurée initialement dans la solution.

A_s = radioactivité restante, mesurée dans la solution après l'échange.

A_a = radioactivité du mercure après l'échange.

Le taux de radioactivité dans les deux phases étant directement proportionnel au nombre total de particules, on peut mettre

$$(\mathrm{Ag_a})/(\mathrm{Ag_s^+}) = (A_a/A_s) \cdot (V_s/V_{\mathrm{Hg}}) \tag{7}$$

(V_s et V_{Hg} étant les volumes de la solution aqueuse et de la goutte de mercure) et comme $A_a = A_0 - A_s$, il en suit (en introduisant l'éqn. (6)):

$$\frac{(\mathrm{Ag_a})}{(\mathrm{Ag_s^+})} = \left(\frac{A_0}{A_s} - 1\right) \frac{V_s}{V_{\mathrm{Hg}}} = \left(\frac{100}{100-Q} - 1\right) \frac{V_s}{V_{\mathrm{Hg}}} = \left(\frac{Q}{100-Q}\right) \frac{V_s}{V_{\mathrm{Hg}}} \tag{8}$$

D'autre part, l'échange se base sur la réaction électrochimique suivante:

$$^{*}Ag^{+} + Hg \rightleftharpoons {}^{*}Ag_{a} + \tfrac{1}{2}Hg_{2}^{2+}$$

de sorte que le bilan stoechiométrique est le suivant:

$$(Hg_{2}^{2+}) = \tfrac{1}{2}[(Ag_{0}^{+}) - (Ag_{s}^{+})] = \tfrac{1}{2}(Ag_{0}^{+})[1 - (Ag_{s}^{+})/(Ag_{0}^{+})] \qquad (9)$$

Le taux de radioactivité dans la même phase étant directement proportionnel à la concentration de l'ion argent, on peut mettre:

$$(Hg_{2}^{2+}) = \tfrac{1}{2}(Ag_{0}^{+})(1 - A_{s}/A_{0}) = \tfrac{1}{2}(Ag_{0}^{+}) \cdot Q/100 \qquad (10)$$

En introduisant les valeurs pour $(Ag_{a})/(Ag_{s}^{+})$ et pour (Hg_{2}^{2+}) (éqn. (8) et (10)) dans l'équation de NERNST[5], on obtient:

$$0.058 \log \tfrac{1}{2} \cdot \frac{Q}{100} \cdot (Ag_{0}^{+}) \cdot \frac{Q^{2}}{(100-Q)^{2}} \cdot \left(\frac{V_{s}}{V_{Hg}}\right)^{2} = 2\,\Delta E_{0} \qquad (11)$$

Cette équation permet de calculer facilement la valeur que la différence du potentiel ΔE_0 doit atteindre pour que l'extraction des ions argent par réduction au mercure devienne quantitative (quantitative dans un sens analytique, c'est-à-dire $Q \geqslant 97\%$).

A titre d'exemple, nous effectuons le calcul avec une concentration initiale en ions argent (Ag_0^+) de 5 μg/ml et un $V_s/V_{Hg} = 40$, valeurs maintenues lors des essais cinétiques dont il est question dans la partie expérimentale de ce travail. Pour une série de valeurs de Q supposées, on obtient les ΔE_0 suivants:

Q (%)	*ΔE_0 (V)*	*Q (%)*	*ΔE_0 (V)*
10	−0.125	90	+0.014
50	−0.049	95	+0.033
70	−0.024	99	+0.046
80	−0.008		

Dans le cas d'une solution acide d'ions argent de la dite concentration, le ΔE_0 est pratiquement zéro, de sorte que l'on peut s'attendre à un rendement d'extraction de 80 à 90%. Pour des concentrations plus faibles cette valeur augmente, pour des solutions plus concentrées en argent elle diminue, ΔE_0 variant avec le log de $[Ag_0^+]$. Dans notre exemple, la valeur de ΔE_0 doit être supérieure à 0.04 V pour que l'extraction soit quantitative. On l'obtient de la façon suivante: en nous basant sur les considérations générales concernant l'influence de la formation de complexes en phase aqueuse sur le comportement électrochimique d'un tel système[6], nous avons cherché un complexant susceptible d'augmenter ΔE_0 afin d'obtenir une réduction quantitative de l'ion argent par le mercure pur. Après différents essais préliminaires, nous avons choisi un milieu ammoniacal tamponné, semblable à celui qu'avaient proposé SCRIBNER ET REILLEY[7] lors de leur dosage d'argent par titration des ions mercureux formés.

La concentration du complexant en phase aqueuse est 1 *M* en NH_3 et 0.2 *M* en NH_4Cl (tampon pH 10). Avant d'effectuer le calcul du ΔE_0 dans ces conditions, remarquons que dans ce milieu:

(*a*) seul l'ion mercurique peut se former en phase aqueuse. Le calcul doit donc se baser sur le potentiel standard du couple Hg/Hg^{2+} qui se situe à +0.852 V (voir éqn. (4));

(*b*) il existe plusieurs complexes des ions Hg^{2+} et Ag^+ dont il faut connaître ceux qui prédominent dans ce milieu. A côté de NH_3, il faut en effet tenir compte de la présence des ions hydroxyles. Or, la quantité totale en Hg(II) en solution aqueuse se compose des particules suivantes:

$$(\mathrm{Hg(II)})_{\mathrm{tot}} = (\mathrm{Hg^{2+}}) + (\mathrm{HgOH^+}) + (\mathrm{Hg(OH)_2}) + (\mathrm{Hg(OH)_3^-}) + (\mathrm{Hg(NH_3)^{2+}}) + \ldots + (\mathrm{Hg(NH_3)_4^{2+}})$$

En remplaçant les diverses particules par leur valeur en fonction du ligand (OH^- et NH_3) et des constantes globales des complexes (β_1, β_2 et β_3 pour OH^- et β_1', β_2', β_3' et β_4' pour NH_3), on obtient:

$$(\mathrm{Hg(II)})_{\mathrm{tot}} = (\mathrm{Hg^{2+}})\,[1 + \beta_1(\mathrm{OH^-}) + \ldots + \beta_3(\mathrm{OH^-})^3 + \beta_1'(\mathrm{NH_3}) + \ldots + \beta_4'(\mathrm{NH_3})^4] \qquad (12)$$

De plus, en tenant compte de la constante K_a du couple NH_4^+/NH_3, la concentration en NH_3 libre est d'environ 1 *M*, celle des ions hydroxyles de 10^{-4} *M*.

En introduisant les constantes globales (valeurs de littérature) dans l'éqn. (12), on constate que les complexes dominant largement tous les autres sont en effet $Hg(NH_3)_4^{2+}$ et $Ag(NH_3)_2^+$. Nous pouvons donc négliger l'effet des ions hydroxyles sur les ions mercure et argent bien que le pH soit alcalin.

On a donc:

$$(\mathrm{Hg(NH_3)_4^{2+}})/(\mathrm{Ag(NH_3)_2^+}) \cong (\mathrm{Hg^{2+}})_{\mathrm{tot}}/(\mathrm{Ag_s^+})_{\mathrm{tot}} \qquad (13)$$

En remplaçant dans l'équation de NERNST

$$0.058 \log \{(\mathrm{Hg^{2+}})(\mathrm{Ag_a})^2/(\mathrm{Ag_s^+})^2\} = 2\Delta E_0$$

les termes (Hg^{2+}) et (Ag_s^+) par leurs valeurs tirées des constantes de stabilité

$$K_{\mathrm{Hg}} = 10^{19.3} \text{ et } K_{\mathrm{Ag}} = 10^{7.2}$$

des complexes sus-mentionnés, on obtient:

$$0.058 \log \{10^{14.4}(\mathrm{Hg(NH_3)_4^{2+}})(\mathrm{Ag_a})^2/10^{19.3}(\mathrm{Ag(NH_3)_2^+})^2\} = 2\,\Delta E_0$$

ou, avec l'éqn. (13):

$$0.058 \log \{10^{14.4}(\mathrm{Hg^{2+}})_{\mathrm{tot}}(\mathrm{Ag_a})^2/10^{19.3}(\mathrm{Ag_s^+})^2_{\mathrm{tot}}\} = 2\,\Delta E_0 \qquad (14)$$

Suivant la concentration finale en argent dans l'amalgame, la différence des potentiels standard en milieu non complexé peut être, d'après KIRCHMAYR[4]:

$$0 \leqslant E_0 \leqslant -0.053 \text{ V (voir les éqns. (2) et (4))}$$

de sorte que dans le cas le plus défavorable, c'est-à-dire lorsque l'amalgame est saturé en argent, on a à l'équilibre: $2\,\Delta E_0 = -0.106$ V.

Le facteur 0.058 log ($10^{14.4}/10^{19.3}$) de l'éqn. (14) suscite un déplacement de ΔE_0 de +0.284 V. Il en résulte:

$$\Delta E_0 = \tfrac{1}{2}(-0.106 + 0.284)\text{ V} = +0.089\text{ V},$$

suffisant pour la réduction quantitative de l'argent par le mercure.

PARTIE EXPÉRIMENTALE

Mode opératoire

Les conditions d'échange sont en principe celles des essais précédents[2]:
Extraction effectuée à l'aide de l'électrovibreur CHEMAP E 1.
Volume de la phase mercurique 300 μl (dans une ampoule de 5 ml).
Volume de la phase aqueuse 4 ml.
Température ordinaire.
Temps d'agitation variable de 10 sec à 7 min.
Chaque point de la courbe a été mesuré 3 fois.

Composition de la phase aqueuse: Série A: $5 \cdot 10^{-5}$ *M* en $^*AgNO_3$ (^{110m}Ag) et 0.2 *M* en HNO_3. Série B: $5 \cdot 10^{-5}$ *M* en $^*AgNO_3$ (^{110m}Ag), 1 *M* en NH_3 et 0.2 *M* en NH_4Cl (tampon pH 10).

Mesures spectrométriques-γ

On effectue successivement les opérations suivantes:

(*a*) Accumulation du spectre-γ de l'^{110m}Ag sur SAIP SAM 60. La solution aqueuse avant l'échange donne l'activité A_0. L'amalgame séparé de la solution et rincé après échange donne l'activité A_a.

(*b*) Sommation des impulsions des canaux représentant le pic photoélectrique à 0.657 ± 0.06 MeV.

(*c*) Comparaison directe de A_0 et A_a pour la détermination de Q. (Les pertes en activité par auto-absorption dans la phase mercurique sont négligeables.)

RÉSULTATS

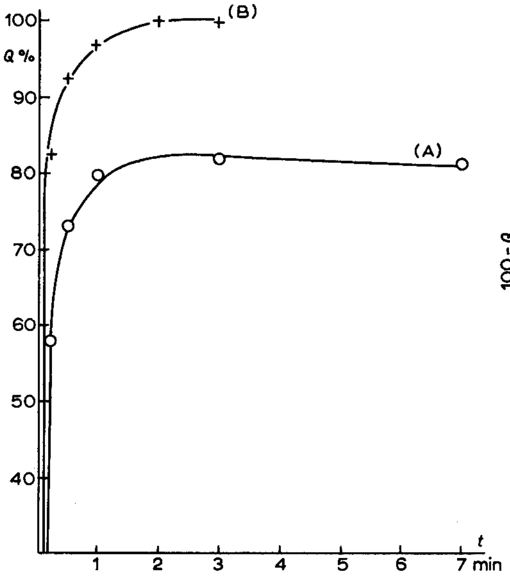
Les courbes $Q = f(t)$ obtenues lors des deux séries d'essais sont représentées Fig. 1. En milieu acide, non complexé (série A), un palier est atteint lorsque les 82% de l'argent ont été extraits, ce qui correspond à la théorie (voir p. 469). Cette valeur a tendance à diminuer lorsqu'on prolonge le temps de vibration. En milieu ammoniacal, l'échange quantitatif à 97% est atteint après 1.5 min d'extraction. Les valeurs moyennes obtenues en fonction du temps de vibration t introduites dans l'expression cinétique

$$\ln \{(100 - Q_{(t)})/100\} = -k_e t \tag{15}$$

on obtient une ligne droite bien dessinée indiquant que la cinétique de l'échange est du premier ordre (Fig. 2).

Analyse spectrométrique de l'^{110}Ag ($T = 24.2$ sec) après séparation chimique

Des deux radioisotopes de courte période de l'argent formés lors de l'activation aux neutrons thermiques (^{108}Ag, $T = 2.3$ min et ^{110}Ag, $T = 24.2$ sec), l'^{110}Ag présente un intérêt particulier par sa haute activité spécifique et le bon emplacement de son pic photoélectrique principal (0.657 MeV). C'est pourquoi nous nous sommes efforcés d'augmenter encore la vitesse de l'échange. Pour ce faire, nous avons tout d'abord étudié l'effet du volume de la goutte de mercure en maintenant le volume constant de la phase aqueuse. Lorsqu'on passe de 300 à 500 μl le temps t_a (temps minimum pour que Q soit $>97\%$) passe de 1.5 min à moins de 30 sec, sans diminuer les % d'échange à l'équilibre. Il n'y a pas avantage à augmenter encore le volume. Les ampoules soudées de 5 ml ont été remplacées par des godets cylindriques de 2 ml en plexi dans lesquels on introduit 1.5 ml de la solution à irradier. On ferme par une membrane de caoutchouc renforcé de toile, fixée par une colle spéciale séchant spontanément.



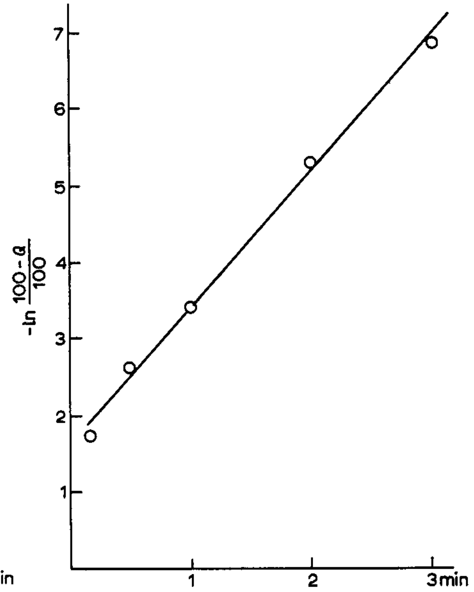


Fig. 1. Echange amalgamique du système $Hg_{mét}/{}^{*}Ag^{+}$. Influence du milieu: (A) HNO_3 0.2 *M*; (B) NH_3 1 *M* et NH_4Cl 0.2 *M*

Fig. 2. Cinétique de l'échange $Hg_{mét}/{}^{*}Ag^{+}$ en milieu ammoniacal.

L'irradiation terminée, le mercure est injecté à travers cette membrane au moyen d'une seringue, puis le tube est soumis à l'électrovibration. La membrane est alors arrachée, la phase mercurique transvasée, rincée et placée dans la sonde du spectromètre-γ.

Le temps nécessaire à toutes ces opérations est:

Ejection pneumatique de l'échantillon et injection du mercure	10 sec
Extraction	30 sec
Préparation de la goutte mercurique pour la mesure	30 sec
Temps total	70 sec

De cette façon, quand il est nécessaire de faire une séparation, l'^{110}Ag peut être mesuré après 3 périodes, ce qui fait qu'avec un flux relativement faible de 10^{10} $n \cdot sec^{-1} cm^{-2}$ et une irradiation à saturation (3 min) on arrive à doser environ 1 p.p.m. de l'argent avec une précision de ±10%.

Sélectivité

Par l'opération ci-dessus, on sépare l'argent de tous les ions métalliques dont le potentiel est inférieur à celui du mercure. D'autre part, Au, Pt et Hg passent dans le mercure avec l'argent mais ils ne s'activent pratiquement pas dans ces conditions et ne gênent donc pas la détermination radiochimique de l'argent.

Par contre, l'extraction de Ag^+ peut être gênée s'il est en présence de quantités importantes d'ions Au^{3+} et Pt^{4+}, non pour des raisons radiochimiques, mais par le fait que le mercure est ainsi rapidement saturé en ions étrangers inactifs, ce qui fait que l'argent réduit ne passe-t-il plus quantitativement dans la phase mercurique, il reste dans la phase aqueuse sous forme de suspensions noirâtres.

Lors de deux séries d'essais, nous avons constaté que le pourcentage d'échange de 1.5 ml d'une solution de $AgNO_3$ $3.5 \cdot 10^{-3}$ *M* (15 µg de Ag) baisse considérablement lorsque la solution renferme 200 µg de Pt^{4+} ou 200 µg de Au^{3+}.

D'autre part, l'échange de l'argent peut être quantitativement bloqué par adjonction d'un excès d'ions cyanure.

Nous remercions le Fonds National Suisse de la Recherche grâce auquel ce travail a pu être réalisé.

RÉSUMÉ

Il est proposé une séparation rapide de l'argent sur le mercure dans le but de doser l'argent par activation et formation d'isotopes à courte période. Dans une étude préalable, les auteurs examinent les conditions permettant une réduction quantitative de l'argent par le mercure. Les constantes des complexes amminés de Hg^{2+} et Ag^+ font qu'en présence de NH_3, l'argent est quantitativement complexé au PH 10. Le mode opératoire est décrit; l'étude cinétique montre qu'après une minute et demie, sous une vibration convenable, 97% de l'Ag^+ passent dans le mercure. L'analyse spectrométrique de l'^{110}Ag est aussi examinée. La sélectivité de l'analyse radiochimique est très grande. Seuls les métaux d'un potentiel ox/réd. plus grand que le mercure s'amalgament, mais dans les conditions d'irradiation, ils ne présentent pratiquement aucune activité.

SUMMARY

A rapid separation of silver on mercury is proposed in order to utilize short-lived isotopes for the determination of silver by activation. The conditions allowing quantitative reduction of silver were studied; a kinetic study showed that after 90 sec, 97% of silver could be transferred to the mercury. The spectrometric analysis of ^{110}Ag was also examined. Only metals with a redox potential greater than that of mercury form amalgams, and under the irradiation conditions these metals produce virtually no activity.

ZUSAMMENFASSUNG

Es wird eine Methode zur schnellen Abtrennung von Silber durch Amalgam Austausch beschrieben. Das Verfahren eignet sich für kurzlebige Silberisotope bei der Aktivierungsanalyse. Die Bedingungen, die eine quantitative Reduktion des Silbers ermöglicht, wurden untersucht. Es zeigte sich, dass nach 90 sec 97% in das Quecksilber überführt werden können. Ferner wurde die spektrometrische Analyse

des ^{110}Ag geprüft. Nur Metalle mit grösseren Redoxpotentialen als die des Quecksilbers bilden Amalgamme, ergeben jedoch unter den Bestrahlungsbedingungen keine Aktivität.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SEPARATIONS RADIOCHIMIQUES RAPIDES PAR ECHANGE SUR LE MERCURE

ÉCHANGE REDOX DE L'OR ET DU PLATINE ET DOSAGE TRÈS SÉLECTIF DE CES ÉLÉMENTS PAR ACTIVATION AUX NEUTRONS THERMIQUES

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(Reçu le 27 mai, 1967)

Dans un article précédent[1] nous avons étudié la séparation rapide d'ions argent radioactifs par réduction de ceux-ci sur le mercure métallique; elle se fait selon l'équilibre:

$$2\,\mathrm{Hg} + {}^*\mathrm{M}^{n+} \rightleftharpoons (\mathrm{Hg}){}^*\mathrm{M} + \tfrac{1}{2}n\,\mathrm{Hg_2}^{2+} \qquad (1)$$

$^*\mathrm{M}^{n+}$ = ion de charge $n+$ d'un métal noble marqué.

Dans le but de compléter la liste des métaux susceptibles d'être extraits par du mercure, nous avons étudié les phénomènes chimiques et électrocinétiques de réduction rapide et sélective de l'or trivalent et du platine tétravalent*. Ces ions formant le plus souvent des anions complexes en phase aqueuse, les réactions d'échange avec le mercure correspondent aux équations suivantes:

$$8\,\mathrm{Hg} + 2\,{}^*\mathrm{AuX_4}^- \rightarrow 2(\mathrm{Hg}){}^*\mathrm{Au} + 3\,\mathrm{Hg_2X_2} + 2\,\mathrm{X}^- \qquad (2)$$

$$5\,\mathrm{Hg} + {}^*\mathrm{PtX_6}^{2-} \rightarrow (\mathrm{Hg}){}^*\mathrm{Pt} + 2\,\mathrm{Hg_2X_2} + 2\,\mathrm{X}^- \qquad (3)$$

X^- = complexants monovalents (Cl^- par ex.)

CONDITIONS EXPÉRIMENTALES

Le milieu chimique

Les conditions chimiques d'échange sont bien différentes de celles des échanges mercure/mercure et argent/mercure. En milieu alcalin l'or(III) et le platine(IV) sont difficiles à maintenir en solution. En milieu ammoniacal notamment il se forme des précipités aminés de composition variable. L'échange se fait donc de préférence en milieu acide nitrique ou chlorhydrique dilué. Il se forme des sels mercureux insolubles qui s'adsorbent à la surface du mercure. Aussi l'extraction doit-elle être suivie d'un lavage minutieux de la goutte de mercure à l'ammoniaque, surtout si l'échantillon irradié contient des ions halogénés.

Mode opératoire

L'appareil permettant l'étude cinétique de l'échange est décrit dans un article précédent[2]. Les conditions sont les suivantes:

Volume de la phase mercurique 300 μl.

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* Etats d'oxydation ordinaires après traitement de l'échantillon renfermant de l'or ou du platine à l'eau régale.

Volume de la phase aqueuse 4 ml.

Température ordinaire.

Temps d'agitation de 10 sec à 5 min.

Composition de la phase aqueuse: (A) Au(III): $3.6 \cdot 10^{-5}$ *M* en $HAuCl_4$, renfermant de l'^{198}Au ($T_{\frac{1}{2}}=65$ h) et 0.2 *M* en l'acide nitrique. (B) Pt(IV): $3.6 \cdot 10^{-5}$ *M* en H_2PtCl_6 traité à l'acide nitrique jusqu'à disparition du chlore (Formation de ^{38}Cl, lors de l'irradiation, gênant la mesure spectrométrique du ^{199}Pt.), puis irradié pendant une heure sous un flux de $2.7 \cdot 10^{12}$ $n \cdot cm^{-2} \cdot sec^{-1}$ (formation de ^{199} Pt, $T_{\frac{1}{2}}=31$ m).

Lavage de la phase mercurique après l'échange: 2 fois à l'acide nitrique 0.2 *M*, 3 fois à l'ammoniaque 2 *M* et 2 fois à l'eau.

Mesures spectrométriques

(*A*) ^{198}*Au*. Sommation du pic photoélectrique à 0.411 MeV, accumulé sur "SAIP SAM 40". Détermination de A_0 et A_s. Le pourcentage d'extraction Q se calcule alors d'après la formule

$$Q\% = \{(A_0 - A_s)/A_0\} \cdot 100$$

A la place de $A_0 - A_s$, on peut également mesurer A_a, en tenant compte d'un facteur d'autoabsorption q dans le mercure:

$$q = A_a/(A_0 - A_s) \quad (0 < q < 1)$$

Dans le cas de l'^{198}Au, $q = 0.76 \pm 0.02$.

(*B*) ^{199}*Pt*. Accumulation de l'activité différentielle sur "Single channel Wellcounter, Philips", muni d'un cristal à puits et d'un discriminateur d'énergie à bande (bande Δ5, seuil inférieur à 2.3, correspondant à 0.51 MeV). Comparaison directe de A_a et A_0, q étant de l'ordre de 1.

A_0 = radioactivité initiale de la solution.

A_s = radioactivité de la solution après extraction.

A_a = radioactivité mesurée de l'amalgame après extraction.

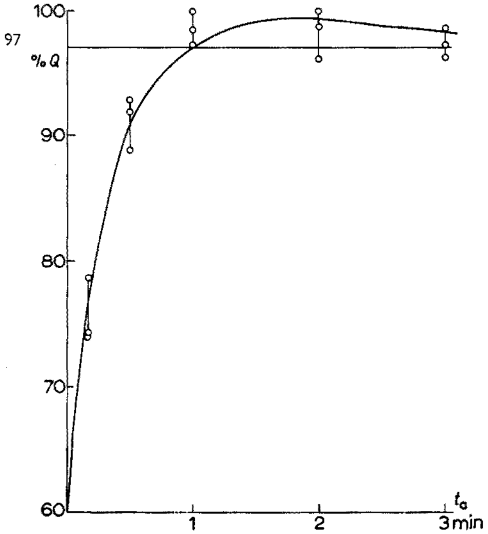
DISCUSSION DES RÉSULTATS

L'échange or/mercure

Cinétique d'échange. Les résultats obtenus lors d'une triple série d'échanges et le diagramme cinétique correspondant sont représentés dans la Fig. 1. Dans les conditions expérimentales un temps de vibration $t_a = 1$ min permet une extraction quantitative ($Q \geqslant 97\%$).

Sélectivité. La grande sensibilité de la méthode basée sur la formation de ^{198}Au et la période relativement longue de cet isotope (65 h) font que les trois autres ions métalliques (Hg, Ag et Pt) susceptibles de passer dans le mercure ne gênent pas la mesure spectrométrique même s'ils sont présents en grand excès. Par contre, de grandes quantités de ces ions étrangers sont alors réduits, s'amalgament et saturent le mercure. C'est ainsi qu'à partir d'une conc. >150 µg/ml en argent ou en platine, l'échange de l'or cesse d'être quantitatif. Ce phénomène a déjà été observé à propos de l'échange de l'argent[1]. Mais grâce à la très grande sensibilité de dosage de l'or, il est en général possible de diluer la solution afin que la saturation du mercure ne soit pas atteinte. (Ce phénomène est plus important que l'oxydation partielle du mercure. La saturation du mercure par un élément étranger fait que le métal à doser ne s'amalgame plus quantitativement.)

Limites de dosage. La limite inférieure de dosage dépend tout d'abord du temps d'activation et du flux disponible. Pour un temps d'activation de 3 h et un flux de $2 \cdot 10^{13}$ n·sec^{-1}·cm^{-2} (neutrons thermiques uniquement) on peut encore doser 0.1 ng d'or. La grande sensibilité de la méthode a permis d'étudier de façon précise la quantitativité de l'échange ox/red de l'or. L'équilibre est atteint lorsque les potentiels qui dépendent des concentrations (activités) des métaux en jeu sont égaux[3]. Une certaine concentration des ions à réduire reste donc obligatoirement en solution. Or on sait qu'en présence de mercure métallique, il y a toujours des traces d'ions mercures en solution aqueuse provenant, en partie du moins, de l'oxydation lente du mercure par l'oxygène dissous. Ces ions peuvent gêner la réduction des ions du métal plus noble si la concentration initiale de ceux-ci dans la solution est très faible. Pour confirmer ces considérations, nous avons effectué l'échange ox/red dans les conditions ordinaires, mais sur des solutions renfermant de submicroquantités d'ions or (avec traceur). Les rendements d'extraction après un temps d'agitation $t_a = 3$ min sont donnés dans le Tableau I. L'examen des résultats montre que l'extraction redox sur mercure de quantités d'or de quelques ng/ml est incomplet et peu reproductible, de sorte qu'il est indispensable d'ajouter après l'irradiation un entraîneur, en l'espèce des ions Au^{3+} inactifs, afin d'obtenir une concentration globale de l'ordre du µg/ml.



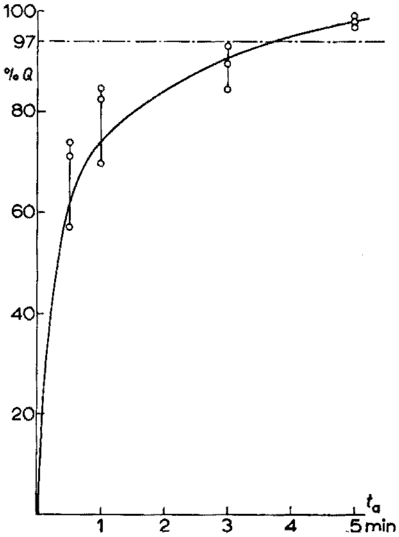


Fig. 1. Echange amalgamique du système $Hg_{mét}/Au^{3+}$. Vitesse d'échange en milieu HNO_3 0.2 *M*.

Fig. 2. Echange amalgamique du système $Hg_{mét}/Pt^{4+}$. Vitesse d'échange en milieu HNO_3 0.2 *M*.

La quantité maximum susceptible d'être extraite dans un volume défini de mercure dépend davantage de l'effet gênant de la pellicule de chlorure mercureux se formant à la surface de la goutte métallique, que de la solubilité de l'or dans le mercure (0.13% en poids). Cet effet se manifeste à partir de 100 µg/ml d'or.

L'échange platine/mercure

Cinétique d'échange. Le diagramme cinétique obtenu lors d'une triple série d'échanges pour un temps de vibration variant de 30 sec à 5 min est représenté dans la Fig. 2. L'amalgamation du platine étant plus difficile que celle de l'or ou de l'argent, l'échange est considérablement plus lent et un $Q \geqslant 97\%$ n'est obtenu qu'après 4 min de vibration.

TABLEAU I

LES RENDEMENTS D'EXTRACTION DE L'OR

Solution	$^*Au^{3+}$ *(ng/ml)*	*Q (%)*	*Remarques*
A	37.5	94.3	
	37.5	91.6	
	37.5	95.7	
B	2.0	64	
	2.0	50	
	2.0	58	
C	1550	98.0	Solution B avec
	1550	98.5	entraîneur
	1550	97.2	inactif

Sélectivité. Lors de l'échange platine/mercure, l'argent gêne lorsque le rapport en poids Ag/Pt $> 10^2$ (formation de ^{110m}Ag, $T_{\frac{1}{2}} = 270$ j) et le mercure à partir d'un rapport Hg/Pt $> 10^3$. La plus grande partie de l'argent peut être séparée après l'activation par précipitation du chlorure (avec du nitrate d'argent inactif comme entraîneur).

Dans le cas où le mercure est en très grand excès dans l'échantillon, les ions du platine et du mercure passent dans la goutte de mercure dont la mesure de l'activité donne la somme des activités des deux isotopes. On peut réextraire quantitativement le platine amalgamé en traitant la goutte de mercure par une solution aqueuse concentrée de cyanure (Fig. 3). Nous avons montré que les ions platine ne sont pas réduits par le mercure en présence de grandes concentrations d'ions cyanure, comme c'est le cas des ions de l'or.

L'or gêne déjà à quantité égale et doit être séparé préalablement par une méthode d'extraction classique.

Afin d'illustrer la haute sélectivité de l'extraction amalgamique d'un métal noble, des mélanges synthétiques renfermant, à côté de traces de platine, les principaux éléments susceptibles de gêner d'une façon ou d'une autre, ont été activés. La composition de cette solution est donnée dans le Tableau II (la quantité de chaque élément a été calculée pour une activité globale comparable à celle du ^{199}Pt présent dans la solution à $t'' = 0$). Les sels en quantités données dans la colonne 3 sont dissous dans 50 ml d'acide chlorhydrique 5 M (solution A). 50 μl (voir colonne 4) de cette solution (A) et 50 μl d'une solution renfermant uniquement 87.4 μg de Pt^{4+} (solution B) sont pipetés sur papiers filtre. Celui-ci est soigneusement séché et irradié dans un sachet de polyéthylène, pendant 60 min à $2.7 \cdot 10^{12}$ n·cm^{-2}·sec^{-1}. Les papiers filtre sont ensuite lavés par 5 ml d'acide chlorhydrique 5 M et le volume porté à 25 ml avec de l'eau bidistillée. 4 ml de cette solution sont extraits pendant 5 min avec 300 μl de mercure. La phase mercurique est lavée comme décrit sous *Mode opératoire*. Puis les spectres-γ de cette goutte d'amalgame (spectre II) et des 4 ml de la solution avant l'extraction (spectre I) sont établis à l'aide de l'analyseur multicanaux TMC 256 muni de l'enregistreur potentiométrique 2D2-XY-Recorder, SL-Moseley Co. La

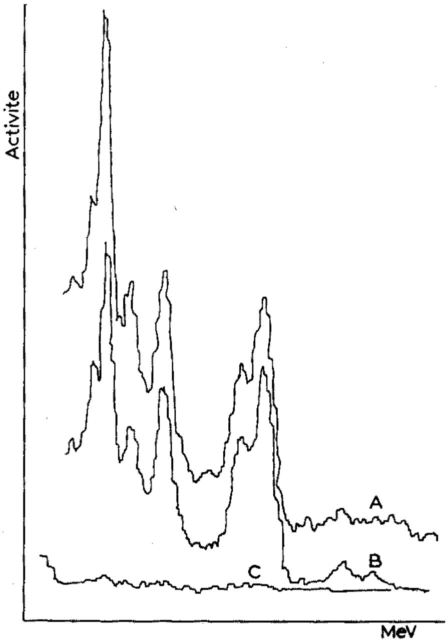


Fig. 3. Influence de l'anion sur l'échange amalgamique du système $Pt^{4+}/Hg_{mét}$. (A) Spectre-γ de la solution de H_2PtCl_6 avant l'échange. (B) A_s après extraction de la même solution. (C) A_s après extraction de la solution renfermant un excès de CN^-.

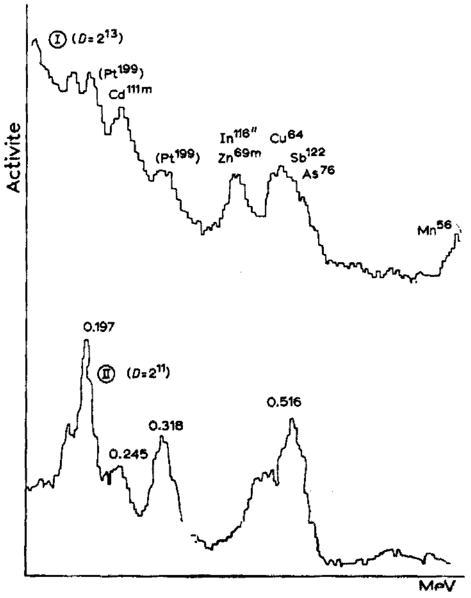


Fig. 4. Sélectivité de l'échange $Pt^{4+}/Hg_{mét}$. (I) Spectre-γ de la solution A non échangée. (II) Spectre-γ de la goutte mercurique après échange de la même solution (^{199}Pt).

TABLEAU II

LA COMPOSITION DE MÉLANGE SYNTHÉTIQUE

Radioisotope par réaction (n,γ)	*Sel utilisé*	*mg de sel pour 50 ml de solution*	*μg d'élément par 50 μl*
^{55}Mn	$MnSO_4 \cdot 4H_2O$	1.0	0.25
^{64}Cu	$Cu(NO_3)_2 \cdot 3H_2O$	27.2	7.15
^{69m}Zn	ZnO	907.6	729.0
^{76}As	As_2O_3	22.2	16.8
^{111m}Cd	$CdSO_4 \cdot 8/3H_2O$	58.4	25.6
^{116m}In	$In(NO_3)_3 \cdot 3H_2O$	0.2	0.065
^{122}Sb	$SbCl_3$	51.2	27.2
^{199}Pt	H_2PtCl_6	232.2	87.4

Fig. 4 montre la grande sélectivité de cet échange, II représentant le spectre quasi-pur du ^{199}Pt. Le niveau très élevé du spectre I (quoique développé avec une sensibilité 4 fois plus faible) est imputable à la grande quantité d'ions chlorures actifs présents dans la solution.

Limites de dosage. Nous avons effectué une série d'échanges avec des solutions de concentrations extrêmement faibles en Pt^{4+}. Si l'on admet que le dosage est encore possible lorsque l'activité mesurée A_a est plus grande ou égale au bruit de fond, *la limite inférieure* de dosage se situe autour de 5 ng/ml de platine pour un temps d'irradiation de 2 heures (95% de la saturation), un flux de $2.7 \cdot 10^{12}$ n·cm^{-2}·sec^{-1} (réacteur SAPHIR de l'EIR à Wurenlingen) et un temps de décroissance de 10 min, imposé par la séparation.

La quantité maximum susceptible d'être échangée quantitativement dans nos conditions d'échange se situe autour de 50 μg de platine par 4 ml de solution. Au-delà de cette valeur le rendement et la reproductibilité de l'échange diminuent, par suite d'une amalgamation incomplète du platine réduit.

Nous tenons à remercier vivement le Fonds National Suisse de la Recherche et l'Institut Fédéral de Recherche Nucléaire pour l'appareillage mis à notre disposition.

RÉSUMÉ

Il est proposé une méthode d'extraction très rapide des ions platine et or en solution par une goutte de mercure. On se base sur la différence des potentiels redox des divers couples en présence. Le phénomène est très rapide et quantitatif entre des limites de concentration des ions or et platine qui ont été déterminées. La sélectivité est très bonne, l'argent gêne mais cet effet peut être évité. La sensibilité est très grande dans le cas de l'analyse par activation aux neutrons, elle est de 5 ng/ml pour le platine (si le flux est $7.7 \cdot 10^{12}$ n·cm^{-2}·sec^{-1} et le temps d'irradiation de 2 h) et la sensibilité pour l'or est de même ordre de grandeur. La séparation se fait en quelques minutes.

SUMMARY

A rapid extraction method of platinum and gold ions by means of a mercury drop is proposed. This is based on the different redox potentials of the various couples present and gives a separation from most other elements. The phenomenon is rapid and quantitative between defined concentration limits. The selectivity is good; silver interferes but this can be avoided. The sensitivity is excellent; with neutron activation in a flux of $7.7 \cdot 10^{12}$ n·cm^{-2}·sec^{-1} for 2 h, the lower limit is about 5 ng/ml.

ZUSAMMENFASSUNG

Eine schnelle Extraktionsmethode für Platin- und Goldionen mit einem Quecksilbertropfen wird vorgeschlagen. Sie beruht auf den unterschiedlichen Redoxpotentialen der verschiedenen anwesenden Paare und ergibt eine Trennung von den meisten anderen Elementen. Die Methode ist schnell und quantitativ zwischen defi-

nierten Grenzen. Die Selektivität ist gut; Silber stört, jedoch kann das vermieden werden. Die Empfindlichkeit ist ausgezeichnet; sie beträgt bei Anwendung der Neutronenaktivierungsanalyse mit einem Fluss von $7.7 \cdot 10^{12}$ n cm^{-2} sec^{-1} und einer Bestrahlungszeit von 2 Stunden etwa 5 ng/ml als untere Grenze.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

DOSAGE DE L'ACIDITE LIBRE DANS LES SOLUTIONS AQUEUSES CONCENTREES DE PLUTONIUM(IV)

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(Reçu le 26 octobre, 1967)

Les cations présentent la fonction acide, conformément à la définition de BRONSTED, puisque, par suite des réactions d'hydrolyse, ils libèrent des protons. Pour tenir compte de ce fait, une terminologie courante désigne par "acidité libre" d'une solution contenant des cations et un acide fort la quantité de protons apportés par l'acide fort[1]. Dans le cas de l'ion plutonium(IV), 4 réactions successives d'hydrolyse peuvent être écrites. Cependant, la littérature[2] ne donne que les constantes caractérisant les équilibres relatifs à la neutralisation de la première fonction acide d'une part et à la neutralisation globale des 4 fonctions acides du plutonium tétravalent d'autre part:

$$Pu^{4+}, H_2O \rightleftarrows PuOH^{3+} + H^+ \qquad pK_1 \sim 1.5 \qquad (1)$$

$$Pu(OH)_4\downarrow \rightleftarrows Pu^{4+} + 4OH^- \qquad pK_S = 55.15 \qquad (2)$$

De ces valeurs, on peut déduire que Pu^{4+} consommera des ions hydroxyles bien avant que le dosage de l'acidité libre soit terminé. Cette interférence est fonction:

(*a*) du rapport des concentrations $\varrho = [Pu^{4+}]/[H^+]$. Si ce rapport est égal à l'unité, l'hydrolyse complète du cation consomme 4 fois plus d'ions hydroxyles que l'acide libre.

(*b*) de la concentration du plutonium. En effet, plus celle-ci est grande et plus il est difficile de complexer le plutonium ou de le séparer quantitativement de l'acide libre, en raison des limitations qu'imposent les propriétés physiques des produits utilisés (solubilité, capacité des résines, etc.). Une dilution préalable de la solution est cependant à proscrire pour les raisons suivantes:

(*i*) le domaine d'acidité utilisable pour le dosage diminue. En effet, si nous diluons d'un facteur 10, le pH initial augmente d'environ 1 unité. D'après l'équilibre (1), le pH de début de neutralisation du plutonium augmente d'une valeur comprise entre 0.5 et 1 unité. D'après l'équilibre (2), le pH de début de précipitation augmente de 0.25 unité seulement. Cela revient à dire qu'il y a, au moins en partie, compensation entre le gain résultant de la possibilité d'atteindre, par séparation, un facteur ϱ plus petit, et l'augmentation, pour un facteur ϱ constant, de l'interférence due au plutonium, lorsque l'on dilue.

(*ii*) la dilution favorise la dismutation du plutonium(IV), ce qui entraine une augmentation de l'acidité libre. En effet, l'équilibre de dismutation peut s'écrire:

$$3\ Pu^{4+}+2\ H_2O \rightleftharpoons PuO_2^{2+}+2\ Pu^{3+}+4\ H^+ \qquad (3)$$

avec

$$K = [Pu^{3+}]^2[PuO_2^{2+}][H^+]^4/[Pu^{4+}]^3 = [Pu^{3+}]^2[PuO_2^{2+}][H^+]/\varrho^3 \qquad (4)$$

$[H_2O]$ est pratiquement constant.

Il est évident, au vu de la relation (4), que la dilution favorise la dismutation. Celle-ci a d'ailleurs été mise en évidence par spectrophotométrie: le spectre de la solution diluée présente le pic caractéristique du plutonium(VI) à 830 nm, alors que ce pic n'apparait pas dans le spectre de la solution initiale.

Le but de cette étude est de proposer une méthode permettant de doser une acidité libre normale dans une solution molaire en plutonium ($\varrho=1$).

PRINCIPE DES MÉTHODES DE DOSAGE

De nombreuses méthodes de dosage d'acidité libre ont été décrites[3-8]. Nous pouvons les classer en 4 catégories.

(1) Dosage de l'acidité totale

La méthode consiste à doser l'acidité totale et à retrancher de celle-ci l'acidité apportée par les cations. L'acidité totale peut être obtenue par:

(i) Protométrie directe. Dans le cas du plutonium(IV), au fur et à mesure que la soude est introduite dans l'échantillon, nous observons une dismutation de plus en plus importante, ce qui, d'après l'équilibre (3), ne modifie pas l'acidité totale. Il y a aussi polymérisation (apparition d'un front vers 450 nm dans le spectre d'absorption); nous n'avons pu déterminer quelle était l'influence de ce phénomène sur le résultat. Enfin, la précipitation de l'hydroxyde engendre tous les inconvénients du dosage en milieu hétérogène: cinétique, adsorption etc.

(ii) Fixation des cations sur résine échangeur de cations mise sous forme H^+ [9]. Une quantité de protons équivalente en charge est libérée suivant le schéma:

$$n\ H_R^+ + M_S^{n+} \rightleftarrows n\ H_S^+ + M_R^{n+} \qquad (5)$$

L'acidité totale de la solution est dosée dans l'éluat. Cependant les cations alcalins, éventuellement présents, se fixent, mais non quantitativement: on ne peut connaître exactement leur participation à l'acidité mesurée. En outre, au cours du rinçage de la résine, une hydrolyse partielle peut se produire: l'hydroxyde formé enrobe les grains et s'oppose aux échanges, ce qui conduit à des résultats supérieurs à la valeur réelle.

(iii) Dosage des anions. Connaissant le nombre total des charges négatives de la solution, on obtient, par application du principe de l'électroneutralité, l'acidité totale.

Outre les sources d'erreurs déjà citées, cette méthode de dosage comporte tous les inconvénients des dosages par différence: nécessité de connaître exactement la composition de la solution (nature et degré d'oxydation des divers composants), et imprécision inhérente au calcul d'une différence entre deux valeurs très voisines l'une de l'autre.

(2) Protométrie après séparation

La méthode consiste à séparer quantitativement les cations hydrolysables sans modifier la concentration de l'acide fort, et à doser celui-ci seul. Cette séparation peut être obtenue par:

(i) Précipitation, par exemple sous forme d'iodate dans le cas des métaux lourds, et, en particulier, du plutonium[10]. Lorsque nous avons dosé l'acidité libre sur une fraction de la solution surnageante, nous avons souvent obtenu des résultats inférieurs à la valeur vraie, par suite de l'adsorption sur le précipité, notamment dans le cas où celui-ci était abondant. Si, au contraire, nous lavions le précipité, nos résultats étaient, en général, supérieurs à la valeur vraie, ce qui peut s'expliquer par la formation d'hydroxyde au sein du précipité.

(ii) Fixation des cations hydrolysables sur une résine échangeur de cations mise sous forme Na^+. On remplace alors les cations gênants par des ions sodium qui ne perturbent pas le dosage. Mais au cours du lavage, il se forme, comme dans le cas de la résine mise sous forme H^+, des hydroxydes au sein de la résine.

(iii) Fixation sur résine échangeur d'anions, sous forme de complexe anionique. Cette fixation exige, dans le cas du plutonium dont les complexes anioniques sont souvent peu stables, une telle concentration de l'anion que celle-ci ne peut être obtenue que par addition de l'acide correspondant: les sels ne sont pas suffisamment solubles ou augmentent trop la densité des solutions pour permettre le passage sur la résine. De plus, dans ce cas également, il y a hydrolyse au cours du lavage. KERGREIS[1] propose d'opérer en milieu eau–alcool afin d'éviter ces inconvénients. Néanmoins, les résultats obtenus sont encore supérieurs à la valeur réelle.

(iv) Extraction par solvant. Ce procédé exige des conditions assez strictes d'acidité que les échantillons analytiques satisfont rarement. Mais ce qui condamne le procédé c'est que, dans la plupart des cas, l'acide lui-même est extrait.

(3) Protométrie après complexation

La méthode consiste à former un complexe très stable pour retarder l'influence de l'hydrolyse. L'anion complexant doit être une base suffisamment faible pour éviter que l'excès ne consomme des protons, ou tout au moins pour permettre de doser la forme acide avant que l'hydrolyse n'intervienne.

(4) Protométrie après modification des propriétés acide–base du solvant

La méthode consiste à effectuer le dosage dans un milieu pour lequel l'échelle d'acidité se trouve étendue dans le domaine des acides forts. Dans les solutions aqueuses, cette échelle est limitée par la basicité de l'eau. L'acide Pu^{4+} est trop proche de cette limite pour que l'on puisse le distinguer de l'acide nitrique. On peut espérer, en reculant cette limite, améliorer la distinction des deux réactions: neutralisation de l'acide fort et hydrolyse du plutonium.

Cette modification des propriétés acide–base du milieu réactionnel peut être obtenue par l'utilisation de solvants ou celle de solutions très concentrées de sels dont l'anion est une base faible. En effet, dans les solutions salines concentrées, l'interaction du proton et des molécules d'eau est moins forte, ce qui a pour effet de diminuer la basicité de l'eau[11]: la limitation se rapproche alors de celle imposée par la basicité de l'anion.

L'utilisation des solutions salines concentrées présente d'autres avantages. L'augmentation de la concentration s'accompagne d'une diminution de la constante diélectrique ε du milieu[11], ce qui a pour conséquence de favoriser la formation d'associations d'ions et donc de stabiliser les composés du type $Pu^{4+}(A^-)_4$. Cela augmente aussi la stabilité de l'acide nitrique, ce qui est défavorable puisque cela revient à diminuer la force de cet acide, mais la présence des cations du sel, en très forte concentration, capables de complexer NO_3^-, diminue cet effet. Enfin, dans ces solutions, il y a moins de molécules d'eau disponibles pour entourer l'ion Pu^{4+}, ce qui le rend plus facilement complexable.

Etant donné les avantages et les inconvénients respectifs des différentes méthodes énoncées ci-dessus, nous avons choisi d'orienter plus systématiquement notre recherche vers l'utilisation des solutions salines concentrées, et la formation de complexes.

PROTOMÉTRIE EN SOLUTION SALINE CONCENTRÉE

Le choix du sel utilisé pour préparer la solution-support est guidé par les critères suivants:

(*i*) le sel doit être suffisamment soluble dans l'eau pour permettre d'atteindre des concentrations de 5 à 10 *M*, et doit exister à l'état très pur, exempt notamment de cations hydrolysables.

(*ii*) l'anion doit présenter des propriétés complexantes pour le plutonium afin d'en retarder la précipitation, et doit être le moins basique possible.

(*iii*) le cation doit avoir une grande affinité pour l'eau afin de diminuer au maximum les interactions H_2O–Pu^{4+} et H_2O–H^+. Les cations très acides sont à proscrire, puisqu'il s'agit d'un dosage d'acidité.

TABLEAU I

PROTOMÉTRIE D'UNE SOLUTION DE PLUTONIUM EN MILIEU SALIN CONCENTRÉ

Sel utilisé	*Résultats*
$CaCl_2$ 6 *M*	Précipitation de l'hydroxyde dès le début du dosage
$ZnBr_2$ 9 *M*	Cation trop acide. Domaine d'acidité trop faible: acidimétrie impossible
$LiNO_3$ 6.5 *M*	Deux points d'inflexion sur la courbe correspondant au dosage de l'acidité libre +3 acidités du plutonium et de la quatrième acidité du plutonium
LiCl 10 *M*	Même résultat qu'avec $LiNO_3$
LiSCN 10 *M*	Même résultat qu'avec $LiNO_3$
KCO_2CH_3 9 *M*	Mesures non reproductibles
KSCN 9.5 *M*	Quatre points d'inflexion correspondant à l'acidité libre +1 acidité du plutonium, puis à la 2e, à la 3e et à la 4e acidité du plutonium.

Les résultats des essais que nous avons effectués avec des sels répondant à ces critères sont rassemblés dans le Tableau I. Aucun de ces sels ne permet d'atteindre les conditions favorables au dosage direct de l'acidité libre.

PROTOMÉTRIE APRÈS COMPLEXATION

Les résultats des essais effectués en présence de complexants sont rassemblés dans le Tableau II. Dans tous les cas, l'acidité dosée est supérieure à l'acidité libre. La précipitation prématurée qui se produit dans la plupart des cas fait intervenir des

TABLEAU II

PROTOMÉTRIE D'UNE SOLUTION DE PLUTONIUM À 21 g/l, EN MILIEU COMPLEXANT

(La prise d'essai de 1 à 5 ml est versée dans 50 ml de complexant)

Complexants	*Acidité dosée*	*Observations*
NaF 0.1 *M*	> acidité libre résultats dispersés	Précipitation dès le début du dosage
$Na_2C_2O_4$ 0.3 *M*	> acidité libre résultats dispersés	Précipitation avant la variation rapide de pH
$K_2C_2O_4$ 1.8 *M*	> acidité libre résultats dispersés	
Na_2SO_4 0.2 *M*	> acidité libre	Polymérisation et précipitation avant la variation rapide de pH
$NaCO_2CH_3$ 0.2 *M*	> acidité libre	Précipitation avant la variation rapide de pH
$NaCO_2CH_2Cl$ 0.2 *M*	> acidité libre	– d° –
$NaCO_2CCl_3$ 0.2 *M*	> acidité libre	– d° –
Na_2HX saturé (sel de l'acide nitrilotriacétique ou complexon I)	Acidité libre + 2 fonctions acides du plutonium	

phénomènes cinétiques qui ont pour conséquence d'augmenter considérablement la dispersion des résultats.

Le plutonium, très complexé par les ions hydroxyles, l'est aussi par les complexants chélatants (dans les 2 cas, il s'agit de liaisons oxygène). Trois complexants de ce type maintiennent le plutonium tétravalent en solution jusqu'à pH 11. Nous les avons expérimentés en maintenant, dans tous les cas, le rapport complexant/Pu supérieur à 10. Il s'agit de:

(1) L'acide citrique utilisé par PFLUG ET MINER[12] comme complexant pour le dosage de l'acidité libre en présence de plutonium. Ce composé possède 3 fonctions acides ($pK_A = 3.1–4.8–6.4$). La variation de pH correspondant à la fin du dosage de la troisième acidité est suffisante pour que la détermination du point équivalent soit aisée. En fait, la courbe de titrage, en présence de plutonium, présente 2 points d'inflexion pour des valeurs de pH supérieures à 7: le premier correspond au dosage d'environ 2 fonctions acides du plutonium en plus de l'acidité libre, le deuxième à celui d'une troisième fonction acide. Un écart à la valeur vraie de l'acidité libre avait d'ailleurs été observé par les auteurs. Cet écart pourrait s'expliquer par la formation de complexes mixtes de la forme (Cit) $Pu(OH)_n{}^{1-n}$ d'autant plus probable que le pH de fin de titrage est élevé (voisin de 9).

(2) L'acide tartrique. Ce composé présente, dans l'eau, 2 fonctions acides ($pK_A = 2.5–4.2$). Le tartrate acide de potassium est très peu soluble et précipite au cours du titrage, raison pour laquelle PFLUG ET MINER ont abandonné ce complexant. Cette précipitation, cependant, n'est pas gênante car la redissolution est complète avant la variation rapide du pH avec le volume de titrant versé.

En revanche, nous avons pu faire les observations suivantes: même si nous maintenons constant le rapport tartrate–plutonium, une augmentation de la quantité de plutonium dans la prise d'essai se traduit par: une diminution de la pente de la courbe de titrage au voisinage du point d'inflexion, des mesures moins reproductibles, et un écart à la valeur vraie de l'acidité libre qui augmente et peut atteindre une valeur correspondant à 2 fonctions acides du plutonium.

(3) L'acide éthylènediaminetétracétique ($pK_A = 2.0\text{–}2.7\text{–}6.2\text{–}10.3$). Le complexe étant formé d'un atome de plutonium pour une molécule d'EDTA, le titrage devrait être effectué (dans la mesure où il s'agit du complexe le plus simple PuY et non d'un complexe mixte PuH_nY^{n+}), en présence de la forme totalement dissociée du complexant, Y^{4-} (pH env. 11), pour éviter que la formation du complexe ne libère des protons. Le point équivalent correspondrait alors au quatrième point d'inflexion de la courbe de neutralisation de l'EDTA. L'acidité que nous obtenons, en utilisant ce mode opératoire, est supérieure à l'acidité libre. Ce fait expérimental peut trouver son explication dans la formation de complexes du type $PuY(OH)_n^{n-}$, que nous n'avons pas mis en évidence. Aucun des autres points d'inflexion, quel que soit le pH initial de la solution d'EDTA, ne correspond à la neutralisation de l'acidité libre. De plus, la présence de plutonium déforme la courbe de titrage de l'EDTA au niveau du domaine d'existence de H_2Y^{2-}: le titrage ne serait donc possible que s'il existait des complexes du type PuH_nY^{n+} où n serait au moins égal à 2, ce qui est peu probable.

L'inconvénient majeur de ces complexants est la multiplicité de leurs fonctions acides faibles ou très faibles qui rend les courbes difficiles à interpréter. C'est pourquoi il nous a paru intéressant de chercher à mettre l'un d'eux sous la forme d'un complexe qui soit un acide relativement fort, dont la neutralisation soit simple (une seule acidité). Ce résultat peut être obtenu dans le cas de l'EDTA par addition d'ions calcium. En effet, il se forme alors un complexe 1:1 assez stable ($pK = 10.6$) qui peut exister sous les formes $CaHY^-$ et CaY^{2-}. L'acidité de ce complexe est relativement forte ($pK_A = 3.1$). Pour que le dosage soit possible en présence de ce composé, il faut que le plutonium forme avec l'EDTA un complexe encore plus stable, ce qui est le cas, puisque les auteurs donnent pour l'équilibre:

$$Pu^{4+} + Y^{4-} \rightleftarrows PuY \tag{6}$$

des valeurs qui varient de 17.7[13] à 25.1[14].

Considérons les échanges qui vont se produire si nous versons la prise d'essai dans une solution de sel monocalcique de l'EDTA préalablement neutralisée jusqu'à une valeur de pH comprise entre 7 et 8 (seule existe alors la forme CaY^{2-}). Au départ, nous sommes en présence des ions:

Pu^{4+}, $Pu(OH)_n^{4-n}$ et H^+ d'une part

CaY^{2-} d'autre part.

L'échange global de particules peut être schématisé de la manière suivante:

$$Pu^{4+} + CaY^{2-} \rightarrow PuY + Ca^{2+} \tag{7}$$

$$n\,H^+ + Pu(OH)_n^{4-n} + CaY^{2-} \rightarrow PuY + Ca^{2+} + n\,H_2O \tag{8}$$

$$H^+ + CaY^{2-} \rightarrow CaHY^- \tag{9}$$

La formation du complexe à partir de l'ion Pu^{4+} (réaction (7)) ne fait intervenir aucun proton. Celle qui s'effectue à partir de l'ion $Pu(OH)_n^{4-n}$ (dont la quantité dépend du rapport ϱ[1]) consomme exactement la quantité de protons apportée par le plutonium, donc qui ne fait pas partie de l'acidité libre. Seuls restent alors en solution, soit sous forme H^+, soit sous la forme complexée $CaHY^-$, les protons apportés par l'acide fort.

Les réactions mises en jeu au cours du titrage sont les suivantes:

$$H^+ + OH^- \rightarrow H_2O \quad (10)$$

$$CaHY^- + OH^- \rightarrow CaY^{2-} + H_2O \quad (11)$$

la réaction (10) ne se produisant que s'il y a un excès de protons par rapport aux ions CaY^{2-} disponibles. Il faut alors pouvoir neutraliser l'acide faible $CaHY^-$ avant que les ions hydroxyles modifient la forme du complexe PuY. La déformation de la courbe expérimentale obtenue laisse supposer que cette modification n'intervient que vers pH 5.5, ce qui permet le dosage, moyennant une construction graphique du point équivalent.

PARTIE EXPÉRIMENTALE

Appareillage utilisé

Ensemble potentiométrique Tacussel "Autotitrigraphe III" utilisé en pH mètre. Le déroulement du papier d'enregistrement et le piston de la burette sont couplés mécaniquement. Leur vitesse est inversement proportionnelle à la dérivée du signal enregistré, ce qui provoque un ralentissement maximal de l'injection du réactif au voisinage du point d'inflexion (point équivalent dans le cas des courbes logarithmiques).

Réactifs

Solution complexante. Sel monocalcique de l'acide éthylènediaminetétracétique (EDTA): dissoudre 27 g de chlorure de calcium dans 500 ml d'eau (solution A). Faire une suspension de 55 g de sel disodique d'EDTA dans 500 ml d'eau (solution B). Verser en agitant la solution B dans la solution A. Neutraliser jusqu'à un pH compris entre 7 et 8 avec de la soude 5 *N* ajoutée goutte à goutte. La solution doit alors être limpide. Le chlorure de calcium et le sel disodique d'EDTA sont choisis très purs afin d'éviter la présence, dans le milieu réactionnel, de cations hydrolysables qui déformeraient la courbe, rendant difficile la détermination du point équivalent, et interviendraient comme un "blanc" dont il faudrait corriger le résultat.

Solutions de plutonium. Deux solutions de nitrate de plutonium ont servi à la mise au point de la méthode: Solution I, titrant 21.3 g/l (0.089 *M*) en plutonium contenant moins de 1% d'impuretés, et 0.93 *N* en acidité libre ($\varrho = 0.09$).

Solution II, titrant 168.5 g/l (0.705 *M*) en plutonium, 1.56 g/l (0.03 *M*) en fer et 1.98 *N* en acidité libre ($\varrho = 0.35$).

Nous verrons plus loin comment nous avons pu déterminer les titres en acidité libre.

Mode opératoire

Faire une prise d'essai contenant moins de 200 mg de plutonium. Dans le cas des solutions très concentrées en plutonium, en raison de la viscosité et du petit volume de la prise, il est nécessaire d'opérer par pesée. Ajouter 40 ml de solution complexante. Immerger les deux électrodes de mesure et maintenir une agitation constante. Choisir la gamme d'enregistrement qui permet l'étalement maximal de l'échelle de pH entre les valeurs 3 et 7. Titrer par une solution de soude normale.

Détermination du point équivalent. Utiliser la méthode de linéarisation proposée par KERGREIS[1,15], la première partie de la courbe étant monologarithmique (Fig. 1). Déterminer sur cette partie de courbe, précédant le point d'inflexion, des points P_1, P_2, P_3... dont les ordonnées sont équidistantes de ΔpH (ΔpH est choisi de façon à disposer d'au moins 4 à 5 points); ils ont pour abscisse x_1, x_2, x_3... Porter, sur l'axe Ox des volumes de soude ajoutée, les points P_1', P_2', P_3'... de même abscisse x_1, x_2, x_3... A partir de P_1', porter sur P_1P_1' un segment égal à $x_2–x_1$; à partir de P_2', porter sur P_2P_2' un segment égal à $x_3–x_2$ etc. Joindre les points P_1'', P_2'', P_3''... obtenus; ils sont alignés sur une droite qui coupe l'axe Ox en un point dont l'abscisse est celle du point équivalent.

Recommencer en choisissant 3 autres valeurs de ΔpH et faire la moyenne des valeurs ainsi obtenues.

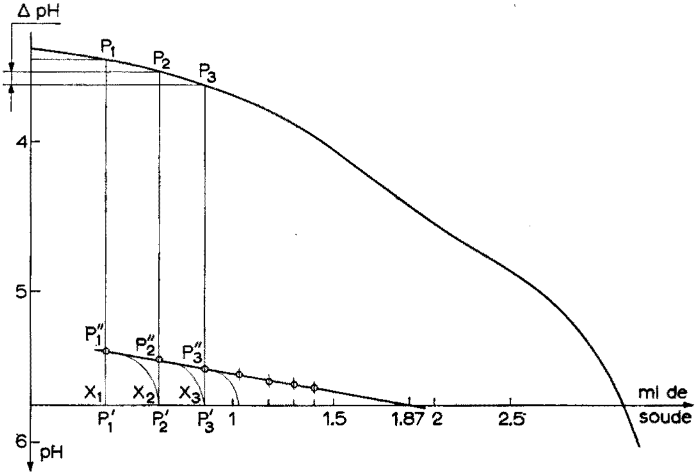

Fig. 1. Courbe de titrage de l'acidité libre d'une solution aqueuse concentrée en plutonium. Détermination du point équivalent par linéarisation.

DISCUSSION

Exactitude de la méthode

Comme il est très difficile de préparer des solutions concentrées de plutonium, ayant une acidité libre bien déterminée, nous avons dû tourner la difficulté de la manière suivante. De façon à rendre plus sensible l'interférence possible du plutonium, nous nous sommes proposés de faire croître le rapport ϱ en maintenant sensiblement constante l'acidité libre.

Sachant, par un dosage de l'acidité totale, que la solution I était voisine de la normalité en acide libre, nous avons effectué les essais suivants: nous ajustons avec de l'acide chlorhydrique 1.000 *N* le niveau de 4 fioles jaugées de 25 ml contenant respectivement 5, 10, 14 et 20 ml de la solution I. Nous faisons sur chaque solution obtenue deux prises d'essai de 10 ml.

Pour une solution donnée, nous appelons y le titre correspondant à l'acidité dosée, x l'acidité libre de la solution I et α la fraction hydrolysée du plutonium qui peut prendre la valeur 0 (Pu^{4+}); 0.25 ($PuOH^{3+}$); 0.50 ($Pu(OH)_2{}^{2+}$); 0.75 ($Pu(OH)_3{}^{+}$) ou 1 ($Pu(OH)_4$) au point équivalent, puisque, par définition, celui-ci correspond à la fin du dosage d'une espèce bien déterminée. Les variables x, y et α sont liées par la relation:

$$y = {}^{1}/_{25}\,[nx + (25-n)\,1.000 + 4n\alpha\,[\mathrm{Pu(IV)}]] \qquad (12)$$

où n représente le nombre de millilitres de la solution I contenus dans la fiole de 25 ml et [Pu(IV)] la concentration totale en plutonium(IV) de la solution I.

Pour que le titrage soit exact, il faut que l'on puisse déterminer un point équivalent satisfaisant aux deux conditions suivantes:

(*a*) Si nous donnons plusieurs valeurs à n (c'est-à-dire si nous faisons varier le rapport ϱ), nous devons obtenir, en ce point, un système d'équations proportionnelles. S'il en est ainsi, cela signifie que α est une constante, donc que l'on dose une espèce bien définie.

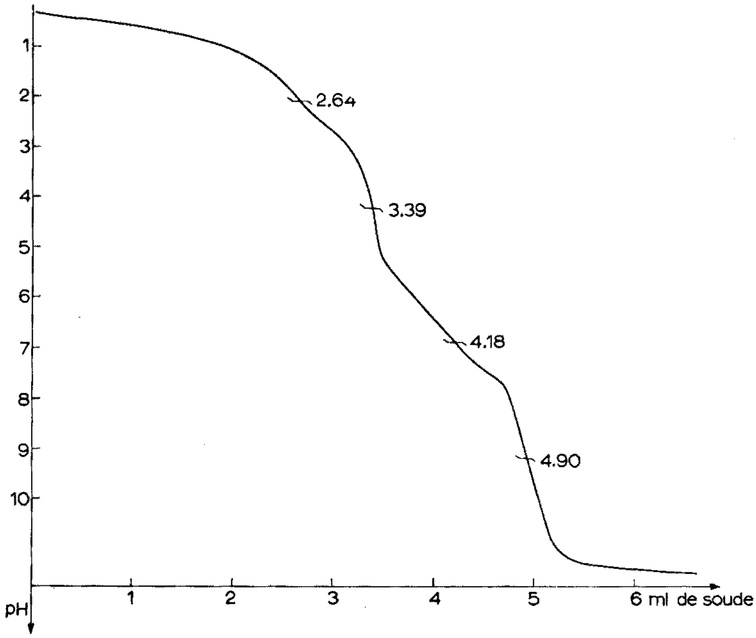

Fig. 2. Titrage de l'acidité d'une solution à 168.5 g/l en plutonium et 1.56 g/l en fer en solution KSCN 9.5 *M*.

(*b*) α doit avoir la valeur zéro pour que, seule, l'acidité libre soit dosée.

Ce test a été appliqué à la méthode de dosage, étudiée plus haut, en milieu thiocyanate saturé, parce que les courbes obtenues dans ce milieu présentent 4 points d'inflexion (Fig. 2): ces points sont d'autant mieux définis que la quantité de plutonium dans la prise est plus importante. En chacun des points d'inflexion, la condition relative aux équations proportionnelles est satisfaite. Comme, par ailleurs, le plutonium est totalement précipité au dernier point d'inflexion, nous faisons l'hypothèse qu'il s'agit de $Pu(OH)_4$, ce qui revient à attribuer la valeur 1 à α en ce point. Ceci nous conduit à prendre comme valeurs de α 0.25, 0.50 et 0.75 respectivement pour chacun des 3 premiers points d'inflexion. On peut donc calculer l'acidité libre; les résultats obtenus dans cette série d'essais sont consignés dans le Tableau III.

Les solutions I et II ont été titrées directement en milieu thiocyanate saturé. Les résultats sont rassemblés dans les Tableaux IV et V. La solution II contenant du fer(III), nous nous sommes assurés par ailleurs que les 3 fonctions acides de ce cation étaient dosées en même temps que la troisième fonction acide du plutonium.

TABLEAU III

TITRAGE DE L'ACIDITÉ D'UNE SOLUTION À 21.3 g/l EN PLUTONIUM EN MILIEU KSCN 9.5 *M*

(Les dosages sont effectués sur 10 ml d'une solution préparée à partir de *n* ml de la solution de plutonium et (25−*n*) ml d'HCl 1.000 *N*)

n(ml)	*Acidité libre (N) calculée à partir du*		
	1er point d'inflexion	*2è point d'inflexion*	*4è point d'inflexion*[a]
5	0.95	0.95	0.93
10	0.94	0.94	0.93
14	0.98	0.93	0.92
20	0.96	0.93	0.93

[a] Le 3ème point d'inflexion est mal défini.

TABLEAU IV

TITRAGE DE L'ACIDITÉ D'UNE SOLUTION À 21.3 g/l EN PLUTONIUM (SOLUTION I) EN MILIEU KSCN 9.5 *M*

Lecture	*Acidité lue (N)*	*Acidité libre calculée (N)*
1er point équivalent	1.02	0.93
2è point équivalent	1.12	0.94
3è point équivalent	Illisible	
4è point équivalent	1.28	0.92

TABLEAU V

TITRAGE DE L'ACIDITÉ D'UNE SOLUTION À 168.5 g/l EN PLUTONIUM ET 1.56 g/l EN FER (SOLUTION II), EN MILIEU KSCN 9.5 *M*

Lecture	*Acidité lue (N)*	*Acidité libre calculée (N)*
1er point équivalent	2.64	1.94
2è point équivalent	3.39	1.98
3è point équivalent[a]	4.18	1.99
4è point équivalent	4.90	2.00

[a] Ce point correspond au dosage des 3 fonctions acides du fer en même temps que de la troisième fonction acide du plutonium.

Le test "α" a été appliqué, par la suite, à la méthode proposée pour le dosage direct de l'acidité libre (complexation par le sel monocalcique de l'EDTA). Les équations obtenues pour le point équivalent, déterminé par "linéarisation" de la courbe, sont proportionnelles, et, en prenant $\alpha = 0$, nous retrouvons $x = 0.93$ *N* comme valeur de l'acidité libre de la solution I. Celle de la solution II est trouvée égale à 1.98 *N*, ce qui est en bon accord avec la valeur déterminée ci-dessus.

TABLEAU VI

TITRAGE DE L'ACIDITÉ LIBRE D'UNE SOLUTION À 21.3 g/l EN PLUTONIUM (SOLUTION 1)

(Le titre trouvé est la moyenne de 6 déterminations)

Prise d'essai (ml)	*Titre trouvé (N)*	*σ (%)*
2.998	0.939 ± 0.012	1.2
3.988	0.933 ± 0.005	0.5
4.989	0.937 ± 0.011	1.0

TABLEAU VII

TITRAGE DE L'ACIDITÉ LIBRE D'UNE SOLUTION À 168.5 g/l EN PLUTONIUM

(Les prises d'essai sont faites par pesée, la densité de la solution étant déterminée par ailleurs)

Prise d'essai (ml)	*Titre trouvé (N)*	*Titre moyen (N)*	*σ (%)*
0.960	1.983	(1.984 ± 0.017)	0.7
0.968	1.987		
0.947	1.975		
0.881	1.990		
0.962	1.986		

Reproductibilité de la méthode

Les Tableaux VI et VII rassemblent les résultats obtenus au cours des essais de reproductibilité. Chaque résultat individuel a été obtenu en effectuant 3 à 4 "linéarisations" de la même courbe, la plus importante source d'erreur provenant de cette construction.

OBSERVATIONS SUR LA MÉTHODE

Eléments interférents

L'influence de 2 éléments souvent présents dans les solutions de plutonium a été examinée. Le fer(III) ne gêne pas lorsque sa concentration atteint quelques grammes par litre. L'uranium(VI) gêne s'il est présent en quantité supérieure à 10 mg dans la prise d'essai.

Remarques

Il est nécessaire de respecter les quantités relatives de complexant et de plutonium. En effet, des essais effectués sur des prises de 340 mg de plutonium en présence de 40 ml de solution complexante ont fait apparaître une erreur positive systématique. En présence de 80 ml de solution complexante, cette erreur disparaît.

En raison de ce rapport Pu–complexant à respecter et de la limitation souhaitée de la consommation de plutonium par le laboratoire d'analyse, la prise d'essai sera d'autant plus petite que la concentration en plutonium sera plus élevée, ce qui risque de rendre non négligeable l'influence de l'évaporation de l'acide, après la prise d'échantillons.

Le domaine d'application de la méthode est limité vers les faibles acidités par l'impossibilité d'atteindre, même en augmentant le volume de la prise d'essai, des valeurs de pH suffisamment petites (pH <4) pour permettre la linéarisation. Si l'acidité libre est importante, le début de la courbe peut être perturbé par l'existence d'autres formes acides que $CaHY^-$. Seule la portion de courbe monologarithmique ($3.5 < pH < 5$) doit être linéarisée.

Enfin, l'examen de la courbe de titrage montre qu'il est nécessaire de la "linéariser" puisqu'elle s'incurve dès pH 5, indiquant qu'une autre espèce commence à être dosée. Cette déformation peut être expliquée par l'existence de complexes $PuY(OH)_n^{n-}$ et $Pu_2Y(OH)_n^{4-n}$ déjà invoquée par FOREMAN ET SMITH[13].

Le calcul de la valeur de la constante du complexe Pu(IV)–Y pour différentes valeurs du pH indique qu'il faut admettre l'hypothèse de la formation de tels complexes afin d'expliquer le maintien en solution du plutonium(IV) à des pH supérieurs à 6. Les derniers points d'inflexion de la courbe ne sont pas assez bien définis pour permettre de déterminer précisément le nombre d'hydroxyles fixés par un atome de plutonium: il semble cependant qu'il y en ait d'abord deux, puis un troisième.

Nous tenons à remercier ici Monsieur F. REGNAUD, Chef de la Section de Chimie Analytique du Plutonium et d'Electroanalyse, sous la direction duquel nous avons effectué ce travail; Monsieur R. MOLINA pour les nombreux conseils qu'il nous a donnés et les critiques qu'il nous a faites; Monsieur M. LUCAS pour les discussions que nous avons eues avec lui au sujet des solutions salines concentrées.

RÉSUMÉ

Une méthode de dosage de l'acidité libre dans les solutions aqueuses concentrées de plutonium est proposée. La neutralisation par la soude est suivie par potentiométrie, après complexation du plutonium par le sel monocalcique de l'acide éthylènediaminetétracétique. Le point équivalent est déterminé en utilisant un procédé graphique de linéarisation. La méthode présente un écart-type relatif de 1%. L'uranium et le fer, en petites quantités, ne gênent pas. La méthode est applicable à des solutions dont l'acidité est au moins voisine de la normalité et dont la concentration en plutonium peut atteindre 200 g/l.

SUMMARY

A method for the determination of free acidity in concentrated aqueous solutions of plutonium(IV) is described. The plutonium–EDTA complex is formed by addition of the calcium–EDTA complex and the neutralization titration with sodium hydroxide is followed potentiometrically, the equivalence point being determined by a graphical method. The relative standard deviation is 1%. Uranium and iron in small amounts do not interfere. The method is applicable to solutions which are *ca.* 1 *N* in acid and which contain up to 200 g Pu/l.

ZUSAMMENFASSUNG

Eine Methode zur Bestimmung der freien Säure in konzentrierten wässrigen Lösungen von Plutonium(IV) wird beschrieben. Der Plutonium–EDTA-Komplex wird durch Zugabe des Calcium–EDTA-Komplexes gebildet und anschliessend wird die Säure mit Natriumhydroxid potentiometrisch titriert. Die relative Standardabweichung beträgt 1%. Uran und Eisen in kleinen Mengen stören nicht. Die Methode eignet sich für etwa 1 *N* Säuren, die bis zu 200 g Pu/l enthalten.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

PHOTOMETRISCHE BESTIMMUNG ALIPHATISCHER AZO- UND HYDRAZO-VERBINDUNGEN

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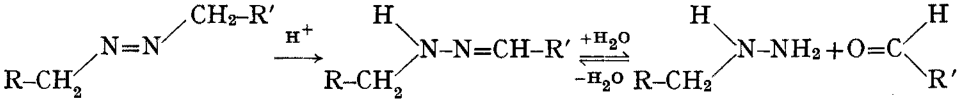
(Eingegangen den 23. Dezember, 1967)

Der Nachweis einer oft stark carcinogenen, mutagenen und teratogenen Wirkung gewisser aliphatischer Hydrazo-[1], Azo-[2] und Azoxy-[2,3] Verbindungen an Versuchstieren macht empfindliche und möglichst spezifische qualitative und quantitative Nachweismethoden für diese Verbindungsklassen erforderlich, insbesondere, da solche Verbindungen auch in der menschlichen Umwelt vorkommen können[3]. Analytische Methoden sind weiterhin notwendig zur Untersuchung des Stoffwechsels dieser Substanzen, die wahrscheinlich nicht als solche wirken, sondern *in vivo* in die eigentlich wirksamen Metaboliten umgewandelt werden[2]. Weiterhin ist eine Reinheitskontrolle synthetischer Substanzen erwünscht, da die Herstellungsmethoden über mehrere Stufen führen und deshalb u.U. Verunreinigungen bzw. Isomere auftreten, die die Ergebnisse biologischer Versuche verfälschen können.

Quantitative Methoden zur Bestimmung von Azoalkanen liegen unseres Wissens bisher nicht vor. Für Alkylhydrazine sind einige neuere titrimetrische[4] und komplexometrische[5] Bestimmungsmethoden bekannt, die auf dem Reduktionsvermögen dieser Stoffe beruhen und daher relativ unspezifisch sind. Eine photometrische Methode zur Bestimmung von Hydrazo-Verbindungen beschreiben SHINE *et al.*[6]. Neuere Arbeiten befassen sich mit der gaschromatographischen Charakterisierung und Bestimmung von Hydrazin-Derivaten[7].

Im folgenden soll eine einfache colorimetrische Bestimmungsmethode für Azoalkane und 1,2-disubstituierte Hydrazine (Hydrazo-Alkane) beschrieben werden. Sie beruht auf der bekannten[8], Säure-katalysierten Umlagerung aliphatischer Azo-Verbindungen (I) zu den entsprechenden Hydrazonen (II). Diese können in saurem Medium hydrolysiert werden, wie im folgenden Reaktionsschema dargestellt:



$$R\text{-}CH_2\text{-}N{=}N\text{-}CH_2\text{-}R' \xrightarrow{H^+} R\text{-}CH_2\text{-}N(H)\text{-}N{=}CH\text{-}R' \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} R\text{-}CH_2\text{-}N(H)\text{-}NH_2 + O{=}C(H)R'$$

(I) (II) (III) (IV)

Die abgespaltene Oxo-Verbindung (IV) wird durch Destillation aus dem Gleichgewicht entfernt und mit Hilfe photometrischer Methoden quantitativ erfasst.

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1,2-Dialkylhydrazine können mit Quecksilber(II)-Sulfat in schwefelsaurem Medium zur Azoverbindung oxydiert werden und lassen sich dann analog bestimmen.

EXPERIMENTELLER TEIL

Die in den Tabellen I und II aufgeführten Azoalkane und 1,2-Dialkylhydrazine wurden, mit Ausnahme des Natulans*, im eigenen Laboratorium nach bekannten Methoden[9] synthetisiert. Die Reinigung erfolgte bei den Azo-Verbindungen durch mehrmalige Destillation und im Falle der 1,2-Dialkylhydrazine durch Umkristallisation der Di- bzw. Mono-Hydrochloride. Die physikalisch-chemischen Daten entsprachen den Literatur-Werten oder wurden durch Elementaranalyse gesichert.

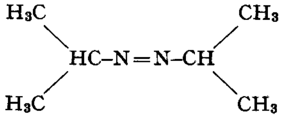
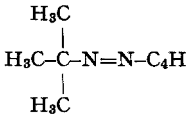
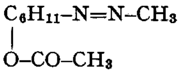
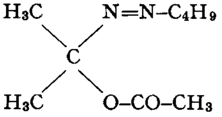
Die verwendeten Reagentien besassen sämtlich Analysen-Qualität.

Zur Messung der Azo–Hydrazon-Umlagerung wurde das automatisch registrierende Spektralphotometer "Bausch und Lomb Spectronic 500" verwandt. Die photometrischen Messungen bei angegebener Wellenlänge erfolgten mit dem "Beck-

TABELLE I

BILDUNG VON OXOVERBINDUNGEN AUS AZOALKANEN NACH SÄURE-KATALYSIERTER UMLAGERUNG

(Ausbeuten beziehen sich auf die Freisetzung *einer* Alkylgruppe (= 100%) als Aldehyd bzw. Keton)

Azo-Alkan	*Formel*	*Gebildete Oxoverbindung*	*Ausbeute (%)*
Azoäthan	$H_5C_2–N=N–C_2H_5$	Acetaldehyd	100±2
Azopropan	$H_7C_3–N=N–C_3H_7$	Propionaldehyd	100±3
Azoisopropan		Aceton	70±10
Azobutan	$H_9C_4–N=N–C_4H_9$	Butyraldehyd	100±3
Methylazobutan	$H_3C–N=N–C_4H_9$	Formaldehyd Butyraldehyd	69±2 31±3
tert.Butylazo-*n*-butan	 $H_3C–C(CH_3)_2–N=N–C_4H_9$	Butyraldehyd	100±3
Cyclohexylazomethan	$C_6H_{10}–N=N–CH_3$	Formaldehyd	100±2
α-Acetoxycyclohexylazomethan	 $C_6H_{11}(O–CO–CH_3)–N=N–CH_3$	Formaldehyd	100±2
α-Acetoxyisopropylazobutan		Butyraldehyd	100±3
Phenylazomethan	$C_6H_5–N=N–CH_3$	Formaldehyd	90±2
Phenylazoäthan	$C_6H_5–N=N–C_2H_5$	Acetaldehyd	95±2
Phenylazobutan	$C_6H_5–N=N–C_4H_9$	Butyraldehyd	100±3

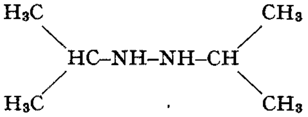
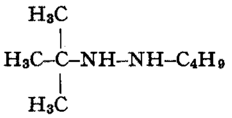
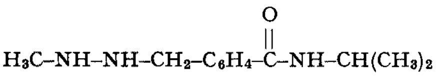
---

* Natulan[R] wurde freundlicherweise von der Hoffmann La Roche & Co., AG, zur Verfügung gestellt.

TABELLE II

BILDUNG VON OXOVERBINDUNGEN AUS 1,2-DIALKYLHYDRAZINEN NACH OXYDATION MIT $HgSO_4$ IN SCHWEFELSAURER LÖSUNG

(Ausbeuten beziehen sich auf die Freisetzung *einer* Alkylgruppe (= 100%) als Aldehyd oder Keton)

Hydrazin	*Formel*	*Gebildete Oxoverbindung*	*Ausbeute (%)*
1,2-Dimethyl-	$H_3C{-}NH{-}NH{-}CH_3$	Formaldehyd	100±2
1,2-Diäthyl-	$H_5C_2{-}NH{-}NH{-}C_2H_5$	Acetaldehyd	100±2
1,2-Dipropyl-	$H_7C_3{-}NH{-}NH{-}C_3H_7$	Propionaldehyd	100±3
1,2-Diisopropyl-	 $(H_3C)_2HC{-}NH{-}NH{-}CH(CH_3)_2$	Aceton	70±10
1,2-Dibutyl-	$H_9C_4{-}NH{-}NH{-}C_4H_9$	Butyraldehyd	100±3
1-Methyl-2-butyl-	$H_3C{-}NH{-}NH{-}C_4H_9$	Formaldehyd Butyraldehyd	52±2 48±3
1-*t*.Butyl-2-*n*-butyl-	 $(H_3C)_3C{-}NH{-}NH{-}C_4H_9$	Butyraldehyd	100±3
1-Methyl-2-cyclohexyl-	$H_3C{-}NH{-}NH{-}C_6H_{11}$	Formaldehyd	85±2
1-Methyl-2-benzyl-	$H_3C{-}NH{-}NH{-}CH_2{-}C_6H_5$	Formaldehyd Benzaldehyd	0 0
1-Methyl-2-*p*-(isopropylcarbamoyl)-benzylhydrazin (Natulan)	 $H_3C{-}NH{-}NH{-}CH_2{-}C_6H_4{-}C(=O){-}NH{-}CH(CH_3)_2$	Formaldehyd	0
1-Methyl-2-phenyl-	$H_3C{-}NH{-}NH{-}C_6H_5$	Formaldehyd	0
1,1-Dimethyl-	$(CH_3)_2N{-}NH_2$	Formaldehyd	100

man Spektralphotometer DB". Die IR-Spektren wurden im "Beckman IR-10" aufgenommen.

Die Schmelzpunktsbestimmungen erfolgten auf einem "Leitz"-Mikroskop-Heiztisch.

Quantitative Bestimmung von Azo-Alkanen

Eine wässrige Lösung von 0.1–2 μMol des Azoalkans wird in einem 50-ml Destillierkolben mit 4 ml 10%iger Schwefelsäure versetzt und mit Wasser auf 25 ml verdünnt. Für die Formaldehydbestimmung werden in einer Mikrodestillations-Apparatur 15 ml des Ansatzes und für die übrigen Aldehyde 10 ml in ein gut gekühltes, graduiertes Schliffreagenzglas bei Normaldruck destilliert. Im Destillat erfolgt die quantitative colorimetrische Bestimmung nach den unten beschriebenen Methoden.

Quantitative Bestimmung von 1,2-Dialkylhydrazinen

Eine wässrige Lösung von 0.1–2 μMol des Dialkylhydrazins als freie Base oder als Salz wird in einem 50-ml Destillierkolben mit 4 ml einer 0.1%igen Lösung von Quecksilber(II)-Sulfat in 10%iger Schwefelsäure versetzt. Die weitere Aufarbeitung erfolgt wie bei den Azoalkanen.

Photometrische Methoden zur Aldehyd- und Keton-Bestimmung

(*1*) *Formaldehyd* nach MACFADYEN[10].

Reagenz. 5%ige wässrige Lösung von Chromotropsäure, Na-Salz (1,8-Dihydroxy-naphthalin-3,6-disulfonsäure).

Ausführung. 10 ml des Formaldehyd enthaltenden Destillats werden mit 2 ml 5%iger Chromotropsäure-Lösung versetzt und mit konzentrierter Schwefelsäure auf 25 ml aufgefüllt. Man erhitzt 30 Min im siedenden Wasserbad, kühlt auf Zimmertemperatur ab und ersetzt den geringen Flüssigkeitsverlust durch Auffüllen mit Wasser. Die violette Lösung wird gegen einen analog behandelten Blindwert bei einer Wellenlänge von 560 nm gemessen.

(*2*) *Acetaldehyd* nach STOTZ[11].

Reagenz. 1 g 4-Hydroxybiphenyl in 25 ml 2 *N* NaOH unter Erwärmen gelöst und mit Wasser auf 100 ml aufgefüllt.

Ausführung. 1 ml des Acetaldehyd enthaltenden Destillats werden mit 0.05 ml der 5%igen Kupfer(II)-Sulfat-Lösung und genau 8 ml konz. Schwefelsäure unter guter Kühlung versetzt. Sodann werden 0.2 ml des Hydroxybiphenyl-Reagenz zugefügt und 30 Min unter öfterem Umschütteln bei 30° belassen. Anschliessend erhitzt man, ebenfalls unter öfterem Umschütteln, 1.5 Min auf 100° und lässt dann auf Zimmertemperatur abkühlen. Die violette Lösung wird gegen eine analog behandelte Blindprobe bei 570 nm gemessen.

(*3*) *Propion- und Butyraldehyd* nach SAWICKI *et al.*[12].

Reagenz. 0.4%ige Lösung von 3-Methyl-2-benzthiazolonhydrazon (MBTH) in Wasser.

Ausführung. 0.5 ml des Destillats werden mit 0.5 ml der MBTH-Lösung versetzt und 30 Min bei Raumtemperatur stehen gelassen. Anschliessend gibt man 2.5 ml der 0.2%igen Lösung von $FeCl_3 \cdot 6\ H_2O$ in Wasser zu und füllt nach 5 Min Stehen mit Aceton p.a. auf 10 ml auf. Propionaldehyd wird bei 662 nm und Butyraldehyd bei 666 nm gegen eine analog behandelte Kontrolle gemessen.

Nach dieser Methode lassen sich auch andere Aldehyde bestimmen.

(*4*) *Aceton* nach BERNTSSON[13].

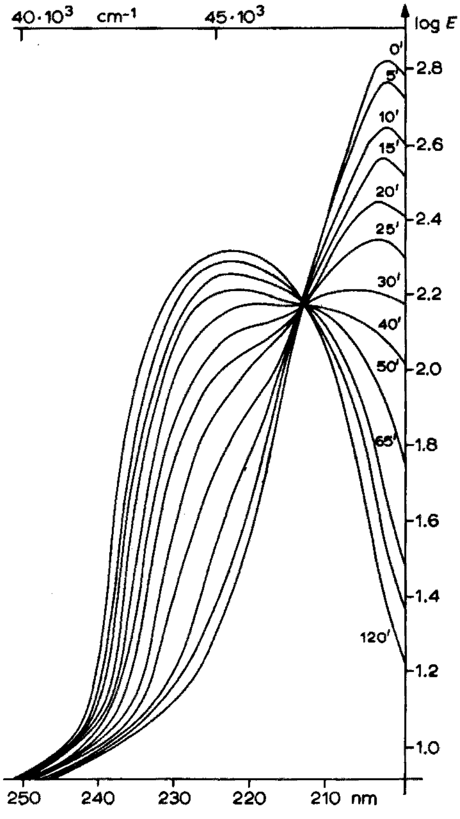
Ausführung. Die gesamten 10 ml des Destillats werden in einen 50-ml Messkolben überführt und mit Wasser auf *ca.* 25 ml verdünnt. Dann gibt man 2 ml NaOH (425 g NaOH auf 1 l H_2O), 0.6 ml reinen redestillierten Salicylaldehyd mit erneut 20 ml NaOH hinzu und füllt mit Wasser auf 50 ml auf. Nach 2 Stunden wird gegen eine analog behandelte Kontrolle bei 474 nm gemessen.

Sämtliche colorimetrischen Bestimmungsmethoden ergeben mit den reinen Oxo-Verbindungen bis zu Konzentrationen von *ca.* 2 μMol lineare Eichkurven.

ERGEBNISSE UND DISKUSSION

Die Protonen-katalysierte Umlagerung des Azoalkans zum Hydrazon gemäss dem Reaktionsschema kann UV-spektroskopisch gut demonstriert werden. Sie ist für den Fall von Azoäthan in Fig. 1 dargestellt. Das Maximum der Azo-Verbindung bei 202 nm verschwindet bei Zusatz eines Tropfens verdünnter Salszäure schnell und es entsteht ein neues Maximum bei 225 nm, das eindeutig dem Acetaldehydäthylhydrazon zuzuordnen ist[14]. Der isosbestische Punkt liegt bei 213 nm (Fig. 1).

Die Umlagerung erfolgt bei den erhöhten Temperaturen der Vorschrift praktisch momentan. Das bei der Spaltung des Hydrazons nach Abdestillieren des Aldehyds zurückbleibende Monoalkylhydrazin kann durch Hydrazonbildung mit *p*-Nitrobenzaldehyd (vgl. OHME UND SCHMITZ[15]) charakterisiert und identifiziert werden. Im Falle des Azoäthans entsteht *p*-Nitrobenzaldehyd-äthylhydrazon, Fp. 88°. Der Mischschmelzpunkt mit einem aus den Ausgangsverbindungen hergestellten Produkt ergab keine Depression, die IR-Spektren waren deckungsgleich.



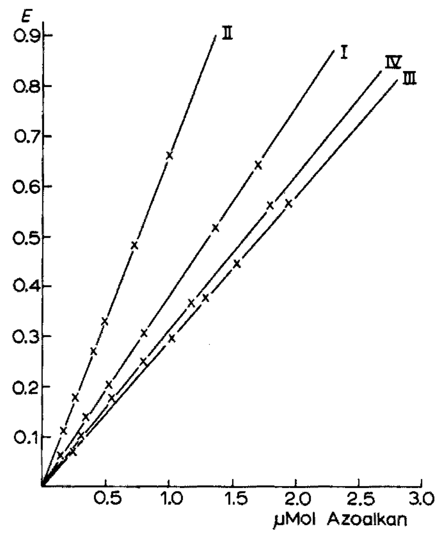


Fig. 1. Säure-katalysierte Umlagerung von Azoäthan ($\lambda_{max} = 202$ nm) zu Acetaldehyd-äthylhydrazon ($\lambda_{max} = 225$ nm).

Fig. 2. Eichkurven zur Bestimmung von Azoalkanen durch colorimetrische Messung freigesetzter Aldehyde nach Säure-katalysierter Umlagerung. (I) Cyclohexylazomethan; (II) Azoäthan; (III) Azopropan; (IV) Azobutan.

Die quantitative Analyse der *Azoalkane* durch photometrische Bestimmung der gebildeten Aldehyde ergibt lineare Eichkurven, die dem Lambert–Beer'schen Gesetz in einem Bereich von 0.1 bis 2 µMol folgen. Beispiele für 4 Azoalkane sind in Fig. 2 dargestellt. Die Ergebnisse für alle untersuchten Azoverbindungen finden sich in Tabelle I. Man sieht, dass gleichartig substituierte, geradkettige Azoalkane quantitativ den entsprechenden Aldehyd liefern. Bei ungleichen Substituenten, wie z.B.

bei Methylazo-*n*-butan, wurden beide möglichen Aldehyde gefunden, wobei der niedere Aldehyd überwiegt. Addition beider Aldehydkonzentrationen ergibt 100% Ausbeute. Bei *tert.*-Butyl-azo-*n*-butan kann die Umlagerung nur nach der Seite der unverzweigten Kette erfolgen.

Kettenverzweigung in α-Stellung, wie im Falle von Azoisopropan, ergibt unter Standard-Bedingungen Aceton-Ausbeuten von nur 70% mit starker Streuung. Dies hat wahrscheinlich sterische Gründe, denn mit Erhöhung der Säurekonzentration steigt auch die Aceton-Ausbeute auf 90%. Dass eine Umlagerung zum Hydrazon und die Abspaltung des Ketons schwerer erfolgt, zeigen auch die Ergebnisse mit Azo-Verbindungen, die einen geradkettigen und einen verzweigten Rest besitzen (Tabelle I). Hier verläuft die Umlagerung ausschliesslich nach dem unverzweigten Alkylrest hin.

Phenyl-azomethan und -äthan spalten den entsprechenden Aldehyd nicht quantitativ ab. Dafür kann eine Erklärung noch nicht gegeben werden.

Aliphatische *Hydrazo*-Verbindungen werden leicht zu den entsprechenden Azo-Verbindungen oxydiert und können somit ebenfalls nach der ausgearbeiteten Methode bestimmt werden. Es erwies sich, dass die meisten gängigen (anorganischen) Oxydationsmittel zu stark wirken und auch die bei der Umsetzung entstehenden Monoalkylhydrazine oxydativ abbauen und somit zu hohe und nicht reproduzierbare Werte ergeben. Es gelang jedoch, durch Oxydation mit Quecksilber(II)-Sulfat in schwefelsaurer Lösung geeignete Reaktionsbedingungen zu finden, die eine quantitative Bestimmung der rein aliphatischen 1,2-Dialkylhydrazine gestatten. Die Ergebnisse mit 12 verschiedenen Verbindungen sind in Tabelle II aufgeführt. Quantitative Aldehydausbeuten werden mit 1,2-Dimethyl- bis 1,2-Dibutylhydrazin erhalten. Aus 1-Methyl-2-*n*-butylhydrazin entstehen wiederum beide möglichen Aldehyde, wobei die Summe, wie bei den entsprechenden Azoverbindungen, 100% Ausbeute beträgt. 1-Methyl-2-cyclohexylhydrazin ergibt nur 85% des theoretisch zu erwartenden Formaldehyds, die Ergebnisse sind jedoch reproduzierbar und die Eichkurven linear. Dagegen ist 1,2-Diisopropylhydrazin (wie die entsprechende Azo-Verbindung) nur schlecht zu bestimmen, die Streuung ist sehr gross.

Überraschend lassen sich die Alkylbenzyl- und Alkylphenylhydrazine unter den angewandten Reaktionsbedingungen nicht zu den entsprechenden Azoverbindungen oxydieren und spalten deshalb auch keinen Aldehyd ab. Diese Ergebnisse stimmen mit manometrischen Messungen der Sauerstoffaufnahme bei der Oxydation von 1,2-disubstituierten Hydrazinen überein[16]. Es stellte sich heraus, dass aliphatische 1,2-Dialkylhydrazine $\frac{1}{2}$ Mol O_2 zu kompletter Oxydation aufnehmen, während Benzyl- und Phenylhydrazin-Derivate 1 Mol O_2 benötigen. Beide Befunde scheinen zu bestätigen, dass die Oxydation dieser beiden Typen von 1,2-disubstituierten Hydrazinen durch unterschiedliche Mechanismen bewirkt werden.

Die untere Nachweisgrenze für aliphatische Hydrazo- und Azo-Verbindungen nach der vorgelegten Methode liegt bei *ca.* 0.1 μMol in der Testlösung. Durch Anwendung empfindlicherer Aldehydbestimmungsmethoden könnte die Empfindlichkeit ohne Zweifel erhöht werden.

Es ist auch möglich, Azo- und 1,2-Dialkylhydrazin-Verbindungen nebeneinander zu analysieren, indem man zuerst die Azo-Verbindung, ohne zu oxydieren, aus der Probe bestimmt und anschliessend den Rückstand oxydiert, wobei nach obigen Methoden die Hydrazo-Verbindung erfasst wird.

Mit Hilfe der Dünnschichtchromatographie kann man ausserdem die Konstitution der Azo- bzw. 1,2-Dialkylhydrazo-Verbindungen ermitteln. Und zwar lässt sich nach bekannten Methoden der Aldehyd (IV) z.B. mit 2,4-Dinitrophenylhydrazin und das Hydrazin (III) mit 2,4-Dinitrobenzaldehyd qualitativ nachweisen und identifizieren.

Bezüglich der *Spezifität* der Nachweismethoden ist zu sagen, dass alle Stoffklassen stören, die unter den sauren Reaktionsbedingungen Oxo-Verbindungen abspalten können. Das sind z.B. alle Oxo-Derivate wie Acetale, Aminale, Mannich-Basen, Hydrazone usw. Mono-, Di- und Trialkylamine stören nicht, ebenfalls negativ sind Monoalkylhydrazine und 1-Acyl-2-alkyl-hydrazine wie z.B. 1-Acetyl-2-äthylhydrazin.

Dagegen fanden wir, dass 1,1-Dialkylhydrazine (Unsymmetrische Dialkylhydrazine) ein Äquivalent Aldehyd mit Quecksilber(II)-Sulfat in saurer Lösung freisetzen. Darüber wird gesondert berichtet[17]. Ebenfalls positiv reagieren Tri- und Tetraalkylhydrazine.

Die Bestimmung von Hydrazo- und Azo-Alkanen gelingt unter den beschriebenen Bedingungen auch in Serum bzw. Urin. Die systematischen Fehler sind hierbei etwas grösser als in wässrigen Lösungen. Ob die Nachweisreaktion in komplexen Gemischen wie z.B. Naturstoffextrakten gelingt, wird in weiteren Untersuchungen geklärt.

Die Untersuchungen wurden durch die Deutsche Forschungsgemeinschaft ermöglicht.

ZUSAMMENFASSUNG

Azoalkane können nach Umlagerung zum Hydrazon in saurem Medium hydrolysiert und durch photometrische Bestimmung der abgespaltenen Oxo-Verbindung quantitativ erfasst werden. 1,2-Disubstituierte Alkylhydrazine (Hydrazo-Alkane) lassen sich analog bestimmen, nachdem sie in schwefelsaurem Medium mit Quecksilber(II)-Sulfat oxydiert wurden. Die untere Nachweisgrenze der beiden Verbindungsklassen liegt bei 0.1 bis 0.2 μMol pro Ansatz. Anwendbarkeit und Spezifität werden diskutiert.

SUMMARY

Aliphatic azo-compounds after rearrangement to hydrazone in acidic medium can be hydrolyzed and the released aldehyde can be determined quantitatively. 1,2-Disubstituted alkylhydrazines (hydrazoalkanes) can be determined by the same principle after oxidation by mercury(II) sulfate in aqueous sulfuric acid. The lower detection limit for both types of compounds is 0.1–0.2 μmoles. The applicability and specificity of this new analytical method are discussed.

RÉSUMÉ

Les composés azo-aliphatiques après réarrangement en milieu acide peuvent être hydrolysés; l'aldéhyde libéré peut être dosé quantitativement. Les alkylhydrazines 1,2-disubstituées (hydrazoalcanes) peuvent être dosées selon le même principe après oxydation au moyen de sulfate de mercure(II) en milieu acide sulfurique. La limite de détection inférieure pour ces deux types de composés est de 0.1–0.2 μmoles. On examine les possibilités d'application et la spécificité de cette nouvelle méthode d'analyse.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE EXTRACTION OF COPPER(I), LEAD(II) AND TIN(IV) FROM HYDROCHLORIC ACID BY SOLUTIONS OF TETRA-*n*-HEXYLAMMONIUM CHLORIDE IN ETHYLENE DICHLORIDE

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(Received December 7th, 1967)

NAKAGAWA[1] has studied the extraction of a number of metal ions from hydrochloric acid solutions using a 10% solution of the secondary amine Amberlite LA1 [N-dodecenyl(trialkylmethyl)amine]. The extraction of copper(II) reached a maximum of 35% from 7 *M* acid; lead(II) showed maximum extraction from 1.5 *M* acid, decreasing to zero at 10 *M*; the extraction of tin(IV) began at 0.5 *M*, reached a maximum between 5 and 6 *M* and then decreased. When the secondary amine Amberlite LA2 [N-lauryl(trialkylmethyl)amine] was used, 98% of tin(IV) was extractable from 5–9 *M* hydrochloric acid; the maximum extraction of lead was again only 40% from 2 *M* acid and the amount decreased rapidly with increasing concentration to become zero at 8 *M* [2]. A method for separating tin and lead was based on these results.

Since marked improvements in distribution coefficients and in selectivity often result from replacing salts of secondary amines by those of tertiary amines, or by quaternary ammonium salts, it was decided to investigate the extraction behaviour of the above-mentioned cations with solutions of tetra-*n*-hexylammonium chloride in ethylene dichloride and to include copper(I) as well as copper(II) in the survey. Since the extraction of copper(II) presented an unusual number of special features, the results for this system will be presented in a separate paper.

THE EXTRACTION OF COPPER(I) FROM CHLORIDE MEDIA

Solutions of copper(II) were reduced by hydroxylamine hydrochloride at pH $\geqslant 2.6$, for preliminary experiments showed this to be quantitative at any pH between 2.5 and 7.0; a 100-fold excess of reductant was used. Extractions were carried out from solutions of sodium chloride in the presence of $10^{-4}M$ hydrochloric acid.

Distribution ratios, defined by the expression

$$D = \frac{\text{Total concentration of metal in the organic phase}}{\text{Total concentration of metal in the aqueous phase}}$$

were obtained by spectrophotometric determinations of the copper content of each phase by the oxalyldihydrazide method[3]. Copper(I) was stripped from the organic phase by an aqueous solution of 0.1 *M* sodium perchlorate containing a little nitric acid. Results were rejected if satisfactory mass-balances were not obtained.

When only the concentration of tetra-*n*-hexylammonium chloride was varied, the plot of log D against log $[NR_4^+Cl^-]_{org.}$ (R = *n*-hexyl; Fig. 1, curve a) was a straight line of unit slope, pointing to the extraction into the ethylene dichloride of the singly charged complex $CuCl_2^-$. Figure 1 (curve b) shows how the distribution ratio is influenced by changes in chloride concentration. The plot of log D against log $[Cl^-]$ is again a straight line but of slope −1.

These results are consistent with the following distribution equilibrium

$$(NR_4^+Cl^-)_{org.} + CuCl_2^- \rightleftarrows (NR_4^+CuCl_2^-)_{org.} + Cl^- \qquad (1)$$

where the subscript *org.* distinguishes species in the organic phase and R = *n*-hexyl. The equilibrium constant ("extraction constant") for this reaction is given by

$$K_{CuCl_2} = [NR_4^+CuCl_2^-]_{org.}\ [Cl^-]/[NR_4^+Cl^-]_{org.}\ [CuCl_2^-] \qquad (2)$$

In the aqueous phase there will be a mixture of chloro-complexes, so that the distribution ratio

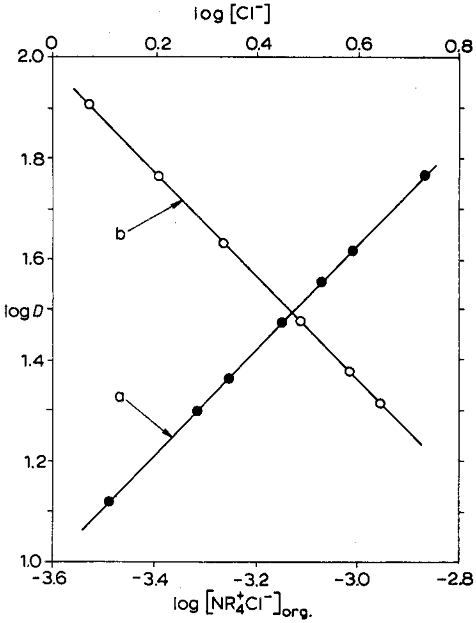

Fig. 1. The extraction of $2 \cdot 10^{-4}$ *M* copper(I) from chloride media by solutions of tetra-*n*-hexylammonium chloride in dichlorethylene. Curve (a) (blackened circles and lower abscissae) variable $[NR_4^+Cl^-]_{org.}$ and constant $[Cl^-]$ as in Table I. Curve (b) (open circles and upper abscissae) variable $[Cl^-]$ and constant total initial concentration of liquid anion-exchanger $[NR_4^+Cl^-]_{org.}$ = $5.532 \cdot 10^{-4}$ *M*.

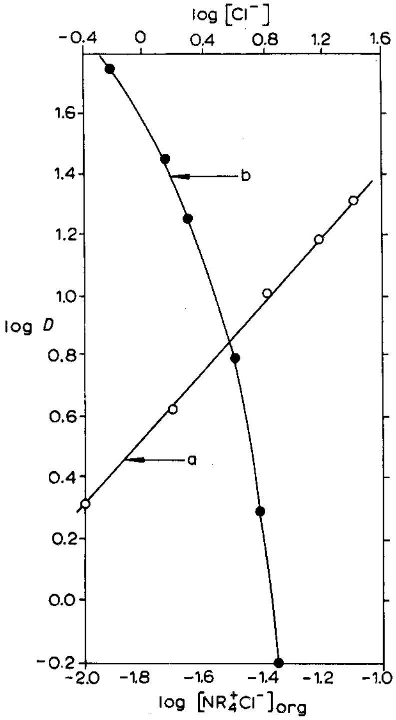

Fig. 2. The extraction of $1.739 \cdot 10^{-3}$ *M* of lead nitrate from hydrochloric acid by solutions of tetra-*n*-hexylammonium chloride in ethylene dichloride. Curve (a) (open circles and lower abscissae) variable $[NR_4^+Cl^-]_{org.}$ and constant chloride, [HCl] = 0.5836 *M*. Curve (b) (blackened circles and upper abscissae) variable $[Cl^-]$ and constant total initial concentration of liquid anion-exchanger, $[NR_4^+Cl^-]_{org.}$ = 0.1 *M*.

$$D = \Sigma[\mathrm{Cu}]_{org.}/\Sigma[\mathrm{Cu}]_{aq.} = [\mathrm{NR_4^+CuCl_2^-}]_{org.}/\sum_{0}^{j}[\mathrm{CuCl}_j]$$

Substituting from eqn. (2), introducing the definition $\beta_j = [\mathrm{CuCl}_j^{1-j}]/[\mathrm{Cu^+}][\mathrm{Cl^-}]^j$, and taking decadic logarithms

$$\begin{aligned}\log D &= \log K_{\mathrm{CuCl_2}^-} + \log [\mathrm{NR_4^+Cl^-}]_{org.} + \log \beta_2 \\ &+ \log [\mathrm{Cl^-}] - \log \Sigma \beta_j [\mathrm{Cl^-}]^j\end{aligned} \tag{3}$$

By differentiation

$$(\partial \log D/\partial \log [\mathrm{NR_4^+Cl^-}]_{org.})_{[\mathrm{Cl^-}]} = +1 \tag{4}$$

as found experimentally (Fig. 1, curve a). Likewise,

$$(\partial \log D/\partial \log [\mathrm{Cl^-}])_{[\mathrm{NR_4^+Cl^-}]} = 1 - \bar{n} \tag{5}$$

where $\bar{n}$ is the degree of formation of the chloro-complexes in the aqueous phase. Equation (5) predicts that the plot of log D against log$[\mathrm{Cl^-}]$ should consist of a curve with a maximum at $\bar{n} = 1$. Since only the descending portion of the curve predictable theoretically is realisable experimentally, it is clear that, under the conditions of these experiments, the degree of formation, $\bar{n}$, had already attained the value of two. This is a consequence of the high stability of the copper(I)–chloride ion complexes which reflect the pronounced class (b) character of copper in this lower oxidation state[4,5]. Thus values of log β_2 from 4.6 to 5.5 are quoted for the overall stability constant of $\mathrm{CuCl_2^-}$ (μ various). Values for log β_3 range from 5.3 to 5.8, indicating the much lower tendency to coordinate a third chloride ion; one author gives evidence for $\mathrm{CuCl_2^-}$ and $\mathrm{Cu_2Cl_3^-}$ but not for $\mathrm{CuCl_3^{2-}}$ [6]. Clearly Fig. 1, curve b, simply represents the effect of increasing concentration of chloride ion in displacing $\mathrm{CuCl_2^-}$ from the organic phase *i.e.* eqn. (1) right to left.

TABLE I

EXTRACTION OF COPPER(I) FROM CHLORIDE MEDIUM BY SOLUTIONS OF TETRAHEXYLAMMONIUM CHLORIDE IN ETHYLENE DICHLORIDE

($[\mathrm{Cu^{2+}}] = 2 \cdot 10^{-4} M$; $[\mathrm{NH_2OH}] = 5 \cdot 10^{-2} M$; $[\mathrm{H^+}] = 10^{-4} M$; $[\mathrm{Cl^-}] = 3.770\ M$)

log D	$[NR_4^+Cl^-]^a_{org.}$ *(× 10⁴)*	$[NR_4^+CuCl_2^-]^a$ *(× 10⁴)*	*log* K_{CuCl_2}
1.140	0.902	1.865	6.11
1.301	2.235	1.905	5.88
1.440	3.591	1.930	5.82
1.576	4.970	1.948	5.81
1.628	6.325	1.954	5.76

[a] At equilibrium.

By assuming the values log $\beta_2 = 5.2$ and log $\beta_3 = 5.5$, calculated values of log $K_{\mathrm{CuCl_2}}$ are 5.88 ± 0.13 for results at constant total chloride ion concentration and a variable concentration of quaternary ammonium salt (Table I), and 5.86 ± 0.03 for results with a constant total amount of ligand exchanger and variable chloride concentration (Table II).

TABLE II

EXTRACTION OF COPPER(I) FROM MEDIA OF VARIABLE CHLORIDE CONTENT

($[Cu^{2+}] = 2 \cdot 10^{-4} M$; $[NH_2OH] = 5 \cdot 10^{-2} M$; $[H^+] = 10^{-4}\ M$; total initial $[NR_4^+Cl^-]_{org.} = 5.532 \cdot 10^{-4} M$)

$\log D$	$[Cl^-]^a (M)$	$[NR_4^+CuCl_2^-]^a_{org.}$ $(\times 10^4)$	$[NR_4^+Cl^-]^a_{org.}$ $(\times 10^4)$	$\log K_{CuCl_2}$
1.425	4.467	1.9272	3.605	5.86
1.471	3.767	1.9348	3.597	5.84
1.588	3.048	1.9494	3.583	5.89
1.699	2.051	1.9608	3.571	5.82
1.950	1.050	1.9782	3.554	5.89

[a] At equilibrium.

Taking the values $\beta_1 = 3.0$, $\beta_2 = 5.2$, $\beta_3 = 5.5$, one can calculate that $\bar{n} = 2$ when $[Cl^-] \cong 5 \cdot 10^{-2} M$, and from eqn. (3) and the value $\log K_{CuCl_2} = 5.87$, we find $\log D \cong 6.4$ when $[NR_4^+Cl^-]_{org.} = 5.532 \cdot 10^{-4} M$. Clearly, copper(I) should be extractable effectively quantitatively over a very wide range of chloride ion concentrations.

Since the stabilities of copper(I) halides increase in the order $Cl^- < Br^- < I^-$ with $\beta_{CuCl_2^-} \sim 5.2$, $\beta_{CuBr_2^-} \sim 5.9$ and $\beta_{CuI_2^-} \sim 9$ [4,5], it is to be predicted that the extraction of copper(I) from bromide or iodine media will be still more effective than from chlorides and D should attain a value of (say) 10^4 at increasing low concentrations.

THE EXTRACTION OF LEAD(II) FROM CHLORIDE MEDIA

In preliminary experiments, low concentrations of lead (*ca.* $10^{-5} M$) were found not to be extracted by solutions of *n*-hexylammonium iodide in ethylene dichloride or by solutions of the corresponding chloride in hexone. These results appeared to conflict with those of MAEK *et al.*[7], who reported almost quantitative extraction of macro-quantities by the quaternary iodide from hydrochloric acid. It was then found that the metal could readily be extracted by solutions of either the quaternary chloride or iodide provided that the concentration of lead was high enough—$1.739 \cdot 10^{-3}\ M$ in the present experiments.

The plot of $\log D$ against $\log [NR_4^+Cl^-]_{org.}$ at constant $[Cl^-]$ is a straight line of unit slope (Fig. 2, curve a) implying that under these conditions ($[HCl] = 0.5836\ M$) the complex $NR_4^+PbCl_3^-$ is formed and extracted according to the equation

$$(NR_4^+Cl^-)_{org.} + PbCl_2 \rightleftarrows (NR_4^+PbCl_3^-)_{org.} \tag{6}$$

The plot of $\log D$ against $\log [Cl^-]$ for a constant excess amount of quaternary chloride (Fig. 2, curve b) is a steeply descending curve with a slope varying from -1 to -3. If K_{PbCl_2} is the equilibrium constant for the extraction process formulated in eqn. (6) and

$$\beta_j = [PbCl_j^{2-j}]/[Pb^{2+}][Cl^-]^j, \text{ we can write}$$

$$D = K_{PbCl_2} [NR_4^+Cl^-]_{org.} \beta_2 [Cl^-]^2 / \sum_0^j \beta_j [Cl^-]^j \tag{7}$$

whence $(\partial D/\partial [NR_4^+Cl^-]_{org.})_{[Cl^-]} = 1$ as found experimentally, and

$$(\partial D/\partial [Cl^-])_{[NR_4^+Cl^-]} = 2 - \bar{n} \tag{8}$$

Along the descending part of curve (b), $\bar{n}$ must first be *ca.* 3, consistent with the extraction of the complex $PbCl_3^-$; the increase to *ca.* 6 at higher chloride ion concentrations suggests that higher chloro-complexes are being formed in the aqueous phase, but these are clearly less extractable. A complicating feature (Table III) is the observation that the distribution ratio decreases with decreases in the total lead concentration and this system clearly merits a fuller investigation.

The stability of the chloride complexes of lead have been repeatedly investigated; more than 50 papers are listed in "Stability Constants"[6]. There is definite evidence for the species $PbCl^+$, $PbCl_2$, $PbCl_3^-$ and $PbCl_4^{2-}$ and values for the formation constants of $PbCl_5^{3-}$ and $PbCl_6^{4-}$ have been given by Russian workers. However, the values reported for log K_1 (for $\mu \sim 1\ M$) range from 0.66 to 1.81 and values for log β_2 range from 0.87 to 2.26, and it is quite impossible to derive a "best value" from the conflicting data which cover such a wide range of ionic strengths and temperatures; moreover, log K_2 is reported sometimes as a positive and sometimes as a negative quantity. Estimates of log β_3 and log β_4 are equally uncertain; but the ranges (1.09 to 2.08 and 0.94 to 1.60) all imply values of K_3 and K_4 less than one.

TABLE III

VARIATION IN THE DISTRIBUTION OF LEAD WITH TOTAL LEAD CONCENTRATION

(Solvent, ethylene dichloride; Volume ratio 1:1; [HCl] = 0.5836 *M*; $[NR_4^+Cl^-]_{org.}$ = 0.1 *M*).

$10^3[Pb]_{total}$	1.739	0.869	0.290	0.058	0.029
D	55.0	11.0	3.5	0.17	0.003

TABLE IV

EXTRACTION OF LEAD FROM 0.5836 *M* HCl

log $[NR_4^+Cl^-]_{org.}$	−2.00	−1.70	−1.40	−1.22	−1.10
log D	0.31	0.63	1.04	1.18	1.32
(log D − log$[NR_4^+Cl^-]_{org.}$)	2.31	2.33	2.44	2.40	2.42

Realistic calculations cannot therefore be undertaken to obtain values of log K_{PbCl_2} from eqn. (7). However, when [Cl⁻] is constant the last three terms in eqn. (7) will all be constant and (log D − log $[NR_4^+Cl^-]_{org.}$) = log K_{PbCl_2} + log β_2 + 2 log$[Cl^-]$ − log$\Sigma\beta_j[Cl^-]^j$ should also be a constant. This is illustrated by results in Table IV, where the concentration of extractant and the distribution ratio are varied over a 10-fold range.

THE EXTRACTION OF TIN(IV) FROM HYDROCHLORIC ACID

Figure 3 (curve a) shows a plot of log D against log $[NR_4^+Cl^-]$ for the extraction of $9.0 \cdot 10^{-4}$ *M* tin(IV) from 3.606 *M* hydrochloric acid by solutions of tetra-*n*-hexylammonium chloride in ethylene dichloride: the curve is linear with a slope of ~6. The partition of the tin was measured polarographically. Although species such as $NR_4^+SnCl_5^-$ and $(NR_4^+)_2SnCl_6^{2-}$ might well be expected to be formed and extracted, the observed slope can only be explained if the extracted material is associated with the anion exchanger. Thus GOOD AND SRIVASTAVA[8] postulated that the anomalous slopes found in the extraction or iron(III), indium(III) and gallium(III) by tertiary amines from chloride solutions involved aggregates of $NR_3H^+MCl_4^-$ with $NR_3H^+Cl^-$. A similar explanation may account for the behaviour of tin(IV).

The extraction of tin(IV) by a solution of anion exchanger of constant composition, $[NR_4^+Cl^-] = 4 \cdot 10^{-3}$ M, is shown as a function of hydrochloric acid concentration in Fig. 3 (curve b). Extraction increases with acid concentration to reach a maximum value ($D > 200$) at about 5 M hydrochloric acid and it decreases rapidly for concentrations greater than 6 M. Although these results confirm those obtained with solutions of Amberlite LA1 in xylene and demonstrate the analytical applications of the procedure, it is clearly impossible to draw any conclusions as to the nature of the species that are being extracted.

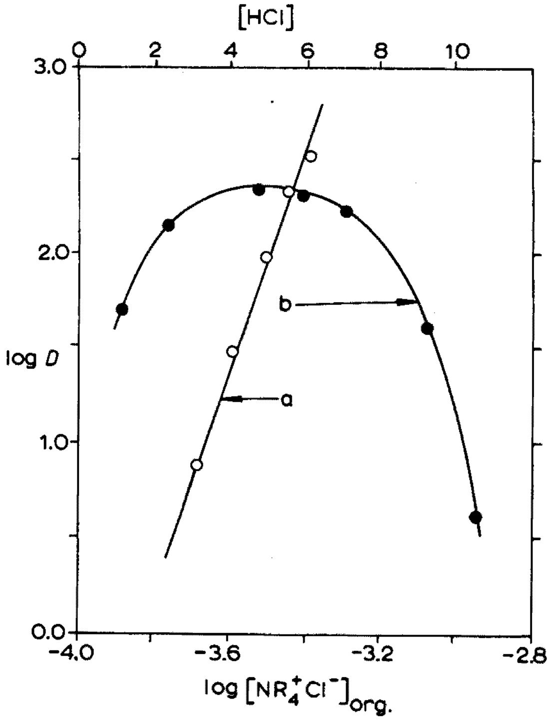

Fig. 3. The extraction of $9 \cdot 10^{-4}$ M tin(IV) chloride from hydrochloric acid by solutions of tetra-*n*-hexylammonium chloride in ethylene dichloride. Curve (a) (open circles and lower abscissae) variable $[NR_4^+Cl^-]_{org.}$ and fixed chloride ion concentration, [HCl] = 3.606 M. Curve (b) (blackened circles and upper abscissae) variable concentrations of hydrochloric acid and a fixed total initial concentration of liquid anion exchanger, $[NR_4^+Cl^-]_{org.} = 4 \cdot 10^{-3}$ M.

Separations of lead(II) and tin(IV) are clearly possible by choice of suitable concentrations of hydrochloric acid for the liquid–liquid extraction and for the stripping stages; the effectiveness of these separations has been confirmed experimentally. The separation of copper and lead is inefficient if the former is in the +1 state. In the copper(II) form the extraction is found to be quite low from 1 M hydrochloric acid and to increase with chloride ion concentration[9]. Separations are thus possible from dilute hydrochloric acid.

EXPERIMENTAL

Reagent

Quaternary *n*-hexylammonium iodide (Eastman Kodak "White Label" grade) or laboratory samples synthesised by heating equivalent amounts of tri-*n*-hexylamine and *n*-hexyl iodide in benzene under reflux, was recrystallized from hot xylene, which gave a silky white free-flowing product.

To prepare the corresponding chloride, anion-exchange resin (100 g of IRA-400 in the chloride-ion form) was packed in a 12" × 1" in column and washed successively with 2 *N* hydrochloric acid, distilled water, and an acetone–water mixture (70%, v/v). A solution of the quaternary iodide (5 g in 100 ml of the same solvent) was added at the rate of 100 ml per hour and the column was eluted with the 70% acetone–water mixture. Ammoniacal silver nitrate was used to test the solvent for the complete absence of iodide.

The acetone in the eluent was removed on a water bath in a current of air and the quaternary ammonium chloride in the resulting viscous solutions was extracted with ethylene dichloride (100 ml); during this process it is advisable to bring the acidity to approximately 1 *M* with hydrochloric acid to prevent emulsification.

The concentration of quaternary ammonium chloride was next determined on the basis of a method described by IRVING AND DAMODARAN[10] for the determination of long-chain amines in effluent solutions. An aliquot portion of the quaternary chloride solution (1 ml) was diluted to 10 ml with hexone in a volumetric flask and 0.1 ml of this solution was diluted to 10 ml; 5 ml of this solution was then equilibrated (3 min) with 5 ml of an aqueous solution of Erdmann's salt (1 g of $(NH_4)[Co(NH_3)_2(NO_2)_4]$ in 10 ml distilled water) in a stoppered centrifuge tube. After centrifugation the aqueous phase was separated and rejected. The organic phase was then treated once more with 5 ml of Erdmannate solution and the separated organic phase was washed twice with 5 ml of water to remove excess reagent. Anhydrous sodium sulphate (0.5 g) was added to dry the organic phase and a portion was filtered through dry filter paper into a 0.5-cm cell. The absorbancy was measured at 353 nm against a hexone blank with a Unicam SP 500 spectrophotometer.

Equilibration procedure and methods of determination

Equilibrations were carried out by vigorously shaking a stoppered centrifuge tube containing 5 ml of an aqueous solution containing a known concentration of copper (which was reduced to copper(I) by hydroxylamine hydrochloride at $\text{pH} \geqslant 2.6$) and known concentrations of hydrogen and chloride ions, together with 5 ml of a solution of tetrahexylammonium chloride of known concentration in ethylene dichloride.

After equilibration, 4 ml of the aqueous phase was transferred to a 100-ml beaker. The excess of hydroxylamine was oxidised by adding 5 ml of saturated potassium bromate solution and 7 ml of 5 *M* hydrochloric acid and the contents of the beaker were taken to dryness on a water bath and the residue taken up in a few drops of nitric acid.

The copper content of the organic phase was first determined after wet oxidation of a 4-ml portion with a mixture of nitric, sulphuric and perchloric acids. Identical results were shown to be given by a more convenient and rapid process of "stripping". In this procedure 4 ml of the organic phase is equilibrated with a 0.1 *M* solution of sodium perchlorate. The perchlorate ion displaces anionic copper from the organic phase. The aqueous phase is removed and the stripping repeated twice more. The organic phase was washed once with water and the combined aqueous extracts acidified with a few drops of nitric acid and taken to dryness. Blank experiments confirmed that two "strippings" removed at least 99% of copper from the organic phase and it was shown that the presence of perchlorate did not interfere with the subsequent spectrophotometric determination of copper. Nevertheless, equivalent amounts of sodium perchlorate were introduced when calibration curves were prepared. Copper(II) was determined spectrophotometrically in aliquot portions of aqueous solutions by the oxalyldihydrazide method[3]; the violet complex has its peak absorption at 536 nm (ε_{max} = 21,700). Beer's law was shown to be obeyed over the range of concentrations used. The mass-balance of copper was always checked against the known total amount added and results were discarded if this proved unsatisfactory.

In studies involving tin(IV) or lead(II), equilibrations were continued for 1 h at room temperature using 10 ml of each phase. With lead, 0.1-ml portions of the aqueous phase were removed and the metal content determined with dithizone by means of IRVING AND BUTLER's reversion method[11]. The lead content of the organic phase was calculated by difference.

With tin(IV), 8 ml of the aqueous phase was removed and the content of metal determined polarographically by GODAR AND ALEXANDER's method[12], which has been verified for the determination of tin in foodstuffs and biological material down to 0.5 p.p.m. The precision was found to be about ±5% at the 10 p.p.m. level. Specpure tin was used to prepare standard solutions.

SUMMARY

Copper(I) is strongly extracted from chloride media as the ion-pair $NR_4^+CuCl_3^-$ by solutions of tetra-*n*-hexylammonium chloride ($NR_4^+Cl^-$) in ethylene dichloride. The distribution coefficient decreases from *ca.* 100 in 1 *M* chloride but is still as high as 13 in 10 *M* chloride. The extraction of lead(II) is shown to be due to the partition of the ion-pair ($NR_4^+PbCl_3^-$). The percentage of 0.0018 *M* lead extracted is 98% from 0.58 *M* hydrochloric acid and falls to 38% from 7.8 *M* acid. The distribution coefficient decreases rapidly with the total lead concentration. The extractions of tin(IV) increased to a maximum of 99.5% in *ca.* 5 *M* hydrochloric acid but decreased rapidly above 6 *M* acid. It proved impossible to identify the extractable species.

RÉSUMÉ

Le cuivre(I) est extrait en milieu chlorure sous forme de $NR_4^+CuCl_3^-$ au moyen de solutions de chlorure de tétra-*n*-hexylammonium ($NR_4^+Cl^-$) dans le dichlorure d'éthylène. L'extraction du plomb est due à la formation de l'ion $NR_4^+PbCl_3^-$. Le pourcentage de plomb 0.0018 *M* extrait est de 98% en solution HCl 0.58 *M* et descend à 38% en solution acide 7.8 *M*. Le coefficient de partage diminue rapidement avec la concentration totale en plomb. Les extractions de l'étain(IV) arrivent à un maximum de 99.5% en milieu HCl env. 5 *M*, mais elles diminuent rapidement au-dessus de 6 *M*. On n'a pas pu identifier la forme extraite.

ZUSAMMENFASSUNG

Kupfer(I) wird in starkem Masse aus einer Chloridlösung als $NR_4^+CuCl_3^-$ mit Tetra-*n*-hexylammoniumchlorid in Äthylendichlorid extrahiert. Der Verteilungskoeffizient fällt von etwa 100 auf 13 beim Übergang von 1 *M* auf 10 *M* Chloridlösung. Bei der Extraktion von Blei(II) wird $NR_4^+PbCl_3^-$ verteilt. Aus 0.58 *M* Salzsäure wird 98% einer 0.0018 *M* Bleilösung extrahiert, dagegen nur 38% aus 7.8 *M* Säure. Der Verteilungskoeffizient nimmt stark mit zunehmen der Bleikonzentration ab. Die Extraktion von Zinn(II) erreicht ein Maximum von 99.5% bei etwa 5 *M* Salzsäure, sinkt jedoch schnell oberhalb 6 *M* Säure. Es war nicht möglich die extrahierbaren Spezies zu identifizieren.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

VERSATILE HIGH-TEMPERATURE LABORATORY PREPARATIVE GAS-LIQUID CHROMATOGRAPHY MANIFOLD AND TRAPPING ASSEMBLY

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(Received November 10th, 1967)

Many problems have plagued preparative gas–liquid chromatography operators in obtaining the maximum yield and purity of individual components. Of these, aerosol formation, thermal sample degradation, component condensation (cold spots) upstream to the traps causing cross-contamination of purified components, and valve leakage at high temperatures are most significant. Other important points include insufficient surface contact for vapors to insure maximum condensation, lack of a second-pass trap to collect uncondensed components that have eluded the first trap and inability to remove a trap from the manifold without disrupting the system until after the last component has been eluted. In addition, the trap exit lines and switching valve are in many cases unheated, which causes some sample condensation which eliminates the usefulness of a second-pass trap assembly unless it is pre-cleaned before different types of samples are charged.

Various methods of routing preparative GLC fractions to traps have been reported. A rotating valve[1] with O-rings compressed between two metal plates (the stationary plate being heated), combination diffusion locks located upstream to the traps[2] with accompanying shut-off valves located in the trap exit line and ball and spring check valves[3] located upstream at the manifold with a downstream rotary fraction collection valve common to all trap exits (when so rotated) have been reported. However, in all of these cases single-pass collection only is used. Pressure actuating devices or rotary valves located downstream to the trap prevent trap removal until after all components are collected.

In the present work a new high-temperature manifold and trapping assembly is described. This assembly prevents:

(*1*) sample condensation losses through the use of second-pass traps;

(*2*) hot and cold spots which cause both degradation and condensation in inlet and/or outlet manifolds, since both are separately heated with demand heating and continuous temperature readout;

(*3*) leak problems in switching valves through the design of new stainless steel valves without dead space or flow restriction;

(*4*) aerosol losses, especially frozen aerosols that emerge from the exit of the first-pass trap by converting them to vapor, before entering the second-pass trap.

In addition, two different traps may be simultaneously used to collect a single component which has the effect of reducing the flow velocity by 50% and increasing the collection efficiency. It has also been found desirable to use different trapping coolants in the first- and second-pass traps such as combinations of ice water and liquid nitrogen.

EXPERIMENTAL

A block diagram of the manifold is shown in Fig. 1*. In operation the manifold functions as follows. The gas stream enters the inlet manifold immediately adjacent to the blocked portion of the ring and, with continuous flushing, flows in sequence through all of the inlet valves to emerge at the opposite extremity of the inlet line blocked portion. It then enters the line and valve common to the inlet and outlet manifolds and thence into the outlet loop of the manifold assembly. Here the gas stream enters adjacent to the blocked portion of the outlet manifold and, with continuous flushing, flows in sequence through all of the outlet valves and finally out of the outlet loop at the opposite extremity of the blocked portion.

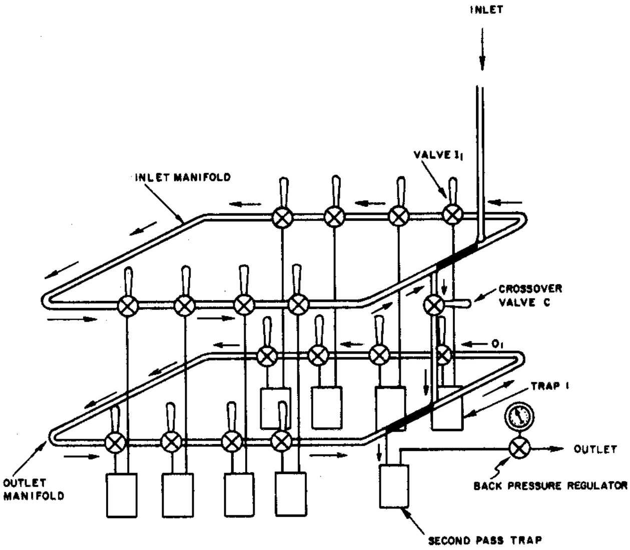

Fig. 1. Dual manifold and trap assembly.

The gas stream now enters the inlet of a second-pass trap, passes through the trap and exits through a back-pressure regulator, before entering either a recycle gas cleanup and compressor, or being vented to a suitable source. In this mode of operation, the sample is passing through the second-pass trap only. This flow path is normally used where the sample is injected to examine the preparative trace before selecting the cut points for component separation. The sample is then removed from the second-pass trap and is reinjected to be fractionated. This flow path is used between each fraction collected to sweep all traces of the previous component continuously through the valves and manifolds and into the second-pass trap.

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* Patent pending.

The trap inlet and outlet manifold are separately heated and controlled (with continuous temperature readout, the crossover line with Valve C is heated with the inlet manifold) at a constant pre-selected temperature. Operating temperatures will vary with both carbon number and functional groups of the components (if known). Nine traps are employed, thus eight separate components can be collected, the ninth trap being used as the second-pass trap.

In practice when it is desired to collect the first fraction, trap inlet valve I_1 and trap outlet valve O_1 are opened and crossover valve C is closed, in that order. The flow path through trap 1 is then open where the first component is collected. Upon emerging from the trap, the flow enters the outlet manifold and continues through the second-pass trap.

Different versions of glass traps used are shown in Fig. 2. Small samples (0.1–1 ml) or the collection of small components necessitate the use of traps with a high surface area and low volume. A trap of this type (with overlapping Vigreaux indentations) is shown with the fitting attachments. The extreme right side of the trap wall is smooth to allow for insertion of a capillary needle for sample withdrawal. Glass

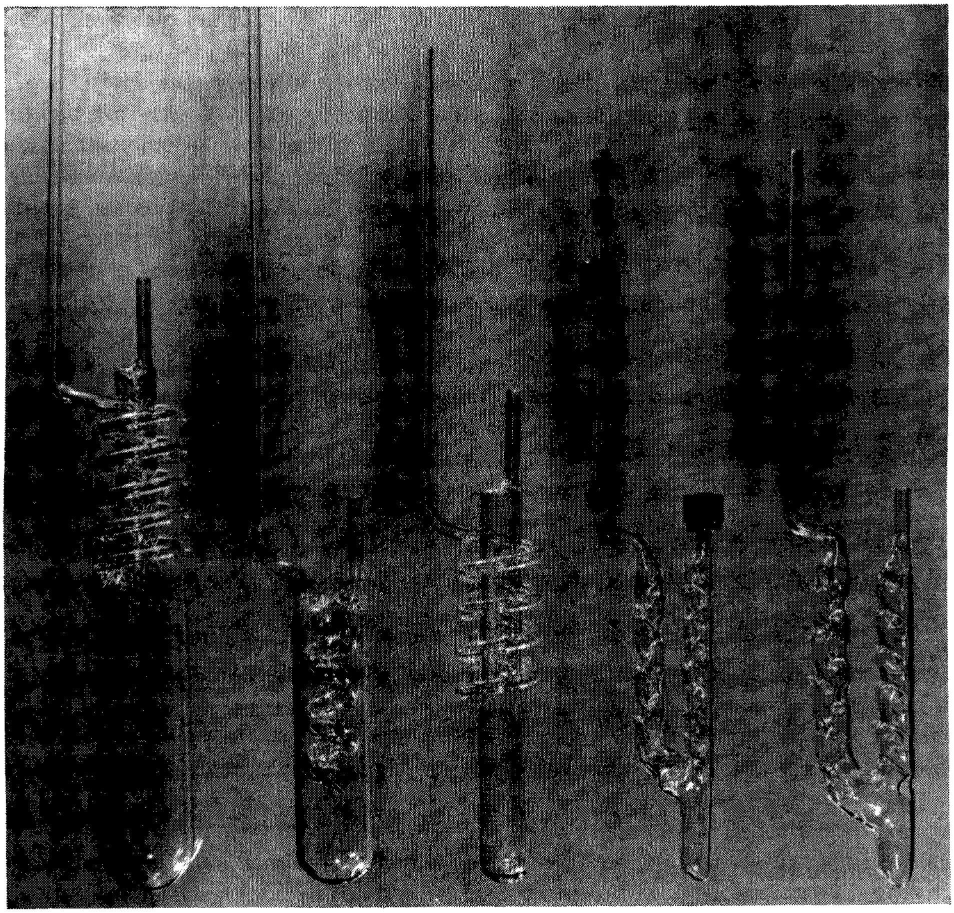

Fig. 2. Different designs of glass trap.

traps of this type are only used on the typical low-volume multicomponent sample. When larger samples (hundreds of ml) are available and a maximum yield of components is desired, the stainless-steel, all-metal trap shown in Fig. 3* is used.

Figures 4 and 5 show the modified 411 series Hoke valves used for high tempe-

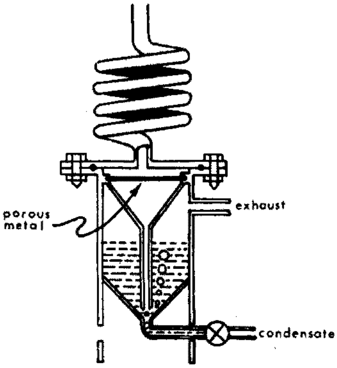

Fig. 3. Stainless steel trap.

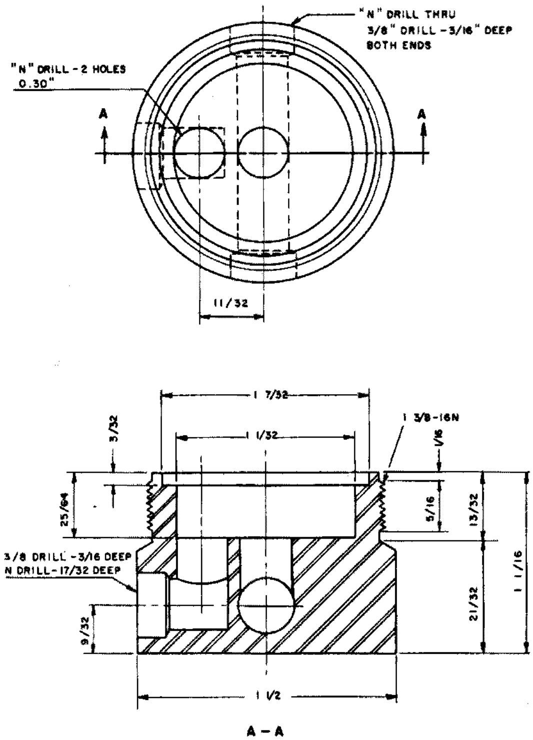

Fig. 4. Modified Hoke stainless steel valve.

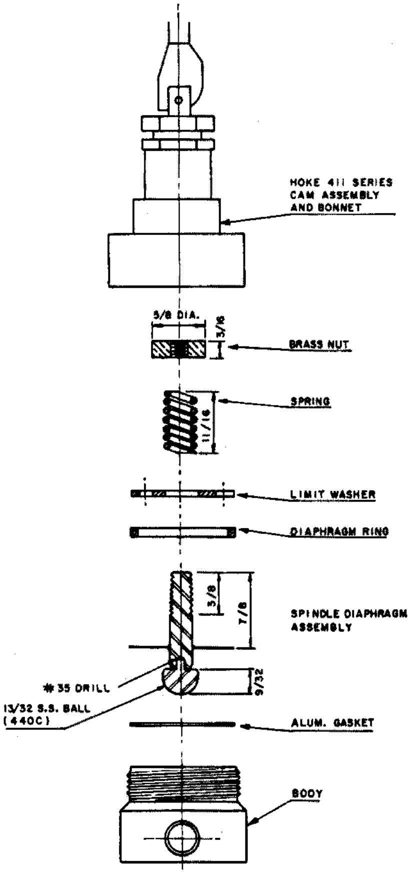

Fig. 5. Bonnet assembly.

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* Patent #3,315,736.

ratures in the manifold assembly. The valve body shown in Fig. 4 is fabricated completely from bar stock 303 stainless steel. Inlet and outlet ports were enlarged from the standard 1/8 to 0.30 in. The outlet port was relocated so that its outer periphery was tangential to the inner wall of the valve chamber body surrounding the stem. In this location the valve is *self draining*. This feature is especially needed when the manifolds are flushed with cleaning solvent. Valve positioning in the manifolds is such that, by simple liquid gravity drain, followed by a slight dry gas flow, removal of solvent traces is easily affected. Figure 5 shows the purchased bonnet assembly. The main revision is the spindle diaphragm assembly where a 13/32 stainless steel ball is used to replace the smaller tapered seat.

The assembled valve has the same high-temperature features of the standard 411 series valves, since an aluminum gasket is used for the bonnet body seal; there is no flow restriction when the valve is joined to a 3/8-in OD stainless steel line and the assembly is self-draining for liquids. The orifice diameter is needed to conform to the internal diameter of 3/8-in connecting lines used in 4- and 6-in diameter preparative GLC columns.

DISCUSSION AND RESULTS

Of the two types of aerosols, solid or liquid, the solid type is much more difficult to retrieve. Since coolants such as liquid nitrogen are commonly used in sample trapping (especially with glass traps) solid aerosol formation results. With the manifold system shown in Fig. 1, aerosols that develop in the first-pass traps emerge into the heated outlet manifold where they are converted to vapor before entering the second-pass trap located at the pressure regulator. Thus sample loss due to aerosol formation is small with this manifold system.

Hot and cold spots are also eliminated since both manifolds are provided with separate controlled demand heating, continuous temperature readout and adequate insulation. Degradation of many organic molecules in line and manifold assemblies can be reduced or eliminated by simply reducing the line or manifold temperature. The ability to remove any first-pass traps during the collection of the components makes it possible to begin immediately the examination of the purified collected fractions to ascertain whether the temperatures and general operating conditions are correct.

The collection efficiency of traps, especially glass traps, varies with the type of coolant used, the freezing point of the component (to some degree) and the type of organic compound. The average collection efficiency of the glass traps shown in Fig. 2 is 75–85% for single pass collection. The dual manifold described in this paper will, however, increase this efficiency to 90%+ since 60–75% of the material lost through the first-pass trap is collected by the second-pass trap. These data are shown in Tables I and II.The efficiency may be increased even further by simultaneous collection of a component in two of the first-pass traps. This increase is due to a 50% reduction in the velocity of the carrier gas through the trap since the same rate of flow is now directed through two traps instead of one.

The stainless steel trap shown in Fig. 3 has a much higher collection efficiency than glass traps have. However, when these traps are used it is undesirable to collect the component other than in the liquid state. Therefore, the coolant used here will normally vary from warm water to ice water. When solidification upon condensation

TABLE I

DATA FOR C_{11}–C_{13} HYDROCARBONS[a]

(Traps, 100 ml glass; sample type, normal C_{11}, C_{12}, C_{13} hydrocarbons; sample volume, 150-ml single injection; number of traps second pass, one; carrier gas, N_2)

Wt. charged (g)	*Wt. recovered (g)*				*% Recovered*		
	Three first-pass traps	*Coolant*	*One second-pass trap*	*Coolant*	*First pass*	*Second pass*	*Total recovery*
110.7	89.0	Ice H_2O	9.2	Ice H_2O	80.4	8.3	88.7
111.2	92.5	Ice H_2O	9.2	Ice H_2O	83.2	8.3	91.5
110.2	90.6	Ice H_2O	14.0	Liq N_2	82.4	12.7	95.1
111.5	86.5	Ice H_2O	15.5	Liq N_2	77.6	13.9	91.5

[a] Purity of individual C_{11}, C_{12}, C_{13} fractions from first-pass traps is 99.9+%.

TABLE II

DATA FOR C_{11}–C_{13} HYDROCARBONS

	Amount recovered (g)	*Coolant*
First fraction (single traps)	2.4	Ice H_2O
Second fraction (single traps)	11.9	Ice H_2O
Secondary trap	1.8	Ice H_2O
Total recovered (g)	16.1	
Total charged (g)	18.8	
% Recovery	85.6	
First fraction (double traps)	4.4	Ice H_2O
Second fraction (double traps)	10.5	Ice H_2O
Secondary trap	1.7	Ice H_2O
Total recovered (g)	16.6	
Total charged (g)	18.8	
% Recovery	88.30	
First fraction (double traps)	4.2	Ice H_2O
Second fraction (double traps)	11.3	Ice H_2O
Secondary trap	2.1	Liquid N_2
Total recovered (g)	17.6	
Total charged (g)	18.7	
% Recovery	94.12	

is suspected, the fritted disc and packing in the down-coming tube are removed to prevent plugged flow. In ideal situations, such as a C_{11}, C_{12}, C_{13} hydrocarbon mixture with an ice water coolant, collection efficiencies of 99+% are obtained with the stainless steel traps with single-trap collection only. An insignificant amount is condensed in the second-pass trap. However, the second-pass stainless steel trap will always decrease the amount of sample lost or unrecoverable through aerosol formation.

SUMMARY

A dual manifold preparative GLC trap assembly is described. The design provides a second-pass trap for increased sample recovery. There is a reduction in component loss by aerosol breakup (vaporization) before entry to the second-pass

trap. The reduction in gas velocity by dual trap collection of single components results in increased trapping efficiency. Isolation for separate heat control of the hot incoming trap inlet gases and the cool trap outlet gases for continuous temperature readout results in a minimum of thermal degradation of purified sample.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ELECTROCHROMATOGRAPHIC SEPARATION OF METAL IONS ON TIN(IV) PHOSPHATE PAPERS

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(Received November 16th, 1967)

Electrochromatography of metal ions has been extensively investigated in order to achieve difficult separations and to separate one metal ion from numerous metal ions[1-6]. If, however, ion exchange is combined with electrophoretic migration, more interesting results are obtained and the potential of this technique increases. Some studies in this direction have shown the superiority of this approach[7-10]. Very little electrochromatographic work on paper impregnated with synthetic inorganic ion exchangers seems to have been reported[11]. In the present report, electrochromatographic studies on tin(IV) phosphate papers are described.

EXPERIMENTAL

Apparatus

Electrochromatography was performed on Whatman No. 1 paper, of 36 × 2.75 cm, with a hanging-strip apparatus (Shandon, Ltd., London).

Reagents

Chemicals and solvents used were either E. Merck (Darmstadt) or British Drug House analytical-grade reagents. Tin(IV) chloride pentahydrate and diammonium hydrogen phosphate were Polish products.

Preparation of ion-exchange papers. Ion-exchange papers were prepared as reported earlier[12].

The paper strips were placed in 0.5 *M* tin(IV) chloride for 3 sec. Excess of reagent was removed by blotting and the strips were then placed in 1.0 *M* diammonium hydrogen phosphate for 5 sec. The strips were again blotted and then dried at room temperature. After 1–2 h, they were washed twice with water of pH 5 and again dried.

Test solutions and detection reagents. These were prepared and used as described previously[12]. The test solutions were generally 0.1 *M* in the metal nitrate or chloride. Conventional spot-test reagents were used for detection purposes[12].

Background electrolyte solutions. Twelve aqueous background electrolyte solutions were used in this study: 0.1 *M* nitric acid, 0.5 *M* nitric acid, 0.5 *M* hydrochloric acid, 1.0 *M* hydrochloric acid, 1 *M* hydrochloric acid + 1 *M* orthophosphoric acid (1:1), 2 *M* hydrochloric acid + 2 *M* orthophosphoric acid (1:1), 0.05 *M* citric acid, 0.1 *M* ammonium carbonate, 0.1 *M* ammonium chloride, 0.1 *M* perchloric acid, 1 *M* nitric acid + 5% tartaric acid (1:1), 1 *M* nitric acid + 5% potassium nitrate (1:1).

TABLE I

MOVEMENTS OF IONS IN DIFFERENT ELECTROLYTES (IN cm)

Ions	1 M HCl + 1 M H_3PO_4 (1:1)[a]	2 M HCl + 2 M H_3PO_4 (1:1)[a]	0.1 M $HClO_4$[b]	0.05 M citric acid[b]	0.1 M NH_4Cl[b]	0.1 M HNO_3	0.1 M HNO_3 + 5% tartaric acid[d]	0.1 M HNO_3 + 5% KNO_3[d]	0.5 M HCl[c]
Ag^+	0.0	0.0	0.0	0.0	0.0	−0.5	0.0	0.0	0.0
Pb^{2+}	0.0	0.0	0.0	0.0	0.0	0.0	−1.9	0.0	0.0
Hg_2^{2+}	+1.2	+1.2	0.0	0.0	0.0	0.0	0.0	+0.7	+1.2
Hg^{2+}	+3.0	+1.7	0.0	−0.7	+7.0	0.0	+2.2	+2.5	+2.9
Tl^+	+0.5	+0.6	−3.2	−2.2	−2.0	−1.2	−1.5	−2.8	0.0
Bi^{3+}	+1.3	+1.2	0.0	0.0	0.0	0.0	0.0	0.0	+1.2
Cd^{2+}	0.0	+3.3	−1.3	−0.7	−1.0	0.0	−5.2	−2.0	+1.1
Cu^{2+}	−0.7	0.0	−1.0	−0.7	0.0	0.0	−2.1	−1.4	0.0
As^{3+}	0.0	0.0	−0.7	−2.0	0.0	−1.5	0.0	0.0	0.0
Sb^{3+}	+0.6	0.0	0.0	−0.5	0.0	0.0	0.0	0.0	0.0
Ni^{2+}	−0.8	−1.1	−1.7	−1.3	−4.2	0.0	−2.5	−3.2	−1.5
Co^{2+}	−0.7	−1.4	−1.8	−1.0	−3.0	0.0	−3.1	−3.3	−1.2
Mn^{2+}	−0.9	−5.3	−1.1	−0.8	−0.9	−0.7	−4.4	−2.8	+4.6
Fe^{2+}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fe^{3+}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Al^{3+}	−0.6	−0.5	0.0	0.0	0.0	0.0	−0.8	−0.7	−1.0
Cr^{3+}	−1.8	−2.1	−1.0	0.0	−2.0	0.0	−3.2	−3.4	−1.8
Zn^{2+}	+0.8	−1.0	−1.0	−1.0	0.0	0.0	−4.2	−1.8	−0.8
La^{3+}	+1.0	0.0	0.0	0.0	0.0	−0.7	0.0	0.0	0.0
Ce^{3+}	+0.8	0.0	−1.2	0.0	0.0	0.0	0.0	0.0	0.0
Ce^{4+}	+0.6	0.0	0.0	0.0	0.0	−1.0	0.0	0.0	0.0
UO_2^{2+}	+0.8	+0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
V^{4+}	0.0	0.0	0.0	0.0	0.0	0.0	−0.9	−1.0	0.0
Te^{4+}	0.0	0.0	0.0	0.0	−0.7	0.0	0.0	0.0	0.0

Mo^{6+}	0.0	+1.0	0.0	+3.1	0.0	0.0	+0.8	0.0	0.0
Pd^{2+}	+3.0	+2.0	0.0	−1.5	+5.0	−1.7	+2.9	+3.2	+1.2
Pt^{4+}	+1.5	+0.3	+3.0	+4.5	—	+2.8	+2.9	+2.5	+2.1
Y^{3+}	0.0	−0.7	−0.8	0.0	0.0	0.0	−0.8	0.0	0.0
Au^{3+}	+1.4	+0.5	−0.7	+1.7	0.0	0.0	0.0	+1.0	+1.0
Ti^{4+}	+0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ga^{3+}	−1.5	0.0	−0.9	0.0	0.0	0.0	0.0	0.0	0.0
K^{+}	−3.2	−1.8	−8.5	−13.1	−8.5	−4.8	−3.2	−9.4	−4.1
Rb^{+}	−3.2	−4.2	−9.6	−9.1	−9.8	—	−4.5	−6.6	−2.7
Cs^{+}	−3.2	−3.3	−9.8	−9.8	−10.3	−4.6	−5.0	−6.7	−3.0
Ba^{2+}	−1.4	−2.5	−4.8	−1.6	−7.0	0.0	−1.2	−3.3	−0.8
Sr^{2+}	−3.8	−2.5	0.0	−3.2	−6.0	−0.5	−3.5	−5.2	−0.7
Ca^{2+}	−3.2	0.0	0.0	−3.1	0.0	−0.6	0.0	0.0	−1.7
Mg^{2+}	−2.0	+1.7	0.0	—	0.0	0.0	0.0	0.0	−1.2
Be^{2+}	+0.6	0.0	0.0	0.0	0.0	−1.0	0.0	0.0	—
Zr^{4+}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Th^{4+}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	+0.6
In^{3+}	0.0	−1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ru^{3+}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ir^{4+}	0.0	−0.5	0.0	0.0	−1.5	0.0	0.0	0.0	—
Nb^{5+}	0.0	0.0	−0.9	—	0.0	—	−1.0	0.0	—
W^{6+}	+0.5	+0.6	0.0	+3.4	0.0	—	+1.0	0.0	0.0
Hf^{4+}	—	—	0.0	0.0	+2.7	—	−1.0	0.0	—
Se^{4+}	—	+0.7	−0.9	0.0	0.0	—	0.0	0.0	—

[a] = 40 V applied potential, 3 h.
[b] = 100 V applied potential, 8 h.
[c] = 100 V applied potential, 3 h.
[d] = 40 V applied potential, 8 h.
[e] = 50 V applied potential, 3 h.

TABLE II

SEPARATIONS ACTUALLY ACHIEVED ON TIN(IV) PHOSPHATE PAPERS BY ELECTROCHROMATOGRAPHY

Background electrolyte	*Electrical potential applied*	*Separations actually achieved*	
0.5 *M* HCl	50 V, 3 h	Cr^{3+} from binary mixtures with	Ag^+, Hg^{2+}, Tl^+, Bi^{3+}, Cd^{2+}, Sb^{3+}, Fe^{2+}, Fe^{3+}, Pt^{4+}
0.1 *M* HNO_3	100 V, 8 h	Tl^+ from binary mixtures with	Ag^+, Pb^{2+}, Hg_2^{2+}, Hg^{2+}, Bi^{3+}, Cd^{2+}, Cu^{2+}, Sb^{3+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Zr^{4+}, In^{3+}
0.1 *M* NH_4Cl	100 V, 8 h	Hg^{2+} from binary mixtures with	Bi^{3+}, Cd^{2+} and Cu^{2+}
		Ni^{2+} from binary mixtures with	Ag^+, Cu^{2+}, Fe^{3+}, Al^{3+}, Zn^{2+}
		K^+ from binary mixtures with	V^{4+}, Ca^{2+} and Mg^{2+}
			(K^+–Al^{3+}–Tl^+)
			(K^+–Fe^{3+}–Co^{2+})
		Cs^+ from binary mixtures with	Mg^{2+}
		Tl^+ from binary mixtures with	Hg^{2+}, Al^{3+}
		Fe^{3+} from binary mixtures with	Mn^{2+}
1 *M* HCl + 1 *M* H_3PO_4 (1:1)	40 V, 3 h	Cr^{3+} from binary mixtures with	Fe^{3+}, Al^{3+}, Zn^{2+}
		Zn^{2+} from binary mixtures with	Al^{3+}
		K^+ from binary mixtures with	Fe^{3+}, V^{4+}, Ti^{4+}, Mo^{6+}
		Sr^{2+} from binary mixtures with	Ba^{2+}, Ca^{2+}, Mg^{2+}, Y^{3+}, Be^{2+}
0.1 *M* $HClO_4$	100 V, 8 h	Ba^{2+} from binary mixtures with	La^{3+}, Sr^{2+}, K^+, Rb^+, Ca^{2+}, Mg^{2+}, Be^{2+}
		Tl^+ from binary mixtures with	Ag^+, Al^{3+}
		K^+ from binary mixtures with	Zr^{4+}
			(K^+–Ba^{2+}–Sr^{2+})
2 *M* HCl + 2 *M* H_3PO_4 (1:1)	40 V, 8 h	Tl^+ from binary mixtures with	Bi^{3+}, Cu^{2+}, Zn^{2+}
		Cd^{2+} from binary mixtures with	Cu^{2+}, Fe^{3+}, Zn^{2+}
		Fe^{3+} from binary mixtures with	Co^{2+}
		Mn^{2+} from binary mixutres with	Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Cr^{3+}
		UO_2^{2+} from binary mixtures with	Tl^+, Co^{2+}, Fe^{3+}, V^{4+}
		Ba^{2+} from binary mixtures with	Ca^{2+}, Mg^{2+}
		Sr^{2+} from binary mixtures with	Ca^{2+}
			(Au^{3+}–Pd^{2+}–Cu^{2+})
1 *M* HNO_3+ 5% tartaric acid	40 V, 8 h	Cd^{2+} from binary mixtures with	Pb^{2+}, Cu^{2+}, Bi^{3+}, As^{3+}
		Zn^{2+} from binary mixtures with	Fe^{3+}, Al^{3+}, Ba^{2+}, Ca^{2+}, Mg^{2+}
0.05 *M* citric acid	100 V, 8 h	K^+ from binary mixtures with	Ba^{2+}, Sr^{2+}, Ca^{2+}, Cr^{3+}
		Rb^+ from binary mixtures with	Ba^{2+}, Sr^{2+}, Ca^{2+}, Cr^{3+}
		Cs^+ from binary mixtures with	Sr^{2+}, Ca^{2+}
		Cr^{3+} from binary mixtures with	K^+, Rb^+
1 *M* HNO_3+ 5% KNO_3	40 V, 8 h	Tl^+ from binary mixtures with	Ag^+, Hg_2^{2+}
		Cd^{2+} from binary mixtures with	Hg_2^{2+}, Bi^{3+}, Sb^{3+}, As^{3+}
		Co^{2+} from binary mixtures with	Fe^{3+}, Pd^{2+}, Mo^{6+}
		Ni^{2+} from binary mixtures with	Ag^+, Fe^{3+}
		Fe^{3+} from binary mixtures with	Cr^{3+}
		Cr^{3+} from binary mixtures with	Al^{3+}, Zn^{2+}, UO_2^{2+}
		Pt^{4+} from binary mixtures with	Cu^{2+}, Sb^{3+}, UO_2^{2+}, Au^{3+}, Ru^{3+}, Ir^{4+}
			(Cu^{2+}–Au^{3+}–Pt^{4+})

Procedure

The electrophoresis apparatus was filled to the mark with background electrolyte and tin(IV) phosphate ion-exchange paper strips, which formed the stabilization medium, were placed in position and allowed to become saturated with the electrolyte. Then a small drop (0.02 ml) of the test solutions containing $2 \cdot 10^{-6}$ moles of the ion was applied separately on each strip in the middle with the help of thin glass capillaries. The time of migration and the potential applied is specified in each case (see Tables). The migration of zones of ions towards anode or cathode was measured from the point of application upto the middle of the zone. On the basis of the results of exploratory experiments and distances of electrical migration of the zones of individual ions, synthetic mixtures of particular ions containing $2 \cdot 10^{-6}$ moles of each ion were prepared and were applied as in the case of individual ions for separation.

RESULTS AND DISCUSSION

As a result of this electrochromatographic study on tin(IV) phosphate ion-exchange papers and with the use of suitable background electrolytes and appropriate potential, a large number of separations was found feasible. The results are described under two heads (*i*) ionic movements in different electrolytes (Table I), and (*ii*) separations actually achieved (Table II). In Table I, the movements of ions towards the anode and cathode are shown respectively by a positive and a negative sign, while ions which do not show movement are marked as 0.0.

A cursory inspection of the results of movements of ions recorded in Table I reveals that a number of interesting and difficult separations are possible. To mention a few, Tl^+, Hg^{2+}, As^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+}, Zn^{2+}, Mo^{6+}, W^{6+}, Pd^{2+}, Pt^{4+}, Au^{3+}, Ba^{2+}, Sr^{2+}, K^+, Rb^+, Cs^+, etc., can be separated from numerous metal ions. This is probably due to the high selectivity shown by the ion exchanger and the background electrolytes. The metal ions were separated as a result of opposite migration or differential migration. Experimental support for some of the separations suggested by the results recorded in Table I was obtained by carrying out various representative and selective separations (Table II). It was found possible to separate chromium(III) from binary mixtures with potassium and rubidium when 0.05 *M* citric acid was used as electrolyte. Both binary and ternary separations were feasible.

The results show that electrochromatography on tin(IV) phosphate papers has many interesting possibilities of analytical importance. Thus Cd^{2+}, Cr^{3+}, Ba^{2+} and Sr^{2+} can be easily separated from numerous metal ions. Some difficult binary and ternary separations, *e.g.*, Fe^{3+}–Cr^{3+}, Pt^{4+}–Ru^{3+}–Cu^{2+}, Au^{3+}–Pd^{2+}–Cu^{2+}, and Sr^{2+}–Ba^{2+} are easily achieved.

The authors are grateful to A. R. KIDWAI for the facilities provided. One of us (A.H.I.) also thanks HAKIM ABDUL HAMEED, President, Institute of History of Medicine and Medical Research, New Delhi, for his interest and encouragement.

SUMMARY

Electrochromatographic separations on tin(IV) phosphate papers in 12 background electrolytes are described. Migration distances for 48 ions are given. Many binary as well as ternary separations are readily achieved, *e.g.* Fe–Cr, Sr–Ba, Pt–Ru–Cu and Au–Pd–Cu.

RÉSUMÉ

On décrit des séparations électrochromatographiques sur papiers au phosphate d'étain(IV) avec 12 électrolytes de base différents. On donne les distances de migration de 48 ions. De nombreuses séparations binaires et ternaires sont ainsi possibles, par exemple: Fe–Cr, Sr–Ba, Pt–Ru–Cu et Au–Pd–Cu.

ZUSAMMENFASSUNG

Es werden elektrochromatographische Trennungen auf Zinn(IV)-Phosphat-Papieren unter Verwendung von 12 Grund-Elektrolyten beschrieben. Die Wanderungsabstände für 48 Ionen werden angegeben. Viele binäre als auch ternäre Trennungen gelingen schnell, z.B. Fe–Cr, Sr–Ba, Pt–Ru–Cu und Au–Pd–Cu.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

THE QUANTITATIVE SEPARATION OF CALCIUM FROM MAGNESIUM, ALUMINIUM AND OTHER ELEMENTS BY CATION-EXCHANGE CHROMATOGRAPHY IN ETHANOL–HYDROCHLORIC ACID

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(Received December 4th, 1967)

Several papers have appeared on the separation of calcium and magnesium by ion-exchange chromatography. The separation can be carried out on a cation-exchange resin merely by eluting the magnesium with about 1 *M* hydrochloric acid, while the calcium is retained and eluted with 3 *M* hydrochloric acid[1,2]. Separation is satisfactory, but only limited amounts (≤ 5 mg) of each element can be present; for larger amounts the elution peaks tend to overlap[1]. The separation factor $\alpha_{Mg}{}^{Ca}$ is only 2.0[3] and fairly large elution volumes (600 ml for magnesium) are required. For enhanced separation complexing agents such as the ammonium salts of formate[4], acetate[5], malonate[6], acetylacetonate[7] and EDTA[8] (this elutes calcium first) have been used as eluants in cation-exchange and ammonium citrate[9] in anion-exchange chromatography. Common volatile inorganic acids seem to be more convenient because the treatment and analysis of the eluate is easier in most cases.

NELSON *et al.*[10] have found large separation factors for the Ca–Mg pair in 9 *M* perchloric or perchloric–hydrochloric acid mixtures and have used 6.4 *M* perchloric acid plus 2.6 *M* hydrochloric acid for the elution of magnesium from a column of Dowex 50-X4 resin. The high concentration of perchloric acid is inconvenient for further analytical work and exchange rates also are reduced considerably.

FRITZ AND WAKI[11] have separated calcium from magnesium by anion exchange in nitric acid–alcohol mixtures. The separation factor is favourable, but exchange rates are rather slow and the evaporation of nitric acid–alcohol mixtures presents problems. Furthermore, of the elements investigated, cadmium, copper and cobalt are not separated from calcium, while the separation of nickel is not satisfactory.

TANAKA[12] has investigated the use of methanolic hydrochloric acid as an eluting agent for the alkaline earth elements, but suggests 0.7 *M* hydrochloric acid as eluting agent for magnesium from a cation-exchange resin. KORKISCH AND AHLUWALIA[13] have undertaken a systematic study of the cation-exchange behaviour of 20 elements including calcium and magnesium in organic solvent–hydrochloric acid media covering the acidity range from 0.15 to 1.2 *M*; from their results they conclude that a separation of magnesium from calcium would be rather difficult.

Because the hydration shells around the calcium and magnesium ions are rather stable, it was considered that a breakdown of the hydration structure around the calcium ion, which leads to a selective increase of the distribution coefficient, should take place at fairly high organic solvent concentrations. A fairly high concentration of hydrochloric acid, therefore, should be present to keep the coefficient of magnesium at a reasonably low value.

A systematic study of the equilibrium distribution coefficients of calcium, magnesium and other elements was, therefore, undertaken in this laboratory covering the ranges from 0.1 to 4 M hydrochloric acid and from 0 to 80% ethanol. Some coefficients in methanol, acetone, dioxane and tetrahydrofuran also were determined, together with coefficients in aqueous and ethanolic hydrochloric acid for a 12% cross-linked resin. The results showed that with increasing concentration of the organic solvent the coefficients for calcium increased considerably faster than those for magnesium. An excellent separation of calcium from magnesium with a separation factor of $\alpha_{Mg}{}^{Ca}=5.6$ (*ca.* 8 for trace amounts) and a reasonably low distribution coefficient for magnesium ($D=12.3$) was obtained in 3 M hydrochloric acid containing 60% ethanol.

EXPERIMENTAL

Reagents and apparatus

Analytical-reagent-grade chemicals were used whenever possible. For the quantitative analysis of synthetic mixtures, ethanol and A.R. grade hydrochloric acid were purified by redistillation. The resins AG50W-X8 and AG50W-X12 (Bio-Rad Laboratories, Richmond, California) are equivalent to the Dowex 50 resins of the same designations. Borosilicate glass tubes of about 20 mm inner diameter, fitted with a glass sinter of No. 2 porosity and a stopcock at the bottom and a B19 ground-glass joint at the top were used as columns. A Perkin Elmer 303 atomic absorption spectrophotometer was used for the measurement of small amounts of calcium, magnesium and some other elements (elution curves).

Distribution coefficients

Distribution coefficients were determined by the batch method using 2.500 g of resin (dry weight at 105°) in the hydrogen form, a total volume of 250 ml solution, 5 meq (exchange equivalents = moles · valency) of the element and a shaking time of 24 h at 20°.

Table I shows coefficients in hydrochloric acid with AG50W-X12 resin which have not been published previously and for comparison includes redetermined coefficients with the 8% cross-linked resin. Magnesium has very similar coefficients

TABLE I

DISTRIBUTION COEFFICIENTS IN HYDROCHLORIC ACID

Molarity of HCl	*AG50W-X8*		*AG50W-X12*	
	Mg	*Ca*	*Mg*	*Ca*
0.1	810	1900	710	2200
0.2	281	580	260	650
0.5	67	131	60	147
1.0	20.2	40.8	19.9	49.5
2.0	6.2	12.2	5.8	16.4
3.0	4.0	7.4	3.5	8.9
4.0	2.9	5.1	2.7	5.9

with both resins, while calcium shows a definite increase at the higher cross-linkage. This leads to an increased separation factor for the Ca–Mg pair, $\alpha_{Mg}{}^{Ca} = 2.7$ in 1.50 *M* hydrochloric acid.

Table II presents coefficients with AG50W-X8 resin for magnesium and calcium at various concentrations of hydrochloric acid and ethanol; and Table III coefficients for magnesium and calcium in 3 *M* hydrochloric acid containing various amounts of methanol, acetone, dioxane, tetrahydrofuran and ethanol, the last results being obtained with AG50W-X12 resin. The coefficients for calcium increase considerably faster with increasing concentrations of the organic solvent than those for magnesium. About 3 *M* hydrochloric acid containing 60% ethanol, acetone or dioxane provides coefficients favourable for a good separation and a high separation factor. The 5 organic solvents show only minor differences in their effects on the coefficients. Increasing the cross-linkage to 12% further increases the separation factor but reduces the rate of exchange.

TABLE II

DISTRIBUTION COEFFICIENTS IN ETHANOL (AG50W-X8 RESIN)

% Ethanol	*1 M HCl*		*2 M HCl*		*3 M HCl*		*4 M HCl*	
	Mg	*Ca*	*Mg*	*Ca*	*Mg*	*Ca*	*Mg*	*Ca*
0	20.2	40.8	6.2	12.2	4.0	7.4	2.9	5.1
10	18.5	45.8	6.4	13.5	3.8	7.5	2.8	5.4
20	19.3	55	7.2	16.3	3.7	8.4	2.7	6.0
30	23.9	73	9.0	21.7	4.5	11.1	3.2	8.0
40	33.0	106	12.1	31.7	5.9	17.2	4.8	14.8
60	71	310	23.8	89.9	12.3	69	—	—
70	—	—	36.2	202	—	—	—	—
80	166	1570	—	—	—	—	—	—

TABLE III

DISTRIBUTION COEFFICIENTS IN 3.00 *N* HYDROCHLORIC ACID WITH VARIOUS ORGANIC SOLVENTS

% Solvent	*Methanol*		*Acetone*		*Dioxane*		*Tetrahydrofuran*		*Ethanol*[a]	
	Mg	*Ca*	*Mg*	*Ca*	*Mg*	*Ca*	*Mg*	*Ca*	*Mg*	*Ca*
20	4.2	10.4	4.1	8.8	4.7	10.2	3.9	9.9	3.6	12.8
30	4.7	12.9	4.4	11.6	5.0	13.0	4.3	12.5	4.0	16.9
40	5.5	18.1	5.0	18.4	6.2	20.8	5.5	17.7	5.7	29.4
60	9.0	52.9	11.3	77.7	9.7	74.3	9.7	50.3	13.9	108

[a] AG50W-X12 resin.

Elution curves

Experimental elution curves were prepared for binary mixtures containing calcium and either magnesium or one other element. Figure 1 shows an elution curve for the calcium–magnesium pair, using a column of 10 g of AG50W-X8 resin; 25 ml of a solution containing 1 mmole of each element in 0.1 *M* hydrochloric acid were adsorbed on the column, and the elements were eluted with 3.00 *M* hydrochloric acid containing 60% ethanol.

Figure 2 shows a similar curve with a column of 23 ml (10 g) of AG50W-X12 resin. For comparison an elution curve with 1.50 *M* aqueous hydrochloric acid from a column of 46 ml (20 g) of the same resin also is presented (Fig. 3); the larger resin

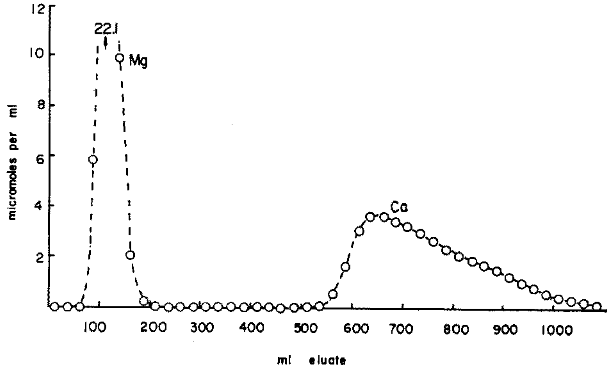

Fig. 1. Elution curve for Mg–Ca with 3.00 *M* hydrochloric acid in 60% ethanol. 30 ml AG50W-X8, 200–400 mesh, resin. Flow rate 1.8±0.3 ml/min. Column 2.0 cm i.d., 10 cm high. 1 mmole of each element.

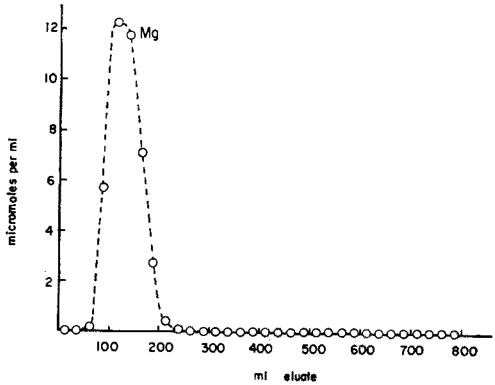

Fig. 2. Elution curve for Mg–Ca with 3.00 *M* hydrochloric acid in 60% ethanol. 23 ml AG50W-X12, 200–400 mesh, resin. Flow rate 1.5±0.3 ml/min. Column 1.9 cm i.d. 1 mmole of each element.

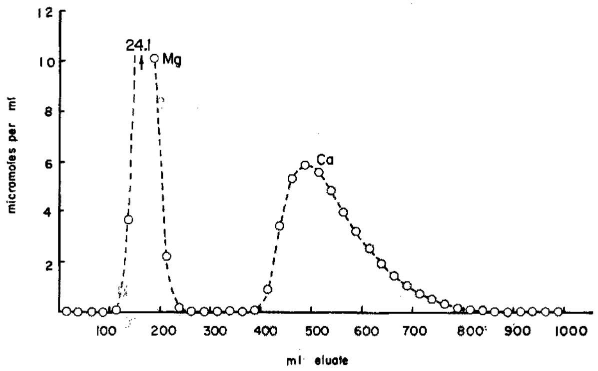

Fig. 3. Elution curve for Mg–Ca with 1.50 *M* hydrochloric acid. 46 ml AG50W-X12, 200–400 mesh, resin. Flow rate 2.5±0.3 ml/min. Column 1.9 cm i.d. 1 mmole of each element.

volume had to be used because separation of 1 mmole amounts was unsatisfactory on a 23-ml column, yet the separation shown on Fig. 3 is considerably better than that obtained by CAMPBELL AND KENNER[1] with Dowex 50-X8 resin. Figures 1 and 2 demonstrate the remarkable improvement obtained by using hydrochloric acid containing ethanol as eluant.

Since the fine resin has a high flow resistance which without application of additional pressure allows only relatively slow flow rates on a 30-ml column, a shorter column was tried out with the aim of reducing both separation time and elution volume. Figure 4 presents an elution curve with 3.00 *M* hydrochloric acid in 60% acetone from an 18-ml (6 g) column of AG50W-X8 resin. The column length was 6.0 cm and its diameter 2.0 cm. About 1 mmole of magnesium and 0.5 mmole of calcium were present, and the flow rate was 3.0±0.3 ml/min.

Figure 5 shows an elution curve for the Ca–Al pair using a column and conditions similar to those described for Fig. 1; 2 mmoles of aluminium plus 1 mmole of calcium were present.

Nickel, cobalt and manganese have elution curves almost similar to that of magnesium. Cu(II), Zn, Cd, Hg(II), Be, Fe(III), Ga, In, Tl(III), V(V), Mo(VI), U(VI) and Ti(IV) (in the presence of hydrogen peroxide) appear in the eluate ahead of magnesium.

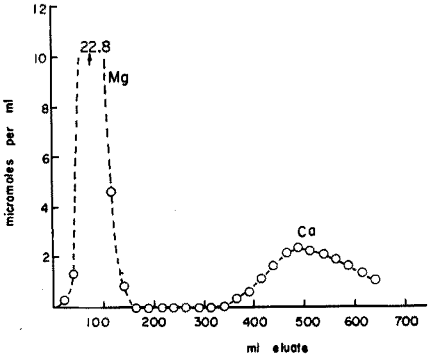

Fig. 4. Elution curve for Mg–Ca with 3.00 *M* hydrochloric acid in 60% acetone. 18 ml AG50W-X8, 200–400 mesh, resin. Flow rate 3.0±0.3 ml/min. Column 2.0 cm i.d. 1 mmole Mg + 0.5 mmole Ca.

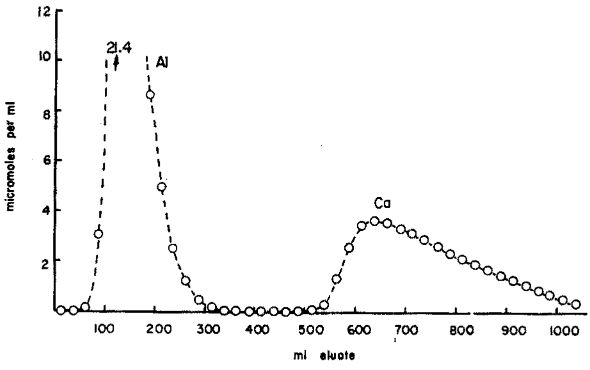

Fig. 5. Elution curve for Al–Ca with 3.00 *M* hydrochloric acid in 60% ethanol. 30 ml AG50W-X8, 200–400 mesh, resin. Flow rate 1.5±0.3 ml/min. Column 2.0 cm i.d. 2 mmole Al + 1 mmole Ca.

Quantitative separations of synthetic mixtures

From the foregoing a method was elaborated and applied to the analysis of synthetic mixtures containing known amounts of calcium and one other element (Table IV). The elements were absorbed from 0.5 *M* hydrochloric acid containing 60% ethanol on a column of 30 ml (10 g dry weight) of AG50W-X8 resin, 200–400 mesh, which had been equilibrated with a solution of the same hydrochloric acid and ethanol concentration. Mixtures with lead(II) were absorbed from 3 *M* hydrochloric acid containing 60% ethanol. The columns were about 10 cm long and 2.0 cm in diameter. The solutions were washed onto the resin with 0.5 *M* hydrochloric acid containing 60% ethanol. A column of about 2 cm of this solution was left on top of the resin to act as a buffer against disturbance of the resin by the concentrated eluant which can lead to "fingering" and premature break-through. Magnesium, iron(III) and other elements were eluted with 3.00 *M* hydrochloric acid containing 60% ethanol at the maximum flow rate attainable; normally this was about 2.0 ml/min. In the case of titanium(IV), 0.2% of 30% hydrogen peroxide also were present in the eluant. For aluminium, 400 ml of the eluant were used. The calcium then was eluted with 200 ml of 3.00 *M* hydrochloric acid at a flow rate of 3.0±0.3 ml/min. After the excess of acid and ethanol had been removed by evaporation, the elements were determined by compleximetric titration or conventional gravimetric methods. Small amounts of calcium and magnesium were determined by atomic absorption spectrometry on a Perkin Elmer 303 apparatus with an acetylene–air flame by means of the 4227 Å and 2852 Å lines, respectively. The experiment was carried out in triplicate or quadruplicate.

TABLE IV

RESULTS OF QUANTITATIVE SEPARATIONS

Taken (mg)			*Found (mg)*[a]	
Ca	*Other element*		*Ca*	*Other element*
40.49	Mg	24.42	40.49 ±0.02	24.40 ±0.03
80.98	Mg	2.44	81.01 ±0.04	2.45 ±0.02
4.05	Mg	122.1	4.06 ±0.02	122.0 ±0.2
404.9[b]	Mg	0.244	405.0 ±0.2	0.246±0.004
0.405[b]	Mg	244.2	0.403±0.006	244.2 ±0.1
40.49	Fe(III)	56.10	40.50 ±0.03	56.08 ±0.06
40.49	Ti(IV)	48.50	40.51 ±0.03	48.53 ±0.05
40.49	Al	55.12	40.51 ±0.02	55.20 ±0.12
40.49	Mn(II)	54.71	40.49 ±0.02	54.73 ±0.04
40.49	Ni(II)	58.58	40.50 ±0.02	58.55 ±0.06
40.49	Co(II)	59.61	40.51 ±0.03	59.63 ±0.07
40.49	Zn	66.05	40.51 ±0.02	66.07 ±0.03
40.49	Cd	113.1	40.50 ±0.02	113.2 ±0.1
40.49	Cu(II)	63.18	40.50 ±0.03	63.17 ±0.04
40.49	Pb(II)	205.4	40.49 ±0.03	205.5 ±0.1
40.49	U(VI)	238.3	40.51 ±0.03	238.4 ±0.2
40.49	Be	18.24	40.51 ±0.02	18.26 ±0.04
40.49	Ga	70.12	40.50 ±0.02	70.14 ±0.08

[a] The results are means of triplicate or quadruplicate experiments.
[b] Mg eluted with 450 ml of eluant from a 60-ml column.

DISCUSSION

The described method provides an excellent means for the separation of calcium from magnesium and also from many other elements which are not separated in aqueous hydrochloric acid, such as Al and Fe(III), or by anion exchange in ethanolic nitric acid, such as Cd, Cu(II) and Co(II)[11]. The separation factor $\alpha_{Mg}{}^{Ca}=5.6$ (*ca.* 8 for trace amounts) is considerably higher than the factor in aqueous hydrochloric acid ($\alpha_{Mg}{}^{Ca}=2.0$)[3] and is comparable to the separation factors in organic complexing agents[6]. Al, Fe(III), Mn(II), Ni(II), Co(II), Zn, Cd, Cu(II), Pb(II), U(VI), Be, Ga, and Ti(IV) in the presence of peroxide, accompany magnesium and can be separated from calcium quantitatively. The behaviour of Mo(VI), V(V), W(VI), Nb(V), In(III), Tl(III), Hg(II), Sn(IV), As(III), Sb(III), Bi(III), Se(IV), Te(IV), Au(III) and the platinum metals has not been investigated in detail, but these elements should be eluted together with magnesium according to their distribution coefficients. Tungsten(VI) and niobium(V) will require the presence of hydrogen peroxide to suppress hydrolysis. Lithium also accompanies magnesium quantitatively. The other alkali metals are eluted between magnesium and calcium. Sr, Ba, Zr, Hf, Th, Sc, La and the rare earths accompany calcium, but all these elements except strontium and barium are retained on a 60-ml (20 g) column of AG50W-X8 resin when calcium is eluted with 2.00 *M* nitric acid. Strontium and barium can be separated from calcium by cation exchange in ammonium malonate[6].

Separations are sharp and recoveries quantitative for up to more than 1 mmole of each element in a binary mixture on a 30-ml (10 g) column of AG50W-X8 resin. When a 60-ml column is used, 0.01 mmole of calcium can be separated from 10 mmole of magnesium and *vice versa*. Blank determinations on reagents and precautions against contamination by atmospheric dust are required for accurate results in this case.

Exchange rates are slower than those in purely aqueous solutions, but faster than those for anion exchange in nitric acid containing 90% ethanol. Resin of 200–400 mesh particle size gives considerably sharper elution peaks and better separations than resin of 100–200 mesh particle size. With the finer resin, flow rates of 3 ml/min (1 ml/min/cm^2) still give a sharp elution peak for magnesium as is shown in Fig. 4. A separation factor of $\alpha_{Mg}{}^{Ca}=8$ (*ca.* 12 for trace amounts) was obtained for the 12% cross-linked resin, yet the lower cross-linkage was preferred because magnesium could be eluted in a smaller volume and because of the superior exchange kinetics.

The method has been applied successfully to the accurate direct determination of calcium in silicates, dolomites, magnesites, and ignited plant material by combining it with a compleximetric titration with EDTA in presence of methylthymol blue as indicator, or with atomic absorption spectrometry.

SUMMARY

Magnesium can be separated from calcium by elution with 3.0 *M* hydrochloric acid containing 60% ethanol from a column of AG50W-X8 cation-exchange resin. Calcium is retained and can be eluted with 3.0 *M* hydrochloric acid or 2.0 *M* nitric acid. The separation factor of $\alpha_{Mg}{}^{Ca}=5.6$ is considerably higher than that in aqueous hydrochloric acid and comparable to those obtained with organic complexing reagents. Separations are sharp and quantitative; up to 10 mmol of magnesium can be separated from 0.01 mmol of calcium and *vice versa* on a 60-ml column. Al, Fe(III), Mn, Ni(II), Co(II), Zn, Cd, Cu(II), Pb(II), U(VI), Be, Ga, Ti(IV) in the presence of H_2O_2 and many other elements accompany magnesium and can be separated from calcium quantitatively. Sr, Ba, Zr, Hf, Th, Sc, La and the rare earths are retained together with Ca, but can be separated by other methods.

RÉSUMÉ

Le magnésium peut être séparé du calcium par élution avec acide chlorhydrique 3.0 *M* renfermant 60% d'éthanol d'une colonne de résine échangeuse de cations AG 50W-X8. Le calcium est retenu et peut-être élué ensuite avec acide chlorhydrique 3.0 *M* ou acide nitrique 2.0 *M*. Le facteur de séparation $\alpha_{Mg}{}^{Ca}=5.6$ est considérablement plus élevé que celui obtenu en solution acide chlorhydrique et comparable à ceux trouvés à l'aide de réactifs complexants organiques. Les séparations sont nettes et quantitatives; on peut ainsi séparer 10 mmoles de magnésium d'avec 0.01 mmole de calcium et vice-versa, sur une colonne de 60 ml. Al, Fe(III), Mn, Ni(II), Co(II), Zn, Cd, Cu(II), Pb(II), U(VI), Be, Ga, Ti(IV) en présence d'H_2O_2 et d'autres éléments accompagnant Mg peuvent être séparés quantitativement d'avec le calcium. Sr, Ba, Hf, Th, Sc, La et les terres rares sont retenus avec le calcium, mais ils peuvent être séparés par d'autres méthodes.

ZUSAMMENFASSUNG

Magnesium kann vom Calcium mit Hilfe der Kationenaustauscherchromatographie abgetrennt werden. Es wird dabei von einer AG50W-X8-Kolonne mit 3.0 *M* Salzsäure, die 60% Äthanol enthält eluiert. Calcium wird zurückgehalten und kann mit 3.0 *M* Salzsäure oder 2.0 *M* Salpetersäure eluiert werden. Der Trennfaktor beträgt 5.6 und ist beträchtlich grösser als der bei Verwendüng von wässriger Salzsäure und vergleichbar mit denen, die mit organischen Komplexen erhalten wurden. Die Trennungen sind scharf und quantitativ. Al, Fe(III), Mn, Ni(II), Co(II), Zn, Cd, Cu(II), Pb(II), U(VI), Be, Ga, Ti(IV) begleiten in Gegenwart von H_2O_2 das Magnesium. Sr Ba, Zr, Hf, Th, Sc, La und die seltenen Erden bleiben beim Calcium.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SEPARATION OF PLATINUM AND PALLADIUM FROM BASE METALS WITH A WEAKLY BASIC CELLULOSE ION EXCHANGER

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(Received September 8th, 1967)

The separation of traces of platinum and palladium from large quantities of base metals, such as aluminum, iron, cobalt, nickel, copper, lead, etc., is often required in concentrating both metals from ores, concentrates, assay buttons, and natural alloys. The major contributions in the field of platinum metal separations have been reviewed by BEAMISH[1].

Effective ion-exchange methods for separating platinum metal ions from large amounts of common base metal ions are rather few, and are mostly based on the use of cation-exchange resin in hydrochloric acid media. Cation-exchange methods for quantitatively separating iron, copper and nickel from trace amounts of platinum and palladium[2-4], rhodium and iridium[5], ruthenium[6] and osmium[7] have been reported. Platinum and rhodium[8] and 4 platinum metals, platinum, palladium, rhodium and iridium[9], have also been separated by cation exchange from base metals including iron, copper, nickel, lead and others. In these methods platinum metal ions are passed through the column as chlorocomplexes in hydrochloric acid solution, while the base metal ions remain adsorbed on the column as cations.

Obviously, it would be better to retain small quantities of precious metals as anions on an anion-exchange column, leaving the large excess of contaminating metals as cations in the effluent wastes so as to avoid use of an excessively large cation-exchange column. However, it has long been recognized that the chlorocomplex anions of platinum metals can be eluted only inefficiently from anion-exchange columns. Thus, BUTLER[8] failed to elute platinum and rhodium chlorocomplexes adsorbed on Amberlite IR4B and Dowex 2 as a complex amine cation, in accordance with observations of MACNEVIN AND CRUMMETT[10]. The same behavior was found by BERMAN AND MCBRYDE for palladium[11]. KRAUS *et al.*[12,13] also found that the adsorbability of the chlorocomplex of palladium, even in concentrated hydrochloric acid, was still sufficiently large to preclude its easy removal from Dowex 1, and they recommended a displacement of the strongly adsorbed palladium(II) complex by other strongly adsorbed chlorocomplexes, *e.g.*, those of zinc(II) or cadmium(II) in 6 *M* hydrochloric acid. BLASIUS AND WACHTEL[14] recorded the quantitative removal of nickel, iron and copper from the platinum on Permutit ES in the chloride form, but failed to elute the platinum (and iridium), suggesting ignition of the resin to recover the metal.

Recently, KOSTER AND SCHMUCKLER[15] described a new type of chelating resin, and effected the separation of platinum from 500 mg each of iron, nickel and copper.

The irreversible strong adsorption of the chlorocomplexes of platinum and palladium on conventional anion-exchange resins makes their use unattractive, although they can be convenient for concentrating traces of platinum and palladium from large quantities of waste metals. A search was therefore made for a more satisfactory ion-exchange method. The moderate affinity of these metal ions towards the cellulose ion-exchanger DEAE[16–18] was found very satisfactory for the quantitative recovery of platinum(IV) and/or palladium(II) from at least twenty to twenty-five thousand times as much of iron, nickel, copper, lead and other base metals.

EXPERIMENTAL

Materials

Cellulose ion exchanger. A weakly basic cellulose anion exchanger DEAE (diethylaminoethylcellulose) (Serva) was obtained from Gallard-Schlesinger Chemical Manufacturing Corp. Before use DEAE was purified and converted to a thiocyanate form as described earlier[17]. DEAE in the chloride form was also used.

Stock solutions of platinum and palladium. A weighed quantity of powdered platinum or palladium metal was dissolved in aqua regia and the solution was evaporated to dryness. The residue was taken up in hydrochloric acid and the evaporation repeated to remove nitrous acid. The final solution was diluted to contain 1 mg Pt(IV) or Pd(II) per ml of 0.1 *M* hydrochloric acid solution.

Wash solutions. Depending on the base metal to be separated the following wash solutions were used:

0.01 *M* ammonium thiocyanate–0.1 *M* hydrochloric acid for iron(III), cobalt, nickel and zinc.

0.01 *M* ammonium thiocyanate–0.1 *M* nitric acid for lead.

0.01 *M* ammonium thiocyanate–1 *M* hydrochloric acid for copper(II).

Buffer solution. Buffer solutions of pH 1 and 2 were prepared by mixing 0.1 *M* potassium chloride solution and 0.1 *M* hydrochloric acid in varying proportions. When necessary, buffer solutions of pH 1, possessing total chloride concentrations of 0.3, 1.0, and 3.0 *M*, respectively, were made up similarly. An acetate buffer solution of pH 3 was prepared by mixing 0.1 *M* sodium acetate and 0.1 *M* acetic acid in proper proportions. The thiocyanate solution of a given pH was prepared by dissolving a known amount of ammonium thiocyanate in a definite volume of the corresponding buffer solution. If any minor displacement of pH occurred, it was readjusted.

Ion-exchange column. 10 g of DEAE in the thiocyanate form were slurried with about 80 ml of the appropriate wash solution and poured into a conventional glass column, I.D. 2.5 cm, pulled to a tip and plugged with glass wool at the outlet. A filter paper disc of the same diameter was placed on to the layer of packed glass wool. The resulting bed was usually 10.5 cm high. For small-scale separations involving less than 1 g of base metals, a small column, I.D. 1.5 cm, which contained 2 g of DEAE, was prepared as described above, the bed being usually 5.0 cm long.

Determination of distribution coefficient

The distribution coefficients of platinum(IV) and palladium(II) on DEAE in the thiocyanate form in buffered thiocyanate solutions and in thiocyanate-hydrochloric acid solutions were determined by a batch equilibrium method. Portions (0.5 g) of DEAE were weighed and placed into stoppered conical flasks, to which 40-ml portions of thiocyanate solutions of varying concentration and 1 ml of the stock solution of either platinum(IV) or palladium(II) were added. After being shaken mechanically for 15 h at 25.0 ± 0.1°, the two phases were separated by filtration and the equilibrium pH of the filtrate was recorded. An aliquot of the filtrate was analyzed for platinum(IV) or palladium(II) colorimetrically by means of the tin(II) chloride and α-nitroso-β-naphthol methods respectively.

The distribution coefficients of platinum(IV) and palladium(II) on DEAE in the chloride form in buffered potassium chloride and hydrochloric acid media were also determined in a similar way at 25.0 ± 0.1°.

The distribution coefficient, K_d, was computed from the following formula:

$$K_d = \frac{\text{Amount of metal ion/g of DEAE}}{\text{Amount of metal ion/ml of solution}}$$

Separation of platinum(IV) and/or palladium(II) from base metals

Before the sample solution is loaded on to the top of the column, it is adjusted to have the same thiocyanate and hydrochloric acid concentrations as those of the wash solution, which varies according to the base metal concerned. The exception is for iron(III); the thiocyanate concentration of the iron(III) solution should differ from that of the wash solution and vary according to the amounts of iron(III) to be separated (see Tables V and VI). The total chloride concentration should not exceed approximately 1.5 *M* to prevent breakthrough of platinum(IV) and palladium(II).

About 1 l of the sample solution containing 20–25 g of a base metal is loaded on to the top of the column at a flow rate of *ca.* 1 ml/ min. After the sample solution has passed, the column is washed with 250 ml of the wash solution. Platinum(IV) and/or palladium(II) is then stripped from the column by elution with about 60 ml of 0.05 *M* thiourea solution. The first effluent fraction corresponding to a void space (about 30 ml) can be discarded. Palladium(II) is directly determined in an aliquot of the effluent colorimetrically with thiourea as the color reagent. For the determination of platinum(IV) an aliquot of the effluent is treated with sodium nitrite and a few drops of sulfuric acid to decompose thiourea, and then evaporated to dryness with nitric acid. The residue is converted to chloride by evaporating with hydrochloric acid and analyzed colorimetrically by the tin(II) chloride method.

Small-scale separations involving 5.0 cm column can be achieved similarly. Usually 100 ml of the sample solution is loaded on to the column at a flow rate of 0.5 ml/min, the column is washed with 50 ml of the wash solution, and finally platinum(IV) and/or palladium(II) is stripped by elution with 20 ml of the thiourea solution.

RESULTS AND DISCUSSION

The K_d values for platinum(IV) and palladium(II) in thiocyanate media on DEAE in the thiocyanate form are listed in Tables I and II, respectively, as functions of the thiocyanate concentration and of the acid strength. If the thiocyanate concentration is kept below 0.1 *M*, the K_d values of both metal ions are well above 10^3 over a wide range of acidity, *i.e.* pH 3 to 0.3 *M* hydrochloric acid concentration. The K_d values are sufficiently great to allow both metal ions to be taken up from

TABLE I

DISTRIBUTION COEFFICIENTS FOR PLATINUM(IV) ON DEAE (SCN form; 25.0±0.1°)

Acidity	*Thiocyanate concentration (M)*						*Total chloride concentration (M)*
	0	*0.010*	*0.050*	*0.10*	*0.50*	*1.0*	
pH 3.0	$>4\cdot10^3$	$>4\cdot10^3$	$>4\cdot10^3$	$\sim4\cdot10^3$	$4.1\cdot10^2$	$1.6\cdot10^2$	0
pH 3.0	$>4\cdot10^3$	$>4\cdot10^3$	$>4\cdot10^3$	$2.8\cdot10^3$	$3.7\cdot10^2$	$1.4\cdot10^2$	0.10
pH 2.0	$>4\cdot10^3$	$>4\cdot10^3$	$>4\cdot10^3$	$\sim4\cdot10^3$	$3.8\cdot10^2$	$1.2\cdot10^2$	0.10
pH 1.0	$>4\cdot10^3$	$>4\cdot10^3$	$>4\cdot10^3$	$\sim4\cdot10^3$	$4.3\cdot10^2$	$1.2\cdot10^2$	0.10
0.30 *M* HCl	$3.9\cdot10^3$	$2.9\cdot10^3$	$1.9\cdot10^3$	$1.5\cdot10^3$	$2.9\cdot10^2$	96	0.30
1.5 *M* HCl	$1.9\cdot10^2$	$1.9\cdot10^2$	$1.9\cdot10^2$	$2.3\cdot10^2$	73	35	1.5

TABLE II

DISTRIBUTION COEFFICIENTS FOR PALLADIUM(II) ON DEAE (SCN form; 25.0±0.1°)

Acidity	*Thiocyanate concentration (M)*						*Total chloride concentration (M)*
	0	*0.010*	*0.050*	*0.10*	*0.50*	*1.0*	
pH 3.0	$>5\cdot10^3$	$>5\cdot10^3$	$>5\cdot10^3$	$\sim5\cdot10^3$	$3.1\cdot10^2$	$1.0\cdot10^2$	0
pH 3.0	$>5\cdot10^3$	$>5\cdot10^3$	$>5\cdot10^3$	$\sim5\cdot10^3$	$3.1\cdot10^2$	$1.0\cdot10^2$	0.10
pH 2.0	$>5\cdot10^3$	$>5\cdot10^3$	$>5\cdot10^3$	$\sim5\cdot10^3$	$2.8\cdot10^2$	$1.0\cdot10^2$	0.10
pH 1.0	$>5\cdot10^3$	$>5\cdot10^3$	$>5\cdot10^3$	$\sim5\cdot10^3$	$2.8\cdot10^2$	$1.0\cdot10^2$	0.10
0.30 *M* HCl	$>5\cdot10^3$	$>5\cdot10^3$	$2.4\cdot10^3$	$1.6\cdot10^3$	$2.4\cdot10^2$	90	0.30
1.5 *M* HCl	$4.5\cdot10^2$	$4.7\cdot10^2$	$4.1\cdot10^2$	$3.8\cdot10^2$	$1.2\cdot10^2$	99	1.5

TABLE III

DISTRIBUTION COEFFICIENTS FOR PLATINUM(IV) AND PALLADIUM(II) ON DEAE (SCN form) IN KCl (pH 1.0) AND HCl MEDIA[a]

(25.0±0.1°)

Ions	*Concn. of KCl (M)*				*Concn. of HCl (M)*		
	0.10	*0.30*	*1.0*	*3.0*	*0.10*	*0.30*	*1.5*
Pt(IV)	$>4\cdot10^3$	$1.5\cdot10^3$	$4.0\cdot10^2$	$1.3\cdot10^2$	$>4\cdot10^3$	$2.9\cdot10^3$	$1.9\cdot10^2$
Pd(II)	$>5\cdot10^3$	$3.5\cdot10^3$	$1.0\cdot10^3$	$3.8\cdot10^2$	$>5\cdot10^3$	$>5\cdot10^3$	$4.7\cdot10^2$

[a] All the KCl and HCl solutions listed are also 0.010 *M* in NH_4SCN.

a large volume of base metal solution. Base metals are not adsorbed at all from the thiocyanate media above, so that platinum(IV) and palladium(II) may easily be separated from base metals.

The chloride dependence of the K_d values for platinum(IV) and palladium(II) is shown in Table III, where the values are given as functions of the potassium chloride and hydrochloric acid concentrations at a constant thiocyanate concentration of 0.01 *M*. Both metal ions exhibit a general tendency for the K_d values to decrease regularly with increasing concentration of chloride ions. The chloride dependence of the K_d values must be taken into consideration, when separations are attempted, to control the allowable chloride concentration of sample solution of base metals.

In Table IV are shown the K_d values for platinum(IV) and palladium(II) on DEAE in the chloride form in potassium chloride media at pH 1 and 3. It may be noted that DEAE in the chloride form lowers the K_d values for platinum(IV) and palladium(II) substantially in chloride media, compared with the values found for DEAE in the thiocyanate form in the same media containing a little amount of thiocyanate ions (Table III). Therefore, when the concentration of chloride is high, as in the usual case, DEAE in the thiocyanate form is decidedly preferable to DEAE in the chloride form to keep the platinum(IV) and palladium(II) adsorbed strongly on the column.

TABLE IV

DISTRIBUTION COEFFICIENTS FOR PLATINUM(IV) AND PALLADIUM(II) ON DEAE (Cl form) IN POTASSIUM CHLORIDE MEDIA

(25.0±0.1°)

Ions	*pH*	*Concn. of Cl^-(M)*			
		0.10	*0.30*	*1.0*	*3.0*
Pt(IV)	1.0	$4.4 \cdot 10^2$	$1.7 \cdot 10^2$	19	5
Pt(IV)	3.0	$2.6 \cdot 10^2$	79	8	<1
Pd(II)	1.0	$7.5 \cdot 10^2$	$2.2 \cdot 10^2$	34	6
Pd(II)	3.0	$1.2 \cdot 10^3$	$3.0 \cdot 10^2$	43	~ 2

To prevent a breakthrough of platinum(IV) and palladium(II), it was decided that the sample solution containing cobalt, nickel or zinc should be adjusted to 0.01 *M* in ammonium thiocyanate and 0.1 *M* in hydrochloric acid. The K_d values for platinum(IV) and palladium(II) in this medium are *ca.* $4 \cdot 10^3$ or more, which is sufficiently high to retain both metal ions from a large volume of the sample solution. In order to avoid the precipitation of lead chloride, the sample solution containing lead must be adjusted to 0.01 *M* ammonium thiocyanate–0.1 *M* nitric acid, from which platinum(IV) and palladium(II) are also retained tightly on the column, while the lead exhibits no adsorption.

A difficulty arose in separating platinum(IV) and palladium(II) from a large quantity of copper(II) in 0.01 *M* ammonium thiocyanate–0.1 *M* hydrochloric acid solution. Because copper(II) ions consume available thiocyanate ions and free thiocyanate ions become deficient in copper(II) thiocyanate solution, an appreciable fraction of palladium(II) precipitates as an insoluble palladium(II) thiocyanate, so that an extremely poor recovery of the palladium(II) results. The recovery of platinum(IV) from the copper(II) thiocyanate solution is also not quantitative (*ca.* 60–70%), although there is no evidence for precipitate formation in this case. Increasing concentrations of the thiocyanate ions allow the palladium(II) to form soluble thiocyanatocomplexes, but at the same time cause copper(II) to precipitate as black copper(II) thiocyanate. These difficulties were overcome simply by increasing the acid concentration to 1 *M* while keeping the thiocyanate concentration constant at 0.01 *M*. The K_d values for platinum(IV) and palladium(II) in this medium are still *ca.* 400 and 10^3 respectively, so that the quantitative uptake is possible, although the adsorption band becomes spread over an appreciable fraction of the column, particularly with the platinum(IV), after as much as 1 l of the sample solution has been passed through.

Iron(III) also reacts with thiocyanate in acid solution to produce stable thiocyanatocomplexes so that insufficient free thiocyanate ions may be available for the formation of the thiocyanatocomplexes of platinum(IV) and palladium(II). It was found that a 1:3 mole ratio of iron(III) to thiocyanate supplies sufficient thiocyanate ions to form soluble thiocyanatocomplexes of palladium(II). Accordingly, platinum(IV) and palladium(II) can be separated without difficulty from as much as 10–20 g of iron(III) in 1 l of sample solution, which is made to 0.1 *M* in hydrochloric acid and contains 3 times as much thiocyanate as iron(III).

TABLE V

SEPARATION OF PLATINUM(IV) FROM BASE METAL IONS[a]

Base metal ions (mg)			*Pt(IV) (mg)*		*Vol. of sample solution (ml)*	*Column used*
	Added	*Found*	*Added*	*Found*		
Co(II)	$1.01 \cdot 10^2$	$1.01 \cdot 10^2$	1.05	1.05	100	S[f]
Cu(II)	$5 \cdot 10^3$	—	1.05	1.03	500	L[g]
Cu(II)	$2 \cdot 10^4$	—	1.05	1.04	1000	L
Fe(III)	10.5	10.5	1.05	1.07	100[b]	S
Fe(III)	$1.05 \cdot 10^2$	$1.02 \cdot 10^2$	1.05	1.06	100[c]	S
Fe(III)	$1.05 \cdot 10^3$	$1.04 \cdot 10^3$	1.05	1.08	100[d]	S
Fe(III)	$1 \cdot 10^4$	—	1.05	1.05	1000[d]	L
Fe(III)	$2 \cdot 10^4$	—	1.05	1.04	1000[e]	L
Ni(II)	12.4	12.5	1.05	1.03	100	S
Ni(II)	$1.24 \cdot 10^2$	$1.24 \cdot 10^2$	1.05	1.06	100	S
Ni(II)	$1.24 \cdot 10^3$	$1.24 \cdot 10^3$	1.05	1.05	100	S
Ni(II)	$1 \cdot 10^4$	—	1.05	1.05	500	L
Ni(II)	$2.5 \cdot 10^4$	—	1.05	1.07	1000	L
Pb(II)	$1.13 \cdot 10^2$	$1.13 \cdot 10^2$	1.05	1.07	100	S
Pb(II)	$2.5 \cdot 10^4$	—	1.05	1.05	1000	L
Zn(II)	8.25	8.24	1.05	1.03	100	S
Zn(II)	82.5	82.2	1.05	1.07	100	S
Zn(II)	$8.25 \cdot 10^2$	$8.25 \cdot 10^2$	1.05	1.07	100	S
Zn(II)	$1 \cdot 10^4$	—	1.05	1.05	500	L
Zn(II)	$2.5 \cdot 10^4$	—	1.05	1.07	1000	L

[a] Base metals added as chloride except for Pb(II). Pb(II) added as nitrate.
[b] Sample solution adjusted to 0.01 *M* NH_4SCN–0.1 *M* HCl.
[c] Sample solution adjusted to 0.06 *M* NH_4SCN–0.1 *M* HCl.
[d] Sample solution adjusted to 0.54 *M* NH_4SCN–0.1 *M* HCl.
[e] Sample solution adjusted to 1.1 *M* NH_4SCN–0.1 *M* HCl.
[f] S: Small column containing 2 g DEAE.
[g] L: Large column containing 10 g DEAE.

The results on quantitative separations of platinum(IV) and palladium(II) from base metals are summarized in Tables V and VI, respectively. In most cases are recorded the runs in which 20–25 grams of base metals were separated from as little as 1 mg of platinum(IV) or palladium(II). Recovery of platinum(IV) and palladium(II) is satisfactory; average deviations of 1.2% for platinum(IV) and 1.6% for palladium(II) were found. In the present method, there seems to be no intrinsic difficulty in increasing the amount of base metals to be separated relative to those of platinum(IV) and palladium(II). Only a small column is necessary to effect the separation, which is in sharp contrast to previously reported cation-exchange methods. No difficulty is found in removing both metal ions from the column; 0.05 *M* thiourea solution is the

TABLE VI

SEPARATION OF Pd(II) FROM BASE METAL IONS[a]

Base metal ions (mg)			*Pt(IV) (mg)*		*Vol. of sample solution (ml)*	*Column used*
	Added	*Found*	*Added*	*Found*		
Co(II)	$1.01 \cdot 10^2$	$1.01 \cdot 10^2$	1.06	1.08	100	S[f]
Cu(II)	$1 \cdot 10^3$	—	1.06	1.03	100	S
Cu(II)	$1 \cdot 10^4$	—	1.06	1.03	1000	L[g]
Cu(II)	$2 \cdot 10^4$	—	1.06	1.09	1000	L
Fe(III)	10.5	10.4	1.06	1.08	100[b]	S
Fe(III)	$1.05 \cdot 10^2$	$1.04 \cdot 10^2$	1.06	0.95	100[c]	S
Fe(III)	$1.05 \cdot 10^3$	$1.04 \cdot 10^3$	1.06	1.06	100[d]	S
Fe(III)	$2 \cdot 10^4$	—	1.06	1.05	1000[e]	L
Ni(II)	12.4	12.5	1.06	1.06	100	S
Ni(II)	$1.24 \cdot 10^2$	$1.24 \cdot 10^2$	1.06	1.06	100	S
Ni(II)	$1.24 \cdot 10^3$	$1.24 \cdot 10^3$	1.06	1.06	100	S
Ni(II)	$2.5 \cdot 10^4$	—	1.06	1.08	1000	L
Pb(II)	$1.13 \cdot 10^2$	$1.13 \cdot 10^2$	1.06	1.06	100	S
Pb(II)	$2.5 \cdot 10^4$	—	1.06	1.06	1000	L
Zn(II)	8.25	8.07	1.06	1.06	100	S
Zn(II)	82.5	81.3	1.06	1.07	100	S
Zn(II)	$8.25 \cdot 10^2$	$8.25 \cdot 10^2$	1.06	1.05	100	S
Zn(II)	$2.5 \cdot 10^4$	—	1.06	1.08	1000	L

[a] See the footnotes to Table V.

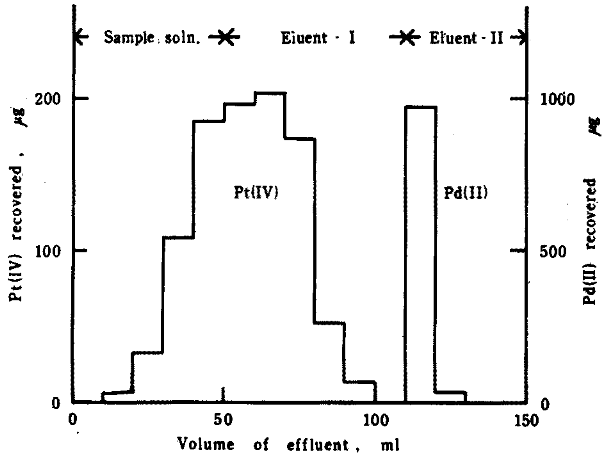

Fig. 1. Separation of Pt(IV) and Pd(II). Sample solution adjusted to 0.02 *M* in NH_4SCN and 2 *M* in HCl. Column pretreated with 15 ml of 0.02 *M* NH_4SCN–2 *M* HCl. Column bed: diam.1.5 cm × 2.5 cm high. Eluent-I: 0.02 *M* NH_4SCN–2 *M* HCl. Eluent-II: 0.05 *M* $(NH_2)_2CS$. Temperature: $<5°$. Flow rate: *ca.* 0.5 ml/min. Recovery: Pt(IV) 1.05 mg added, 1.03 mg found; Pd(II) 1.06 mg added, 1.07 mg found.

most effective, but instead a mixture of hydrochloric and perchloric acids (*e.g.* 4 *M* HCl–2 *M* $HClO_4$) can also be used.

The formation rate of thiocyanatoplatinum complexes is not rapid at lower temperatures. This behavior of platinum(IV) can successfully be used for separating it from palladium(II) at a lower temperature. In Fig. 1 is illustrated an elution profile curve on the separation of platinum(IV) and palladium(II) below 5°. With increasing temperature, some platinum(IV) becomes retained on the column and is eluted along with palladium(II) by a 0.05 *M* thiourea solution or hydrochloric–perchloric acids mixture. The early eluted fraction of platinum(IV) varies with temperature, decreasing with increasing temperature.

SUMMARY

Platinum(IV) and palladium(II) are strongly adsorbed on the weakly basic cellulose ion exchanger DEAE from dilute thiocyanate media, while most other metal ions do not show any marked tendency to adsorb from the same media. It is possible to separate and concentrate the noble metal ions from a large quantity of base metals such as iron, cobalt, nickel, copper, zinc and lead. As little as 1 mg of platinum(IV) and/or palladium(II) can be quantitatively separated from as much as 20–25 g of base metals on a small column of DEAE (thiocyanate form). The noble metal ions adsorbed are easily stripped from DEAE.

RÉSUMÉ

Le platine(IV) et le palladium(II) sont fortement adsorbés sur un échangeur d'ions DEAE cellulose, faiblement basique, de milieux thiocyanate dilué. Il est possible de séparer et de concentrer les ions de métaux nobles d'avec un grand nombre de métaux de base tels que fer, cobalt, nickel, cuivre, zinc et plomb. On peut ainsi séparer quantitativement jusqu'à 1 mg de platine(IV) ou de palladium(II) en présence de 20 à 25 g de métaux de base sur une petite colonne de DEAE (forme thiocyanate).Les métaux nobles adsorbés sont facilement élués.

ZUSAMMENFASSUNG

Platin(IV) und Palladium(II) werden von einem schwach basischen Zellulose-Ionenaustauscher (DEAE) aus verdünnter Thiocyanatlösung stark adsorbiert, während die meisten anderen Metallionen keine deutliche Neigung zeigen vom selben Medium adsorbiert zu werden. Dadurch ist es möglich die Edelmetallionen von einer grossen Anzahl von Metallen wie Eisen, Kobalt, Nickel, Kupfer, Zink und Blei abzutrennen und zu konzentrieren. 1 mg Platin(IV) und/oder Palladium(II) können quantitativ aus 20–25 g der genannten Metalle mit einer kleinen Kolonne gewonnen werden. Die adsorbierten Edelmetallionen können leicht vom DEAE gelöst werden.

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Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

SHORT COMMUNICATIONS

The determination of silver in fine silver bullion by atomic absorption spectroscopy

Previously, at this Branch Mint, fine silver bullion has been assayed by the Gay-Lussac method[1], which involves precipitation, and coagulation by shaking, of most of the silver in a 1-g sample dissolved in nitric acid, with 100 ml of a standard sodium chloride solution; 1-ml additions of decimal sodium chloride solution are then made, each followed by shaking, until only a faint cloud is obtained. The intensity of the cloud is estimated optically and the total amount of sodium chloride is then compared with that added to solutions containing 1-g samples of proof silver. The method has been considered generally satisfactory, although much experience is required for confidence in estimating the cloud accurately.

The concentrations of silver remaining in the supernatant solutions after precipitation of the bulk of the silver, as described above, are in the 10–35 p.p.m. range. Tests showed that sufficient precision can be obtained in measuring these concentrations of silver using atomic absorption spectroscopy.

Apparatus and reagents

Atomic Absorption Spectrophotometer Techtron AA3 with silver hollow-cathode lamp.

Standard sodium chloride solution. Dissolve 5.4 g of sodium chloride in water and dilute to 1 l. For standardisation of this solution, dissolve 1 g of proof silver in 20 ml of 1:2 nitric acid and add exactly 100 ml of the chloride solution. Shake for 3 min and then determine the silver content of the supernate by comparison with standards. Four standards, 5, 15, 25 and 35 p.p.m. of silver should suffice. The author prefers about 13 p.p.m. for a 1-g proof sample. If the prepared solution requires dilution, add 1 ml of water for each litre; this results in an increase of 10 p.p.m. of silver in the supernate of a 1-g proof sample. Similarly, add 0.0054 g of sodium chloride for each litre to decrease the silver content by 10 p.p.m.

Instrument settings

Various concentrations of silver nitrate were prepared and sprayed into a coal gas flame. By adjusting the H.T. on the photomultiplier, so that the strongest solution gave about 20% transmission, the range of solutions could be accommodated on the scale. A straight line calibration graph was obtained over the range 10–22.5 p.p.m. of silver.

Note that the supernatant solution for a 1-g sample of proof silver of 999.8 fineness will contain about 8 p.p.m. more silver than a sample of silver bullion which assays 999.0.

The emission line at 3281 Å was used. The silver hollow-cathode lamp current and slit width were 5 mA and 0.05 mm respectively. The air–coal gas mixture used, gave a nonluminous flame at 17 p.s.i. air pressure.

Precision

Nineteen samples of proof silver, 999.8 fineness, weighing about 1 g were dissolved in 10 ml of 1:1 nitric acid; 100 ml of standard sodium chloride solution was added to each from a Stas pipette and shaken. Without further preparation, these solutions were sprayed into the flame and after adjustment of H.T. as described above, absorbances were read directly. Weights of proofs were plotted against absorbances. Results are shown in Fig. 1. It should be noted that the accuracy of the method depends largely on the precision with which 100 ml of sodium chloride can be delivered.

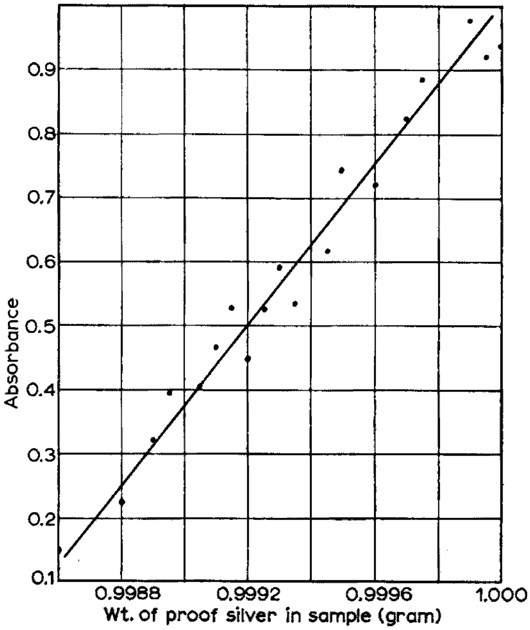

Fig 1. Curve illustrating precision of method by plotting absorbance of silver in supernatant solutions, against weight of proof silver in sample.

Tests for interference

For the range of concentrations referred to above, the effects of nitric acid, sodium and elements likely to be encountered, were examined. Neither nitric acid nor sodium had any significant effect.

The maximum concentration of an impurity in bullion of 999.0 fineness is 0.1%, corresponding to 0.001 g in a 1-g sample, and to about 10 p.p.m. when prepared for assay. None of the elements examined, copper, nickel, zinc, iron, lead, tellurium, selenium, at least up to that concentration, had any significant effect on the absorbance of silver. Similar results have been reported by WILSON[2].

Recommended procedure

Preparation of working curve. Weigh in 4 samples of proof silver whose weights range from 0.9985 g to 1 g. Dissolve in 20 ml of 1:2 nitric acid. Add 100 ml of standard sodium chloride solution through matched Stas pipettes. Shake for 3 min and spray the supernatant solutions directly into the flame. Adjust the H.T. and read the absorbances. Plot absorbance against fineness of proof sample.

Analysis of fine silver bullion. Weigh 1-g samples and treat similarly. Measure the absorbances and read the silver fineness from the working curve.

Comparison of results obtained by different methods

Table I lists the results obtained by the Gay-Lussac and atomic absorption methods. The procedure developed possesses some advantages over the older method. The time-consuming operation of making several 1-ml additions of decimal sodium chloride solution, each followed by shaking, is replaced by spraying the supernatant solution into the flame and simply reading the absorbance.

Replacement of an optical estimation by an instrumental reading is another advantage.

TABLE I

COMPARISON OF RESULTS OBTAINED BY ATOMIC ABSORPTION SPECTROPHOTOMETRY WITH THOSE OBTAINED BY THE GAY-LUSSAC METHOD

Wt. Ag in proof sample (g)	*Silver assay (parts per thousand)*	
	Gay-Lussac	*Atomic absorption*
0.9998	999.8	999.8, 999.7
0.9995	999.4	999.6, 999.5
0.9997	999.5	999.7, 999.7
0.9998	999.8	999.8, 999.8
0.9998	999.8, 999.6	999.8, 999.8
1.0000	999.8, 999.8, 999.9	1000.0, 999.95, 999.9, 999.9
0.9997	999.5, 999.5	999.7, 999.7, 999.6, 999.8
0.9996	—	999.6, 999.6, 999.55, 999.6
0.9995	999.6	999.55, 999.65
0.9993	—	999.25
0.9992	999.1, 999.0	999.25
0.9991	—	999.05, 999.15
0.9990	—	998.95

The author wishes to thank the Deputy Master, Royal Mint, Perth, Western Australia, for permission to publish this paper.

Royal Mint,
Perth (Western Australia)
L. G. HICKEY

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(Received November 15th, 1967)

General formula for the calculation of the hydrogen-ion concentration of aqueous solutions of several polyvalent weak acids

The problem of the calculation of the hydrogen-ion concentration in weak acid solutions has been dealt with in several papers[1-6]. The interest in this problem is largely concerned with the difficulties in deriving correct equations which are amenable to numerical solution. The rather complicated nature of the problem is shown by the fact that the correct equation for even one monovalent weak acid solution is third order with respect to the hydrogen-ion concentration[3]. Clearly, the correct equation for weak polyvalent acids and for several polyvalent acids will be still more complicated. However, if the concept of SIMMS[7], who postulated that polyvalent acids may be considered in a certain sense as a mixture of monovalent acids, is utilized, it is possible to obtain a relatively simple and general solution of the above problem in the following way.

The ion equilibria and equilibrium constants in aqueous solutions of a polyvalent weak acid may be expressed in the usual manner as follows:

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = [H^+]\,[OH^-] \qquad (1)$$

$$HA^{1-n} \rightleftarrows H^+ + A^{n-} \qquad K_n = [H^+]\,[A^{n-}]/[HA^{1-n}] \qquad (2)$$

$$H_2A^{2-n} \rightleftarrows H^+ + HA^{1-n} \qquad K_{n-1} = [H^+]\,[HA^{1-n}]/[H_2A^{2-n}] \qquad (3)$$

$$\ldots$$

$$H_nA \rightleftarrows H^+ + H_{n-1}A^- \qquad K_1 = [H^+]\,[H_{n-1}A^-]/[H_nA] \qquad (4)$$

From the condition of electroneutrality:

$$[H^+] = [OH^-] + [H_{n-1}A^-] + \ldots + (n-1)\,[HA^{1-n}] + n[A^{n-}] \qquad (5)$$

and, according to the material balance, the analytical concentration of the acid is:

$$c = [H_nA] + [H_{n-1}A^-] + \ldots + [HA^{1-n}] + [A^{n-}] \qquad (6)$$

From eqns. (1)–(6), the hydrogen-ion concentration may be expressed as:

$$[H^+] = \frac{K_w}{[H^+]} + c\,\frac{K_1[H^+]^{n-1} + 2K_1K_2[H^+]^{n-2} + \ldots + (n-1)K_1K_2\ldots K_{n-1}[H^+] + nK_1K_2\ldots K_n}{[H^+]^n + K_1[H^+]^{n-1} + \ldots + K_1K_2\ldots K_{n-1}[H^+] + K_1K_2\ldots K_n} =$$

$$= K_w/[H^+] + cR([H^+]) \qquad (7)$$

SIMMS suggested that the function $R([H^+])$ may be more simply, but still exactly, expressed by the sum:

$$R([H^+]) = \frac{G_1}{[H^+]+G_1} + \frac{G_2}{[H^+]+G_2} + \ldots + \frac{G_n}{[H^+]+G_n} \qquad (8)$$

where the ionization constants (2 to 4) are related to the constants G in the following manner[7]: monovalent acid $K = G$, bivalent acid $K_1 = G_1 + G_2$, $K_1K_2 = G_1G_2$, trivalent acid $K_1 = G_1 + G_2 + G_3$, $K_1K_2 = G_1G_2 + G_2G_3 + G_1G_3$, $K_1K_2K_3 = G_1G_2G_3$ etc.

The total hydrogen-ion concentration on the left side of eqn. (7) equals the sum of the partial concentrations of hydrogen ions contributed by the water ($K_w/[H^+]$) and the acid ionized to the consecutive degrees according to eqn. (8):

$$[\mathrm{H}^+] = \frac{K_\mathrm{w}}{[\mathrm{H}^+]} + \sum_{i=1}^{n} \frac{cG_i}{[\mathrm{H}^+]+G_i} \tag{9}$$

Equation (9), which expresses the hydrogen-ion concentration in a solution of an n-valent acid is analogous in form and meaning to the equation for a solution of n monovalent acids[6].

(Some simplifications are indicated. If $[\mathrm{H}^+] \ll G_n$, total ionization of the acid occurs, and then $[\mathrm{H}^+] = K_\mathrm{w}/[\mathrm{H}^+] + nc$. If $[\mathrm{H}^+] \gg G_1$, *i.e.* for a very weak acid, then $[\mathrm{H}^+] = \sqrt{(K_\mathrm{w} + \sum_{i=1}^{n} cG_i)}$, and if $[\mathrm{H}^+] > 10^{-5}$, then $[\mathrm{H}^+] = \sum_{i=1}^{n} cG_i/([\mathrm{H}^+]+G_i)$.)

For a solution of several polyvalent weak acids, $\mathrm{H}_n\mathrm{A}$, $\mathrm{H}_m\mathrm{B}$...$\mathrm{H}_u\mathrm{D}$, with the analytical concentrations c_A, c_B...c_D and the constants assigned $G_{\mathrm{A}i}$, $G_{\mathrm{B}i}$...$G_{\mathrm{D}i}$, the total hydrogen-ion concentration would comprise the contribution by the water and by all the acids in the system, so that the total hydrogen-ion concentration may be expressed analogously to eqn. (9):

$$[\mathrm{H}^+] = \frac{K_\mathrm{w}}{[\mathrm{H}^+]} + \sum_{i=1}^{n} \frac{c_\mathrm{A}G_{\mathrm{A}i}}{[\mathrm{H}^+]+G_{\mathrm{A}i}} + \sum_{i=1}^{m} \frac{c_\mathrm{B}G_{\mathrm{B}i}}{[\mathrm{H}^+]+G_{\mathrm{B}i}} + \ldots + \sum_{i=1}^{u} \frac{c_\mathrm{D}G_{\mathrm{D}i}}{[\mathrm{H}^+]+G_{\mathrm{D}i}} \tag{10}$$

For the calculation of the hydrogen-ion concentration from eqn. (10) (eqn. (9) is simply the partial case of eqn. (10) under the conditions: $c_\mathrm{B} = \ldots = c_\mathrm{D} = 0$), it is not necessary to calculate the constants G_i by means of the equilibrium constants K_i, if the consecutive constants differ markedly from each other ($K_i/K_{i+1} \simeq 1000$). In this case, $G_i = K_i$ (within *ca.* 0.1 %). For other cases, the values of the constants G_i are available in the paper by SIMMS[7].

The calculation of the hydrogen-ion concentration itself may be done by the methods of consecutive approximations, of iteration or any other method[8] for numerical solution of equations.

The above technique can obviously be applied to the calculation of hydroxyl-ion concentration by appropriate conversion.

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(Received November 18th, 1967)

The thermal and atomic-fluorescence emission of germanium in a nitrogen–oxygen–acetylene flame

HERRMANN AND ALKEMADE[1] state that the emission spectrum of germanium has not been observed from aqueous solutions aspirated into conventional flames, whilst GILBERT[2] has observed the chemiluminescent emission of germanium (as H_2GeF_6) in isopropyl alcohol solutions in an air–hydrogen flame. With a total consumption burner he observed a limit of detection of 5 p.p.m. at 2651 Å. The limit of detection at 2651 Å from aqueous solution in the inner cones of an oxy–acetylene flame was given as 250 p.p.m., whilst it was 1000 p.p.m. in an oxy–hydrogen flame[1].

In a current programme of work, slight germanium emission from aqueous solutions was observed in the primary reaction cones of an air–acetylene flame, but this emission is not useful analytically because of the poor sensitivity (limit of detection of *ca.* 50 p.p.m. Ge) and the very high background-to-signal ratio which would result in a "noisy" determination.

This communication describes the determination of germanium by thermal emission and the first reported instance of an atomic-fluorescence signal for this element, in a nitrogen–oxygen–acetylene flame. Measurements of germanium in the atomic state have so far been restricted to absorption studies in a nitrous oxide–acetylene[3] flame, because germanium normally tends to form a refractory oxide species, probably owing to the presence of considerable quantities of atomic oxygen in conventional flames. This oxidising effect can only be overcome by using very high temperature flames to ensure efficient dissociation of the oxides, or by employing highly reducing atmospheres such as are present in the nitrous oxide–acetylene flame. In this instance the high population of reducing CN radicals is thought[4] to induce dissociation of metal oxide species by removal of atomic oxygen in the equilibrium

$$MO \rightleftharpoons M + [O]$$

The nitrogen–oxygen–acetylene flame is thought to lower the availability of atomic oxygen and so give rise to a higher concentration of atomic germanium.

Apparatus

The apparatus used in both studies was a Unicam SP900A spectrophotometer in its "emission" mode of operation[5], with a standard 1.8 × 7.5 cm air–acetylene emission burner-head.

The test solution was nebulised on nitrogen (thus eliminating risk of an explosive blowback even when organic solvents were used) at an optimised pressure of 20 psi using the conventional SP900A nebulising system. Acetylene was introduced at the base of the burner *via* the di-*n*-butyl phthalate manometer gauge and oxygen was passed through a pressure regulator into the burner *via* a slightly enlarged acetylene jet in the burner base[6]. The flame was lit on nitrogen and acetylene, and then the oxygen was introduced. The flame was safely extinguished by turning off the acetylene flow.

Thermal emission studies

When a 500-p.p.m. germanium solution was nebulised as above, emission was observed at 2592, 2651, 2691, 2710 and 2755 Å. The emission at 2651 Å was the most intense, probably because it is the sum of emission of two unresolved lines at 2651.2 and 2651.6 Å. The optimum emission occurred in a slightly fuel-rich flame with sharply defined primary cones and with the top of the burner-head about 2 mm below the bottom of the monochromator slit. The emission decreased very rapidly as the flame was made fuel-lean. The emission also decreased rapidly as the burner was lowered, thus indicating that it occurred just above the inner cones of the flame. When the top two-thirds of the monochromator slit was blanked-off, the emission signal hardly decreased whilst the signal-to-background ratio increased. The nitrogen pressure was found not to be very critical and was maintained at 20 psi. The instrument settings used are described below.

Under these conditions almost linear calibration curves were obtained over the range 10–2000 p.p.m. germanium and the limit of detection (signal:noise of 1) at 2651 Å was 5 p.p.m. (using a slit-width of 0.07 mm and gain 4, 5). The limit of detection was decreased by using organic solvents, *e.g.* a 800 p.p.m. germanium solution, 50% w/v in isopropyl alcohol, gave a 50% increase in the emission signal at 2651 Å. Organic solvents can be nebulised on nitrogen with complete safety.

When argon was used in place of nitrogen, increased emission signals were obtained. From a slightly luminous argon–oxygen–acetylene flame on the same burner, the emission from the same aqueous concentration of germanium was about twice that of the optimised nitrogen-diluted flame. However, the burner system used is not entirely satisfactory for supporting an argon flame because flame-blowback could only be prevented by using a minimum argon pressure of 20 psi (relative to nitrogen flow of 12 psi) and with the acetylene and oxygen pressures reduced to about half their previous values. When the corresponding nitrogen flame was used with similar acetylene and oxygen flow rates the germanium emission was *ca.* 7 times weaker. It would obviously be desirable to redesign the burner to support an argon–oxygen–acetylene flame so that the maximum benefit of increased sensitivity could be obtained.

Because the rate of sample uptake was found to be similar in the two flames, it would appear that the argon-diluted flame exhibits considerably higher thermal emission for germanium than does the nitrogen-diluted flame. This could be due to a higher flame temperature because of the lower heat capacity of argon and also to less quenching of excited germanium atoms by argon atoms than by diatomic nitrogen molecules. This latter effect has already been noticed in conjunction with certain atomic-fluorescence studies[7]. The differences observed in the emission intensities cannot be explained by the differences in the flow rates of argon and nitrogen; at an argon pressure of 20 psi (flow rate of 3.8 l/min) the flame readily blew back, but was quite stable with a nitrogen pressure of 15 psi (3.7 l/min).

Atomic-fluorescence studies

A germanium microwave-excited electrodeless discharge tube was prepared as previously described for antimony[8], from *ca.* 10 mg of germanium and *ca.* 20 mg of iodine. The 4-cm long tube was sealed under an argon pressure of 1 mm Hg and was operated using a "Microtron 200" generator and a 214 L cavity[8].

The discharge tube was run at a rating of 40 W and was slightly cooled with compressed air *via* the cooling vents in the cavity. The only useful atomic-fluorescence signal observed was at 2651 Å and was only one-third of the intensity of the thermal emission signal at the same germanium concentration and wavelength. The fluorescence signal could not be improved in intensity by adjusting the flame conditions or the position of measurement in the flame.

With the experimental arrangement used here, the detector system amplifies the background radiation from the flame, the thermal emission and the atomic-fluorescence signal because the source is not modulated. The limits of detection could be lowered by using a modulated source tuned to the amplifying frequency. Previously we have chiefly used flames of low background for atomic-fluorescence spectroscopy because we have used unmodulated sources. The present work indicates that high background flames could also have considerable use in atomic-fluorescence spectroscopy in conjunction with a modulated source, particularly where flames of low background do not produce any degree of atomisation of the element under examination.

The relatively weak atomic-fluorescence signal indicates that the observed thermal emission is chemiluminescent in nature and that the few atoms which exist do so in a region just above the inner cones of the flame. This was further investigated by carrying out atomic-absorption measurements under similar conditions.

Atomic-absorption studies

A conventional Unicam SP900A air–acetylene burner-head of 7 cm path length was used for the nitrogen–oxygen–acetylene flame and the instrument was operated in its "absorption" mode. The electrodeless discharge tube was used as source, but was operated, with slight cooling, only at 20 W to prevent too much radiation from striking the photomultiplier.

The absorption at 2651 Å was found to be maximal when the upper two-thirds of the monochromator slit was blanked off and the light from the source was passed through the flame just above the inner cones of a slightly fuel-rich flame. Under these conditions, a 1000-p.p.m. germanium solution gave only about 10% absorption, thus confirming the suspected low concentration of germanium atoms in the flame gases.

Preparation of thermal emission calibration curve

Apparatus. Unicam SP900A flame emission/atomic-absorption spectrophotometer with standard 1.8×7.5 cm air–acetylene emission head and EMI 9601B photomultiplier.

Reagents. 2000-p.p.m. germanium solution. Add 10 ml of distilled water to 1.441 g of germanium dioxide and about 8 pellets of potassium hydroxide in a small beaker and boil gently until dissolution. Allow to cool, make acid with 2 *F* sulphuric acid and dilute to 500 ml with distilled water.

Procedure for 40–400 p.p.m. Ge. Pipette 2–20 ml of the standard 2000-p.p.m. germanium solution into a series of 100-ml volumetric flasks and dilute to the mark with distilled water. Nebulise these into the nitrogen–oxygen–acetylene flame under the following experimental conditions: nitrogen pressure 20 psi, oxygen pressure *ca.* 2 psi, acetylene flow rate corresponding to 32 cm on the di-*n*-butyl phthalate filled manometer gauge (sufficient to give a slightly luminous flame), top of burnerhead *ca.* 2 mm below the bottom of monochromator slit, slit-width 0.04 mm, gain 3, 10 and bandwidth 3. Cut down the flame background by blanking off the upper two-thirds of the monochromator slit and measure the emission at 2651 Å. The background signal is measured by nebulising distilled water.

The plot of emission signal *vs.* concentration of germanium is linear. Other ranges can be prepared by suitable dilution of the above standard germanium solution.

One of us (K.C.T.) wishes to thank the S.R.C. for the award of a Research Studentship. We also wish to thank Unicam Instruments Limited for the loan of the spectrometer used in this study.

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(Received December 11th, 1967)

Anal. Chim. Acta, 41 (1968) 551–554

Sur la détermination quantitative précise des éléments légers par fluorescence X. Une comparaison des méthodes de fusion

La méthode des perles de borax de CLAISSE[1] a été appliquée avec succès à la détermination des éléments légers (Al, Si) notamment par TERTIAN *et al.*[2] qui ont utilisé comme fondant un mélange de borax et de carbonate de lithium, et par ROSE *et al.*[3] qui ont utilisé le tétraborate de lithium, précédemment proposé par ANDERMANN ET ALLEN[4], en l'additionnant d'un constituant absorbant, en l'occurrence La_2O_3.

Il est aisé de voir en examinant les tables de coefficients d'absorption massique que le mélange de $B_4O_7Li_2$ et de La_2O_3 préconisé par ROSE est *moins* absorbant pour les radiations de l'aluminium et du silicium que le borax lui-même. En conséquence nous estimons que le véritable intérêt de l'oxyde de lanthane à la fusion est de favoriser l'obtention d'un verre homogène et d'une perle (ou disque) d'un très bel aspect et d'une excellente conservation.

Il semble dommage dans ces conditions de broyer les dites perles pour les homogénéiser et les repastiller ensuite à la presse comme il est décrit dans la méthode de ROSE et comme l'ont fait à la suite d'autres applicateurs, dont WITTMANN *et al.*[5] par exemple. A l'opposé VON EUW[6] a décrit d'excellents résultats obtenus en analyse des ciments en utilisant les mêmes perles simplement coulées.

Pour préciser ce point de discussion nous nous sommes mis en devoir de comparer, strictement au point de vue de la *reproductibilité,* la technique de ROSE et la technique des perles simplement coulées que nous utilisons, à la suite de CLAISSE, depuis près de 10 ans.

L'analyse témoin choisie est celle d'une bauxite et on utilise une seule formulation, voisine de celle de ROSE, et qui est: $B_4O_7Li_2$: 8.500 g; La_2O_3: 1.500 g; bauxite: 0.925 g.

Un certain nombre de perles de cette composition sont coulées par la technique usuelle au creuset de platine, au diamètre de 30 mm, et mesurées telles quelles pour Al et pour Si. Un autre lot de perles identiques a été broyé finement, homogénéisé et recomprimé en pastilles (pellets) de 30 mm également que l'on mesure à leur tour pour Al et Si.

Les mesures sont conduites en accumulant sur chaque perle ou pastille un nombre suffisant d'impulsions pour amener l'erreur statistique de comptage à une valeur très faible de manière à bien laisser paraître l'erreur de préparation proprement dite. De même on enchaîne sur tous les échantillons d'une même série de nombreux comptages *alternatifs* de manière à éliminer toute cause d'erreur due à une dérive ou à des fluctuations accidentelles de l'appareillage. Ces résultats sont résumés dans le Tableau I.

Le Tableau I permet de constater que dans le cas des perles broyées l'erreur globale déborde nettement l'erreur statistique tandis que dans le cas des perles coulées l'erreur globale constatée demeure *inférieure* à l'erreur statistique évaluée au niveau 3 σ. C'est-à-dire que dans ce dernier cas l'erreur de préparation proprement dite est très faible. L'expérience, qui a été répétée sur une seconde bauxite, nous permet de dire que cette erreur est *inférieure ou égale* à ±0.25% (relative) alors que dans la technique du broyage l'erreur est de l'ordre de ±0.75%.

L'excellence de la méthode des perles coulées a été encore démontrée par un travail complémentaire portant sur 6 bauxites françaises très soigneusement analysées par voie chimique et qui ont été mesurées pour l'aluminium et pour le silicium avec un appareil bien réglé et stable mais *une seule fois* pour chacun des 2 éléments (2 minutes de comptage pour Si, 1 minute pour Al) et *sur une seule préparation.*

TABLEAU I

REPRODUCTIBILITÉ DE PRÉPARATION DANS LA MESURE DE L'ALUMINIUM ET DU SILICIUM (BAUXITE)

Grandeurs[a]	*Méthode utilisée*	
	$B_4O_7Li_2 + La_2O_3$ *perles broyées* *(12 pastilles)*	$B_4O_7Li_2 + La_2O_3$ *perles coulées* *(6 perles)*
	Mesure de l'aluminium	
N	580.000	990.000
ε(%)	±0.37	±0.28
Δ(%)	±0.74	±0.22
	Mesure de silicium	
N	276.000	140.000
ε(%)	±0.54	±0.74
Δ(%)	±0.85	±0.52

[a] N = Nombre d'impulsions accumulé sur chaque perle ou pastille.
ε = L'erreur statistique correspondante qui est, au niveau de sécurité 3 σ: $\varepsilon = \pm 3\sqrt{N}/N \cdot 100$ (en %).
Δ = Considéré comme *erreur de préparation*, en % également. En fait Δ englobe aussi l'erreur de mesure ε.

TABLEAU II

PRÉCISIONS

Constituants	*Teneurs moyennes et écarts absolus (%)*	*Précisions relatives (%)*
Al_2O_3	60.0±0.3	±0.25
SiO_2	6.0±0.1	±1
Fe_2O_3	25.0±0.25	±0.5
TiO_2	3.0±0.05	±1
CaO	1.0±0.05	±1

Les résultats obtenus en une seule mesure sont excellents et des résultats de même qualité ont été produits pour les éléments Fe, Ti, Ca avec un seul comptage de 24 sec. Le Tableau II résume, dans la colonne 2, les précisions globales obtenues pour les divers éléments ou, en d'autres termes, le degré d'accord entre les concentrations chimiques et les intensités de fluorescence. Si nous admettons, bien légitimement, que la moitié au moins de la dispersion constatée est imputable à l'erreur d'analyse chimique, encore que celle-ci ait été faite avec un soin tout particulier, nous pouvons considérer que la précision relative propre à la méthode physique est celle indiquée par les chiffres de la colonne 3, Tableau II.

En résumé: nous avons attiré l'attention sur le rôle bénéfique de l'oxyde de lanthane comme agent de coulée favorable à l'obtention de perles parfaitement homogènes et reproductibles. Il nous semble parfaitement illogique et désavantageux de broyer ces perles pour les repastiller ensuite à nouveau. Nous avons démontré que l'application de la méthode originale de CLAISSE usant de la formulation de ROSE permet d'atteindre, dans l'analyse des bauxites par exemple, à de hautes performances surpassant de très loin, au point de vue rapidité et précision, ce qui peut être atteint par les méthodes courantes.

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(Reçu le 29 novembre, 1967)

Controlled deactivation-hydrolysis and determination of aluminum in aluminum alkyl compounds

The need for safe, rapid, and accurate analyses of pyrophoric aluminum organic compounds has involved development of new analytical techniques. These compounds are instantly flammable in air or moisture and are also altered in composition in the presence of traces of these materials as well as other contaminants. Known hydrolysis techniques, in addition to being difficultly air and/or moisture free, were not suitable for routine analysis of large numbers of samples. Hydrolysis by addition of the pyrophoric material to a hydrocarbon solvent and dilute acid in a pressure bottle also proved cumbersome.

Pyrophoric organic aluminum compounds are pronounced electron-acceptors, and form very stable complexes with electron-rich molecules such as amines and ethers which in the case of the etherates are thermally stable[1]. Chemical hydrolysis of the etherate is complete, and can be followed by compleximetric titration of aluminum with cyclohexanediaminetetraacetic acid[2,3].

In the method described below, duplicate samples require less than 25 min for analysis.

Apparatus and reagents

Cyclohexanediaminetetraacetic acid (CDTA) (Hach Chemical Co., Ames, Iowa). A 0.05 *M* solution was standardized against pure aluminum or zinc metal at pH 4.5 with dithizone as indicator.

Zinc sulfate solution. A 0.05 *M* solution was standardized against CDTA at pH 4.5 with dithizone as indicator.

B-D 1 ml smooth bore syringe with Luer Lok and Teflon plunger and 23-gauge, 1.5-in hypodermic needles.

Procedure

Precautions. Pyrophoric aluminum organic compounds must be treated with extreme care. For obvious reasons transfer of the pyrophoric sample must be done below the surface of ether. A bench top shield is recommended.

Sampling. Clean a 1-ml syringe with 1:1 concentrated hydrochloric acid: acetone. Rinse with water, then acetone, and dry in a stream of dry nitrogen. Insert the greaseless Teflon plunger into the syringe, attach the dry nitrogen-purged needle and cap it with a silicone rubber plug (0.25 × 0.5 in) until required.

Uncap the syringe needle and immediately insert the needle through a 22-mm rubber serum septum into a 25-ml bottle containing the sample, tilting the bottle so as to allow removal of 0.5–0.6 ml of sample. Then draw a few bubbles of the bottle atmosphere into the syringe to free the needle of sample. Withdraw the needle carefully, cap immediately with the silicone rubber plug and weigh. The needle must be free of sample when removed from the bottle; otherwise, smoking will occur and the sample will not be representative.

Hydrolysis. Empty the weighed syringe by carefully removing the silicone plug after applying a slight vacuum to the syringe barrel by pulling the plunger out slightly to free the needle of any sample. Then rapidly immerse the needle *below* the surface of 50–75 ml of diethyl ether in a 250-ml Erlenmeyer flask, and slowly depress the plunger. Remove the syringe, recap and reweigh to obtain the sample weight. Swirl the ether solution to form the aluminum etherate. Complete the hydrolysis by adding 5 ml of concentrated hydrochloric acid slowly with swirling followed by 20–25 ml of distilled water. Extract the aluminum chloride into the aqueous phase and remove the organic phase, by heating on a steam bath. The aqueous solution is ready for titration.

Titration. Add an excess of at least 5 ml of CDTA solution to the acidic aqueous sample solution and heat the reaction mixture to near boiling so that the aluminum complex is formed. Add 50 ml of isopropanol, and 0.5 ml of 1 w/v% dithizone dissolved in acetone to the hot reaction mixture. Adjust to pH 4.5 (yellow-green) with 1:4 ammonia solution and pH 4.5 ammonium acetate buffer and back-titrate the excess of CDTA with standard zinc sulfate solution. The end-point is very sharp from green to red. Preliminary separation is unnecessary unless interfering metals are known to be present.

Other procedures used for comparative data included the classical ignition, 8-oxine, and fluoride methods described in standard texts.

Discussion and results

A Teflon plunger is preferred to the standard glass syringe plunger because no lubrication is needed, and any error due to lubricant is thus avoided; moreover, sample transfer is easier to control.

When the syringe needle is uncapped to take a sample, utmost care must be exercised to prevent any plunger movement and eliminate any minute air contamination. When the sample has been taken, the few bubbles of inert atmosphere pulled into the syringe from the sample bottle serve to prevent oxidation when the needle is withdrawn. If smoking occurs, oxidation has occurred and the sample is slightly altered; for the most precise and accurate results, a new portion of the sample should then be taken. The handling procedure described is satisfactory when followed carefully.

Ether, although flammable, is the most desirable medium for the sample because it can be easily removed. The sample *must* be discharged under the surface of the ether. The etherate forms rapidly and smoothly; swirling is recommended to avoid localized buildup of the sample. Addition of hydrochloric acid before water avoids the formation of hydrated aluminum oxides. The reaction sequence is described below.

$$R_3{=}Al + O{=}(C_2H_5)_2 \rightarrow (C_2H_5)_2{=}O{:}Al{=}R_3$$

$$\xrightarrow[H_2O]{HCl} AlCl_3 + 3\ RH + (C_2H_5)_2O$$

The titration used was first described by Wanninen and Ringbom[2] and later improved by Nydahl[3]. Substitution of CDTA for EDTA results in a more stable complex and thus a sharper end-point, but with both titrants, the aluminum chelate forms only slowly and partially unless heated with an excess of the titrant. Zinc is used to titrate the excess of CDTA with dithizone as indicator. The colored zinc dithizonate is substantially less stable than either the Zn–CDTA or Al–CDTA complexes. The Zn–CDTA complex is more stable than the Al–CDTA complex, but the latter once formed is difficult to decompose, hence the titration sequence is satisfactory. Several metals form colored dithizone complexes, however, and if present would interfere in the analysis, so that a preliminary separation would be necessary. Isopropanol is added to ensure a single phase solution for the final titration.

The data in Table I show comparative results for aluminum by various accepted methods. The standard aluminum powder had been analyzed by 3 different laboratories for trace impurities and aluminum. Each pyrophoric compound was distilled using an inert gas blanket and retained either undiluted or diluted with dry xylene or kerosene.

The compleximetric method proved to be the most precise, accurate and rapid method of analysis. Occlusion occurs with 8-hydroxyquinoline, and the fluoride procedure is subject to too many variable parameters to be suitable for routine use. Extremely high ignition temperatures followed by efficient desiccation are required for the ignition procedure. Pure aluminum triethyl (aluminum alkyl #2) contains 23.63% aluminum; from the data the 8-hydroxyquinoline methods appears to be most

TABLE I

COMPARATIVE ALUMINUM VALUES BY SEVERAL ACCEPTED METHODS AND THE PROPOSED METHOD

Sample		*Ignition*	*Oxine*	*Fluoride*	*Compleximetric*
Std. Al powder (99.64% Al)[a]		102.0±1.00	100.2±0.92	—	99.5±0.20
Al wire (99.71)[a]		101.0±2.60	101.1±1.23	—	99.7±0.22
Std. K. Alum		—	5.90	5.92	5.90
Alkyls	1	12.33	11.87	—	11.73
	2	24.35	23.61	—	23.44
	3	12.71	12.24	—	12.16
	4	4.64	4.41	—	4.43
Alkoxide	1	4.22	4.23	—	4.11
	2	4.76	4.71	—	4.63
Alum	1	4.14	4.03	3.81	4.02
	2	4.14	4.03	3.83	4.02
	3	4.17	4.02	4.01	4.01
	4	4.12	4.03	3.85	4.01

[a] Each result is the average of 10 or more analyses. All other results are the average of 3 or more analyses.

TABLE II

ALUMINUM RESULTS OBTAINED ON A VARIETY OF TYPICAL ALUMINUM ALKYLS BY THE DESCRIBED PROCEDURE

Sample	*No. of replicates*	*% Al*		
		Range	*Ave.*	*Dev.*
A	3	22.50–22.64	22.58	±0.07
B	5	20.90–21.01	20.95	±0.05
C	4	20.00–20.09	20.03	±0.05
D	3	23.45–23.55	23.51	±0.05
E	3	23.49–23.58	23.54	±0.04
F	4	9.84– 9.91	9.88	±0.03
G	4	—	10.35	±0.00
H	4	13.85–13.87	13.86	±0.01
I	5	—	0.09	±0.00
J	4	—	0.16	±0.00
K	4		0.2c	±0.00
L	4	0.88– 0.90	0.89	±0.01
M	4	4.05– 4.07	4.06	±0.01

accurate but experience[4] has shown that all low-molecular-weight aluminum pyrophorics are slightly contaminated with aluminum oxygenates, which, of course, change the matrix and slightly reduce the true aluminum content of the solution. Actually, aluminum triethyl has been used in this laboratory as an extremely efficient scavenger for trace electron-rich gases such as oxygen and moisture in so-called pure inert gases.

Table II shows aluminum results obtained by the described procedure under routine conditions. The lower values represent either samples with extreme solvent dilution or very high molecular weight. Neither the molecular weight nor the solvent have any effect on the final results. Of course, as the molecular weight increases, the pyrophoricity decreases and handling becomes progressively easier.

The described procedure has been used without difficulty to analyze several thousand pyrophoric aluminum samples without matrix effect or interference.

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1 E. Bonitz, *Chem. Ber.*, 88 (1955) 742.
2 E. Wanninen and A. Ringbom, *Anal. Chim. Acta*, 12 (1955) 308.
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(Received November 17th, 1967)

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Anal. Chim. Acta, 41 (1968) 557–560

Quantitative separation of selenium from metal ions on tin(IV) tungstate papers

Although ion-exchange papers for the separation of metal ions have recently received much attention, few quantitative separations have been described for papers impregnated with inorganic ion exchangers. The ion-exchange separation of selenium has been little studied[1]; the present work was undertaken to investigate the quantitative separation of selenium from important cations.

Apparatus

Glass jars (20 × 5 cm) were used to develop Whatman No. 1 paper strips 14 by 3 cm in size. A Bausch and Lomb Spectronic-20 was used for the spectrophotometric work.

Reagents and chemicals

Chemicals were either E. Merck (Darmstadt) or British Drug House analytical-reagent grade. Tin(IV) chloride pentahydrate was a Polish product. Demineralized, distilled water was used throughout.

Preparation of tin(IV) tungstate papers. Solutions containing 8.8% tin(IV) chloride pentahydrate and 3.3% sodium tungstate were prepared in water. Paper strips were passed through the tin(IV) solutions for 3–5 sec. The excess of tin(IV) was removed by placing the strips on a filter paper sheet. The strips were then dipped in a hot sodium tungstate solution for 5 sec and the excess drained off. These strips were dried at 40–45° in an oven and then washed with water in order to remove any excess of the reagents. The strips were again dried at 40–45°. These papers were first washed with 30 ml of 5% nitric acid and then with water to remove any excess of nitric acid. The papers were then dried and used as such.

Metal solutions. 0.1 *M* solutions of nitrates or chlorides of cations under study, containing a little acid to prevent hydrolysis, were used.

Standard selenium solution (10,000 p.p.m. Se). 2.190 g of anhydrous sodium selenite was dissolved in 20 ml of 1:1 hydrochloric acid and the solution was made upto 100 ml with water.

Qualitative tests

Yellow ammonium sulphide was used to detect lead and bismuth. Copper and iron were detected with hexacyanoferrate(II). Zinc and manganese were detected with diphenylcarbazide. Hydrochloric acid–tin(II) chloride reagent was used to detect selenium and tellurium.

Procedure

The solution containing selenium with other metal ions as impurities was applied as a thin uniform streak by means of a μl-pipette. The strips were conditioned for 10 min and then the developing solvent (0.1 *M* ammonium tartrate in 4 *M* ammonia solution) was allowed to ascend 11 cm on the paper. In order to ascertain the actual positions of the respective spots after development, pilot chromatograms were run under similar conditions and visualized. The selenium spots moved with the solvent front while all other ions remained at the point of application or moved only very slightly. For elution of the selenium spot the paper was cut and its upper end tapered to a point; the lower end was supported in a Petri dish by a glass rod. The spot was then eluted first with 10 ml of water and then with 5-ml portions upto a total volume of 30 ml. The volume was reduced to about 1 ml by evaporation in a beaker over a water bath. For the determination of selenium 9 ml of 5 *N* sulfuric acid were added to the concentrate, the precipitate was filtered and washed, and the filtrate was collected in a 25-ml volumetric flask. Then 2 ml of 5 *N* sulfuric acid were added and the selenium was determined using the starch-iodide method[2].

Results

Qualitative separation of selenium from important cations in varying ratios. Qualitative separation of selenium from traces of iron(III), copper(II) and zinc(II) was achieved (Table I).

Determination of selenium in presence of iron, copper, zinc, lead, bismuth and tellurium. Selenium solution containing various other elements was applied to the ion-exchange paper and the quantitative separation of selenium was studied. The sample contained selenium and the impurities in the ratio 10:1. A synthetic mixture containing selenium and six metal ions was also analyzed. The selenium content after

TABLE I

QUALITATIVE SEPARATION OF SELENIUM FROM SOME IMPORTANT CATIONS

Cations	*Ratio* $Se^{4+}:M$[a]	R_L[b]	R_T[b]	*Cations*	*Ratio* $Se^{4+}:M$	R_L[b]	R_T[b]
Se^{4+}	(1:1)	0.96	0.85	Se^{4+}	(1:10)	0.95	0.88
Cu^{2+}		0.29	0.00	Cu^{2+}		0.20	0.00
Se^{4+}	(10:1)	0.95	0.81	Se^{4+}	(100:1)	0.95	0.88
Cu^{2+}		0.11	0.00	Cu^{2+}		0.20	0.00
Se^{4+}	(1:1)	0.95	0.85	Se^{4+}	(1:10)	0.95	0.82
Fe^{3+}		0.40	0.00	Fe^{3+}		0.30	0.00
Se^{4+}	(10:1)	0.98	0.90	Se^{4+}	(100:1)	0.94	0.82
Fe^{3+}		0.27	0.00	Fe^{3+}		0.00	0.00
Se^{4+}	(1:1)	0.97	0.87	Se^{4+}	(1:10)	0.85	0.70
Zn^{2+}		0.16	0.00	Zn^{2+}		0.45	0.00
Se^{4+}	(10:1)	0.92	0.80	Se^{4+}	(100:1)	0.92	0.80
Zn^{2+}		0.09	0.00	Zn^{2+}		0.00	0.00
Se^{4+}	(1:1)	1.00	0.87	Se^{4+}	(1:1)	0.93	0.82
Mn^{2+}		0.00	0.00	Pb^{2+}		0.00	0.00
Se^{4+}	(1:1)	0.99	0.87	Se^{4+}	(1:1)	0.96	0.84
Hg^{2+}		0.17	0.00	Bi^{3+}		0.00	0.00

[a] Other cations.

[b] R_L, flow rate of leading front; R_T, flow rate of tailing front.

elution was found to be quantitative. Representative results are summarized in Table II.

The results show that the procedure is applicable for the quantitative separation of selenium from traces of Fe, Cu, Zn, Pb, Bi and Te. Washing of the ion-exchange papers before elution is necessary to eliminate interferences from incompletely precipitated tin(IV) or sodium tungstate. This technique can probably be used for other quantitative separations since the tin(IV) tungstate papers are selective and give fast and sharp separation.

TABLE II

DETERMINATION OF SELENIUM IN PRESENCE OF IMPURITIES

Selenium applied (µg)	*Impurity added*	*Selenium recovered (µg)*	*% Error*
20	Fe^{3+}	19.0	−5.0
20	Fe^{3+}	19.0	−5.0
20	Cu^{2+}	19.0	−5.0
20	Cu^{2+}	19.5	−2.5
20	Zn^{2+}	19.5	−2.5
20	Zn^{2+}	19.25	−3.75
20	Fe^{3+}, Cu^{2+}, Zn^{2+}, Bi^{3+}, Pb^{2+}, Te^{4+}	20.0	0.0
20	Fe^{3+}, Cu^{2+}, Zn^{2+}, Bi^{3+}, Pb^{2+}, Te^{4+}	19.0	−5.0
20	Fe^{3+}, Cu^{2+}, Zn^{2+}, Bi^{3+}, Pb^{2+}, Te^{4+}	19.25	−3.75

The authors are grateful to Dr. S. M. F. RAHMAN for providing research facilities. One of us (K.N.M.) received financial assistance from C.S.I.R. (India) which is gratefully acknowledged.

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1 I. M. KOLTHOFF AND P. J. ELVING, *Treatise on Analytical Chemistry*, Part II, John Wiley, 1961, p. 156.
2 D. F. BOLTZ, *Colorimetric Determination of Nonmetals*, Vol. III, Interscience, New York, 1958, p. 326.

(Received December 21st, 1967)

BOOK REVIEWS

G. H. NANCOLLAS, *Interactions in Electrolyte Solutions*, Topics in Inorganic and General Chemistry, Vol. 8, Elsevier, Amsterdam, 1966, x+214 pp., price Dfl. 40,—.

Information concerning complexes in solution forms an important branch of coordination chemistry, and fundamental work in this field has influenced the development of titrimetry, biochemistry, ocean chemistry and nuclear fuel reprocessing. Analytical chemists, biochemists and nuclear chemists have made important contributions to solution chemistry, especially in elucidating the nature of species formed by chemical equilibria in electrolyte solutions (ionic equilibria). NANCOLLAS is well known for his research in the field of solution chemistry and belongs to the British "zero ionic strength" group, which emanates from C. W. DAVIES. The other group, predominantly Scandinavian, make their measurements in media of high and constant ionic strength. As the reviewer belongs to the latter group, this will be reflected in his criticism of NANCOLLAS' book.

The book deals mostly with very simple equilibria, in which one species is formed from two ($M+A \rightleftharpoons MA$). This is due to the fact that, if one limits the investigation to an ionic strength less than 0.1 M, the concentrations of the metal ion and the ligand cannot be varied over very wide ranges. Thus polynuclear complexes, M_mA_n, or complexes with many ligands, MA_n, may not always be detected. Furthermore, the British group are of the opinion that thermodynamic calculations can only be performed for pure water (zero ionic strength), which is, of course, not true, and activity factors for reacting components X may very well be defined for other media, *e.g.*, $f_X \rightarrow 1$ when $[X] \rightarrow 0$ in 3 M $NaClO_4$.

The British group have spent much time in considering the values of the ΔG ($-RT\ln K$), ΔH and $T\Delta S$ terms of complex formation, while the Scandinavians have directed their research towards finding all possible species that can be formed from M and A in solution. This is then illustrated by distribution diagrams of which the reader will find none in NANCOLLAS' book.

It is therefore natural that Chapters 4 and 5 of the book, which deal with relationships between association constants, enthalpy and entropy changes, are excellent. The reviewer especially enjoyed the parts dealing with the polyamine, carboxylic, amino acid and aminopolycarboxylate complexes. The problem of inner- and outer-sphere complex formation of ion-pairs is also treated very well, but the book does not deal with equilibria in mixed or non-aqueous solvents.

Chapter 3 deals with experimental methods for determining association (stability) constants and Chapter 4 treats the problem of calculating the constants from experimental data. The division of the material in these two chapters into experimental techniques, primary data, relationships between primary data (*e.g.* emf) and concentrations of different species, and, finally, calculation of the parameters in the relationships, is, however, not very strict. Some experimental methods have been treated briefly (*e.g.* solvent extraction) or omitted altogether (*e.g.* vapour pressure osmometry), while other methods (*e.g.* conductance, solubility measurements, and determination of the heats of association) are treated in more detail. A warning should have been given for the possibility of the formation of mixed solid complexes in solubility measurements, and for the variation of the ion-exchange constants at low (trace) concentrations.

SUNNER, well-known for his work in calorimetry, should have had his name spelt correctly. It is irritating to see electroneutrality (p. 39, 41, 79, 87, 89) still in use instead of the analytically known total concentrations of all components (total $TlIO_3$ on p. 39, total M on p. 41, total H on p. 79, 87 and 89).

Chapter 6 gives a limited but very enjoyable treatment of the kinetics and mechanism of metal complex formation and the structure of the complex. The Appendix contains tables of thermodynamic functions, which are discussed further in Chapters 3 and 4.

GEORGE NANCOLLAS has written a very useful book, which can be recommended as an introduction to the field. I have on several occasions examined students at the University of Gothenburg on NANCOLLAS' book with good result, and it is furthermore important that Scandinavian chemists become acquainted with the British way of thinking in the field of ionic equilibria.

D. DYRSSEN (Göteborg)

Anal. Chim. Acta, 41 (1968) 563–564

Supplement to *Official, Standardised and Recommended Methods of Analysis*, Compiled and edited by S. C. JOLLY, for the Analytical Methods Committee of The Society for Analytical Chemistry, London, 1967. Society for Analytical Chemistry, London, 1967, xiv+424 pp., price 147 s (126 s to Society members).

The main publication to which this Supplement is attached was reviewed in this journal (*Anal. Chim. Acta*, 30 (1964) 106) and the same complimentary comments are equally applicable to this extension. For a publication with this coverage to be of maximum benefit to the analyst, it must be reasonably up-to-date, and this prime objective of the A.M.C. has been commendably achieved with the appearance of this Supplement.

Anal. Chim. Acta, 41 (1968) 564–565

Like the 1963 publication, this Supplement is in two parts, the first containing new recommended methods of analysis, and the second a revised bibliography of official, standardised, tentative and recommended methods. The methods in Part I are those that have been recommended on the basis of investigations carried out either by the A.M.C. sub-committees, or joint committees of the A.M.C. with other learned societies or government departments, and have been published in *The Analyst* between the beginning of 1963 and the end of 1966. All 44 sections of the bibliography in Part II of the earlier publication, except that on Soils, have been revised, and a new section on Coffee has been added. Information in the majority of these sections in this Supplement now covers the literature up to the end of 1966, and even later in some cases.

W. T. ELWELL (Birmingham)

Anal. Chim. Acta, 41 (1968) 564–565

ERRATUM

F. W. E. STRELOW, C. R. VAN ZYL AND C. R. NOLTE, Separation of alkaline earth elements by cation-exchange chromatography in ammonium malonate media, *Anal. Chim. Acta*, 40 (1968) 145–153.

The formula at the foot of p. 146 of the above paper should read:

$$D = \frac{\text{Equivalents in resin phase} \cdot \text{ml solution}}{\text{Equivalents in aqueous phase} \cdot \text{g resin.}}$$

Anal. Chim. Acta, 41 (1968) 565

[illegible]

[illegible]

Analytica Chimica Acta
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

ANNOUNCEMENT

MICROCHEMICAL WORKSHOP — 1968

The American Microchemical Society will conduct a Microchemical Workshop August 22 to 24 at the Pennsylvania State University. The program will consist of morning lectures on a number of topics that are of current interest to the chemist, followed by afternoon sessions devoted to demonstrations of equipment and techniques, laboratory work sessions including instruction in the use of thermal microscopy, and discussion groups. The afternoon laboratory sessions will be in charge of the same lecturers who presented the theoretical aspects in the morning sessions.

Topics will include "The Theory and Application of Ion Specific Electrodes", "Determination of Purity by Thermal Methods", "Thermal Microscopy in the Pharamaceutical Industry", and "Current Status and New Ideas in Fluorine Determination". One day will also be devoted to the general topic of "Current Ideas and Practice in the Operation of Microchemical Laboratories".

It is expected that the following lecturers will participate: Prof. R. BELCHER (Birmingham, England), Dr. N. BRENNER (Perkin-Elmer Corp., U.S.A.), Dr. B. BUDEŠINSKY (Prague), Dr. A. DIRSCHERL (Basel), Dr. ALLAN GRAY (Perkin-Elmer Corp., U.S.A.), Mr. D. KETCHUM (Eastman Kodak Co., U.S.A.), Prof. Dr. M. KUHNERT-BRANDSTÄTTER (Innsbruck), Dr. W. PADOWETZ (Basel), Dr. JAMES ROSS (Orion Corp., U.S.A.), Dr. W. SCHÖNIGER (Basel), Prof. Dr. W. SIMON (Zürich), Dr. H. WAGNER (Basel), Prof. C. WILSON (Belfast).

The facilities of Penn State will be utilized, including those of the College of Science, in addition to housing and food services. The total fee for the three-day session will be $35. In order to insure that each participant will receive full benefit of attendance and in view of the limited laboratory space available for the personalized work sessions, it will be necessary to limit attendance. Interested persons are urged to register early to insure their participation. For further information regarding registration and housing write to: Mr. DAVID R. SCHUCKERS, J. Orvis Keller Conference Center, The Pennsylvania State University, University Park, Pa. 16802.

For further information regarding the program write to: Mr. HOWARD J. FRANCIS, JR., Pennsalt Chemicals Corporation, 900 First Avenue, King of Prussia, Pa. 19406.

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PRINTED IN THE NETHERLANDS