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ELECTRON-EXCHANGE PROCESSES ON SIMPLE COLUMNS
OF KEL-F SUPPORTING TETRACHLOROHYDROQUINONE

The preparation of simple electron-exchange columns is reported. An organic porous material (Kel-F powder) is used to support a water-insoluble redox reagent. Of the organic compounds tested, tetrachlorohydroquinone was best. Very stable columns were obtained with a sufficiently high redox capacity (1.59 meq/g dry material) and a satisfactory reaction rate.

The following oxidation reactions were carried out: $Fe^{2+} \rightarrow Fe^{3+}$, $Cu^+ \rightarrow Cu^{2+}$, $Sn^{2+} \rightarrow Sn^{4+}$, $I^- \rightarrow I$, ascorbic acid $\rightarrow$ dehydroascorbic acid, as well as the following reduction reactions: $Fe^{3+} \rightarrow Fe^{2+}$, $I \rightarrow I^-$, $Ce^{4+} \rightarrow Ce^{3+}$, $V^{5+} \rightarrow V^{4+}$, $Cr^{6+} \rightarrow Cr^{3+}$. The effect of hydrogen ion concentration on the redox reactions was also studied.

The Kel-F–tetrachlorohydroquinone columns can be used for indirect titration of redox systems and for selective oxidations or reductions, e.g. Fe^{3+} in presence of Fe^{2+} and vice versa, Cr^{6+} in presence of Fe^{3+}, Ce^{4+} in presence of Ce^{3+}, ascorbic acid in the presence of glucose, and Sn^{2+} in presence of Sn^{4+} or Fe^{2+}.

E. CERRAI AND C. TESTA, *Anal. Chim. Acta*, 28 (1963) 205–216

THE APPLICATION OF MICROCHEMICAL METHODS TO
RADIOCHEMICAL ANALYSIS

PART III. SOLVENT EXTRACTION OF DIETHYLDITHIOCARBAMATES AND
THE RADIOCHEMICAL SEPARATION AND PURIFICATION OF COBALT,
NICKEL, PALLADIUM, SILVER AND CADMIUM

The advantages of solvent extraction of diethyldithiocarbamates in radiochemical separations are discussed. The development of a procedure for the separation and purification of cobalt and nickel from mixtures containing fission products is described; diethyldithiocarbamate extraction is used extensively. A scheme incorporating this procedure is also described whereby the fission products palladium, cadmium and silver are also determined on the same sample.

R. G. MONK, *Anal. Chim. Acta*, 28 (1963) 217–226

SYSTEMATIC STUDY OF THE SOLVENT EXTRACTION OF
METAL β-DIKETONATES

The extraction of 30 metals (Be, Mg, Ca, Sr, Ba, Sc, La, Ti, Zr, Th, Cr, Mo, U, Mn, Co, Fe, Ni, Pd, Cu, Ag, Zn, Cd, Hg, Al, Ga, In, Tl, Sn, Pb and Bi) by solutions of acetylacetone, benzoylacetone and dibenzoylmethane in benzene has been studied in relation to the pH values for extraction. The extraction constants and two-phase stability constants of the β-diketonates were calculated; these can be used to determine the optimum conditions for the separation of many metals. The linear relationship between the distribution coefficients of β-diketones and their corresponding β-diketonates has been confirmed.

J. STARÝ AND E. HLADKÝ, *Anal. Chim. Acta*, 28 (1963) 227–235

TEMPERATURE CHANGES IN SOLVENT EXTRACTIONS OF CADMIUM OXINATE

The extraction of $10^{-5.1}$ M cadmium ion from aqueous solution into chloroform containing oxine has been investigated and the effects caused by changing the temperature were studied. Values of equilibrium constants for all reactions participating in the extraction have been obtained as a function of temperature. Plots of the logarithms of the constants $vs.$ the reciprocal of the absolute temperature gave straight lines. Thermodynamic functions for all reactions involved have been calculated.

COCRYSTALLIZATION OF ULTRAMICRO QUANTITIES OF ELEMENTS WITH 2-MERCAPTOBENZIMIDAZOLE

DETERMINATION OF GOLD IN SEAWATER

The cocrystallization of ultramicro quantities of 25 diverse elements with 2-mercaptobenzimidazole was investigated with the aid of radiotracers. Under optimum conditions Sn, Hg, Ag, Ta and Au were recovered in high yield. Distribution coefficients between mother liquor and solid phase were calculated for gold and were found to vary inversely with the degree of crystallization and the hydrogen ion concentration. The cocrystallization process was applied to the isolation and subsequent determination of the natural gold abundance in seawater. After radiometric correction for chemical yield, the concentration of gold was calculated to be 0.068 ± 0.003 $\mu g/l$.

AMPEROMETRIC TITRATION OF COPPER WITH DIALLYL-DITHIOCARBAMIDOHYDRAZINE

Small amounts of copper(II) can be titrated with diallyldithiocarbamidohydrazine using amperometric end-point detection. The titration may be performed in the presence of air by short-circuiting the dropping mercury electrode with the reference electrode and measuring the limiting current of excess reagent after the end-point with a galvanometer. Few metals interfere. The time required for one determination is 10–15 min.

THE OSCILLOGRAPHIC POLAROGRAPHY OF NOBLE METAL COMPLEXES

The polarographic behaviour of complexes of the noble metals was studied by oscillographic polarography. A method was developed for the polarographic determination of copper, gold and palladium; silver and nickel do not interfere. Applications to the analysis of dental alloys proved successful.

SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF PALLADIUM AFTER COPRECIPITATION WITH TELLURIUM

A spectrophotometric method for the determination of microgram amounts of palladium in the presence of much iron, copper, nickel, cobalt, and other common elements (~ 0.5 g) is described. Palladium is separated by stannous chloride precipitation with tellurium as collector. p-Nitrosodiphenylamine is used as the colorimetric reagent, and diethyl oxalate as extractant for the palladium complex (sensitivity $= 0.0015$ μg Pd/cm$^2 \equiv \log I_0/I = 0.001$). Silver, selenium and tungsten lead to low results and should not exceed ~ 0.1 mg. The weight ratio Au/Pd should not exceed 10, else results for palladium are high. For Pd $>$ 1 μg, recoveries average 90% or better.

SPECTROPHOTOMETRIC DETERMINATION OF SCANDIUM WITH ANTHRARUFIN-2,6-DISULFONIC ACID (DISODIUM SALT)

A new spectrophotometric method for the determination of scandium is described using anthrarufin-2,6-disulfonic acid (disodium salt) as a reagent. The color reaction has a sensitivity of 0.004 μg Sc per cm^2 for $\log I_0/I = 0.001$ and obeys Beer's law up to 2 p.p.m. The effects of pH, time, order of addition of the reagents, temperature, and diverse ions were investigated. A separation procedure was developed and applied to six salt solutions containing scandium plus a variety of foreign ions.

SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM AFTER SEPARATION BY ANION EXCHANGE

A method is outlined for separation of titanium by anion exchange and subsequent spectrophotometric determination. Titanium fluoride is adsorbed quantitatively on a column of strongly basic anion exchanger and thus separated from ions which would normally interfere. The spectrophotometric measurement is achieved by formation of the intensely yellow and stable titanium ascorbate complex which has a maximum absorbance at 355 mμ.

A COMBINED ANION EXCHANGE–SOLVENT EXTRACTION PROCEDURE FOR SEPARATING TRACE AMOUNTS OF Eu, Gd, Dy, Sm AND Er FROM THORIUM TETRAFLUORIDE

A combined anion exchange–solvent extraction procedure has been developed to facilitate the spectrographic determination of trace quantities of Eu, Gd, Dy, Sm and Er in thorium tetrafluoride.

CHEMICAL METHODS FOR THE DETERMINATION OF THE "OXIDIZING (OR REDUCING) POWER" OF CERTAIN MATERIALS CONTAINING A MULTIVALENT ELEMENT IN SEVERAL OXIDATION STATES

General chemical methods for determining the "oxidizing (or reducing) power" of certain materials containing a multivalent element in several oxidation states have been considered. These determinations are important as representing the charge carrier concentration.

The general methods available are listed and the criteria for selecting the best method for a particular material are considered. Experimental procedures and estimates of the accuracy and precision of eight methods for the determination of the "oxidizing power" and the "reducing power" are given. The application of these methods to thermoelectric materials is also described.

DETERMINATION OF TITANIUM AND ZIRCONIUM AND THEIR SEPARATION FROM EACH OTHER WITH CHELIDONIC ACID

(Short Communication)

TITRIMETRIC MICRODETERMINATION OF COPPER AND ZINC WITH EDTA

(Short Communication)

SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

PART VIII. RIGOROUS CALCULATIONS OF THE HYDROGEN ION CONCENTRATION OF ACIDS AND BASES

(Short Communication)

ELECTRON-EXCHANGE PROCESSES ON SIMPLE COLUMNS OF KEL-F SUPPORTING TETRACHLOROHYDROQUINONE

E. CERRAI AND C. TESTA

Laboratori CISE - Segrate, Milano (Italy)*

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In 1949 CASSIDY[1] described his first experimental results and theoretical conclusions on the possibility of preparing polymeric substances capable of reversibly exchanging electrons with the molecules or ions of an adjacent phase. The well-known analogy between acid-base reactions and oxidation-reduction reactions was then carried into the field of exchange resins and a certain similarity was found between the ion-exchange mechanism and the electron-exchange mechanism. The polymeric substances tested, which possessed the electron-exchange properties, were named "redox resins" or "electron-exchange polymers".

In addition to the theoretical interest, one of the aims of the long series of studies that followed the first experiments mentioned above was to supply analytical chemistry with a new tool. The great advantage of a solid insoluble substance capable of oxidizing or reducing molecules or ions in an adjacent phase without the use of any reagent and without gas evolution, but simply by taking or releasing electrons (generally by exchanging electrons with protons) is obvious.

As surveyed in several review articles[2-4] almost all the experimental work has been devoted to the preparation of polymers with a matrix structure similar to that of ion-exchange resins but containing a functional group capable of the redox reaction. The functional group may be either a part of the back-bone of the chain or a substituent on the chain. The hydroquinone molecule has been considered a suitable functional group and therefore attempts have been made to polymerize vinylhydroquinone monomers[5]. Copolymers of vinylhydroquinone with styrene, α-methyl-styrene and 4-vinylpyridine[6] have also been prepared. Two additional examples of the preparation of redox polymers are a resin from hydroquinone, phenol and formaldehyde[7], and a resin from resorcinol, methylene blue and formaldehyde[8].

A different class of redox systems which in effect are redox ion exchangers has also been reported. These have been easily obtained by loading conventional cationic resins with Fe^{2+}/Fe^{3+}, Cu^+/Cu^{2+} and Sn^{2+}/Sn^{4+} or anionic resins with methylene blue/leucomethylene blue or quinone/hydroquinone[9,10].

In spite of the accurate and valuable studies which have been carried out, redox polymers have not been widely used so far in practical work. The reason is, at least partly, that practical applications are seriously limited by the relatively slow reaction rates and, in many cases, by insufficient chemical stability of the resins[4].

The only commercial product is not a redox polymer but a redox ion exchanger, *i.e.* Duolite S10, an anionic resin containing complexed copper(II), which is used for removal of dissolved oxygen from water.

The aim of our work was to study the preparation of a redox system suitable for column operation and simple enough to be easily set up in any analytical laboratory. No lengthy or complicated syntheses of redox polymers would be required but nevertheless the required fundamental characteristics should be preserved. Such characteristics are: (*a*) insolubility in the aqueous solutions passed through the columns; (*b*) enough porosity to allow efficient contact between the redox functions and ions or molecules of the aqueous phase; (*c*) high reactivity to permit an appreciable reaction rate without undesired chemical changes; (*d*) reversibility of the redox process; (*e*) ease of regeneration; (*f*) a redox potential suitable for a wide range of oxidation-reduction reactions; (*g*) for analytical applications, possibly different colours of the oxidized and the reduced forms. For the preparation of such a substance the same philosophy as that suggested by reversed phase column chromatography was followed.

An inert, porous, hydrophobic support was selected and an organic solution, immiscible with water and containing a water-insoluble organic redox substance, was sought; the desired characteristics were that the organic solution should be absorbed by the porous support in such a way that the redox molecules would be stably fixed to the surface and ready to react. Kel-F powder (polytrifluorochloroethylene) was used as the inert support because of the favourable results obtained in some examples of reversed phase column chromatography in which organic solutions of TBP, TNOA[11], TOPO[12] and HDEHP[13] were employed.

For the redox reagent, it was decided to investigate some of the simplest water-insoluble derivatives of hydroquinone or pyrogallol provided that they were appreciably soluble in some organic solvent as well as easily available.

The present paper describes the experiments carried out to test the performance of the organic compounds listed in the following section; a suitable product was found, and the preparation and analytical use of redox Kel-F columns are discussed.

EXPERIMENTAL

Reagents and apparatus

The five organic compounds tested are listed in Table I. Compounds A, B, C and D were supplied by Eastman Organic Chemicals (New York, U.S.A.) and compound E by Fluka (S.G. Buchs, Switzerland).

The Kel-F low-density powder (polytrifluorochloroethylene), grade 300, was supplied by Minnesota S.p.A. (Milano, Italy). All the other chemicals were of analytical grade.

The chromatographic columns were glass tubes of inner diameter 7 or 8.6 mm fitted at the bottom with a fritted glass disc.

Tests of solubility in organic solvents and insolubility in aqueous solutions

Equal amounts of the five compounds were rapidly tested with different organic solvents. The results obtained are collected in Table II. The most effective solvents proved to be ethyl ether and methyl isobutyl ketone (hexone). Therefore solutions of the five compounds in these solvents were tested by placing them in contact with
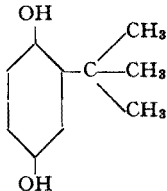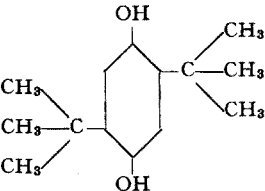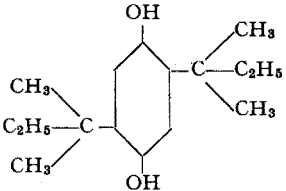
TABLE I

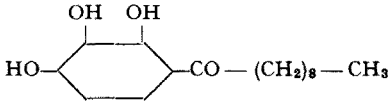### ORGANIC COMPOUNDS INVESTIGATED
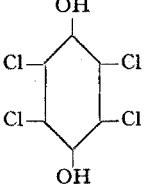
Compound A

Tert.-butylhydroquinone
(M.W. = 166)

Compound B

2,5-Di-*tert.*-butylhydroquin-
one (M.W. = 222)

Compound C

2,5-Di-*tert.*-amylhydroquin-
one (M.W. = 250)

Compound D

2,3,4-Trihydroxydecanophenone (M.W. = 280)

Compound E

Tetrachlorohydroquinone (M.W. = 248)

TABLE II

SOLUBILITY OF THE VARIOUS COMPOUNDS IN ORGANIC SOLVENTS

Solvent \ Compound	A	B	C	D	E
Benzene	Part. sol.	Part. sol.	Part. sol.	Part. sol.	Insol.
Cyclohexane	Insol.	Insol.	Insol.	Insol.	Insol.
Ethyl ether	Sol.	Sol.	Sol.	Sol.	Sol.
Chloroform	Part. sol.	Insol.	Part. sol.	Sol.	Insol.
Trichloroethylene	Insol.	Insol.	Part. sol.	Sol.	Insol.
White spirit 30–50°	Insol.	Insol.	Insol.	Insol.	Insol.
Hexone	Sol.	Sol.	Sol.	Sol.	Sol.

TABLE III

SOLUBILITY IN AQUEOUS MEDIA OF ETHYL ETHER OR HEXONE SOLUTIONS OF THE VARIOUS COMPOUNDS

Solvent	pH = 0		pH = 5		pH = 10	
	ether	hexone	ether	hexone	ether	hexone
Compound A	o	o	o	o	col.[a]	o
Compound B	o	o	o	o	o	o
Compound C	o	o	o	o	t[b]	o
Compound D	o	o	t[b]	o	col.[b] t[a]	o
Compound E	o	o	o	o	col.[b]	p[b]

o = no change, col. = colour formation, t = turbidity, p = precipitation.
[a] In the organic phase.
[b] In the aqueous phase.

aqueous solutions of pH 0, 5 and 10. The results (Table III) indicate that practically no turbidity, coloration or precipitation are produced at pH 0 or 5 whereas such phenomena become more apparent in alkaline medium. This behaviour is due to the presence of the phenolic hydroxyl groups which exhibit a slightly acidic character and consequently undergo some salt formation in the alkaline medium. Therefore in many cases, in order to avoid leaching of the redox reagent, redox columns should not be treated with strongly alkaline solutions.

Redox behaviour of the five products

To investigate the redox properties of the five compounds, five identical columns were prepared each with a theoretical capacity of 5 meq. The organic solutions for treatment of the Kel-F powder were prepared by dissolving in five 10 ml portions of hexone the following amounts of substances: 0.420 g of A, 0.560 g of B, 0.700 g of C, 0.625 g of D, and 0.615 g of E. Five 3 g portions of 100–170 mesh Kel-F powder were placed in five small beakers; 10 ml of each of the prepared organic solutions were added to each beaker in successive 2.5 ml aliquots. After each 2.5 ml addition the solvent was removed by thoroughly mixing the substance with a glass rod under a warm air flow. When the whole 10 ml amount had been added, the solvent was removed until a pasty substance was obtained. Then about 40 ml of 2 M hydrochloric acid were added and floating particles were eliminated. The organic–hydrochloric acid mixtures were then transferred to five 7 mm i.d. columns and a bed about 7 cm high was obtained in each column. Then each bed was fed with a 0.1 N solution of ceric sulphate at a flow-rate of about 0.2 ml/min.

In the reduced form the colour of the bed prepared with compound D (pyrogallol derivative) was brown, whilst those of the other beds (hydroquinone derivatives) were white. When in the oxidized form, *i.e.* after the treatment with cerium(IV), bed D turned red and the others yellow. After 100 ml of the oxidizing solution had passed through each bed, the column was washed with distilled water, and the excess cerium(IV) in the eluates was determined by iodimetry. These determinations indicated a reducing capacity of the beds from 4.6 to 5.1 meq, which is near enough to the theoretical value 5.0. It was therefore concluded that, as expected, such compounds almost completely exhibited their reducing property. From the colour changes from the reduced to the oxidized form it was noted that the oxidized band appeared more cleanly, the simpler the molecular structure of the compound: the order of decreasing sharpness was E-D-C-B-A. Since at a given flow-rate, the band definition is better the higher the exchange rate, it seems that the simpler molecules are more reactive than the more complicated ones. This is probably due to steric effects and to the influence of substituent groups on the normal redox potential of hydroquinone.

To test the reversibility of the five beds once they had been oxidized by cerium(IV), they were washed with 2 M hydrochloric acid and a 0.1 N stannous chloride solution in 2 M hydrochloric acid was passed at a flow-rate of 0.2 ml/min. Only compound E (tetrachlorohydroquinone) proved to be reversible by oxidizing tin(II) to tin(IV). In fact, bed E gradually turned white during elution. At the end of the treatment the bed was washed with 2 M hydrochloric acid and the excess of tin(II) in the whole eluate was determined by iodimetry. The oxidizing capacity was found to be 4.8 meq.

On the basis of the above experiments, tetrachlorohydroquinone was selected for further experiments owing to its reversibility and satisfactory reaction rate.

Redox processes with Kel-F –tetrachlorohydroquinone

Column I

A first series of oxidation-reduction reactions was carried out with a column named column I. This was prepared by mixing 5 g of 100–170-mesh Kel-F powder with 50 ml of a saturated solution of tetrachlorohydroquinone in ethyl ether in successive aliquots of 5 ml. After the addition of each aliquot the solvent was eliminated by stirring at room temperature. A pasty mixture with a weight of 6.8 g was obtained; 40 ml of 2 M hydrochloric acid were added and the whole slurry was transferred to a 8.6 mm i.d. column, the bed being gently pressed with a glass rod to eliminate channels. A 17-cm high bed was thus obtained.

Cycle 1. After the column had been washed with 0.03 M hydrochloric acid, a 0.02 N ferric chloride solution in 0.03 M hydrochloric acid was passed at a flow-rate of 0.5 ml/min. Iron(III) was completely reduced to iron(II) while the bed turned to the yellow form (oxidized quinone form). This cycle was stopped when 9.8 meq of iron(III) had been reduced without reaching saturation of the column. In this case the reaction rate was rather poor.

Cycle 2. The bed, which was about 90% in the oxidized form, was washed with 8 M hydrochloric acid, and then a 2.5% solution of potassium iodide in 8 M hydrochloric acid was passed at 0.5 ml/min. The pale yellow solution of iodide was oxidized to iodine (brown) by the column. Iodine was titrated in the eluate with thiosulfate. After the column had been completely reduced with an excess of the iodide solution, 9.6 meq of iodine were found.

Cycle 3. The column was washed with a buffer solution of pH 7.8 and a 0.05 M solution of iodine in potassium iodide buffered at pH 7.8 was allowed to pass at a rate of 1 ml/min. Under such pH conditions iodine was reduced to iodide ion and did not appear in the eluate even after 10 meq had been reduced. In this experiment the total reducing capacity of the column (completely yellow) proved to be 10.95 meq which corresponds to 1.61 meq/g of dry material.

Cycle 4. The column was washed with 2 M hydrochloric acid and a 0.1 N solution of stannous chloride in this 2 M acid was passed at 1 ml/min. The bed turned white whilst tin(II) gradually oxidized to tin(IV). When the treatment was complete, the oxidizing capacity of the column proved to be 10.7 meq (*i.e.* 1.57 meq/g).

Cycle 5. After the column had been washed with 2 M hydrochloric acid, a 0.1 M solution of vanadium(V) in this acid solution was passed through the bed at a flow-rate of 0.5 ml/min. The solution turned from yellow (V^{5+}) to blue-green (V^{4+}), and the bed from white to yellow. In this case the capacity was not evaluated.

Cycle 6. The column was washed with 2 M hydrochloric acid and quickly reduced with an excess of a 1 N solution of stannous chloride in 2 M hydrochloric acid. In spite of the high concentration of the reducing ion, the reduction band was well defined. In this case also, the capacity was not evaluated.

Cycle 7. The column was washed with distilled water and then a 0.1 N ceric sulphate solution was passed at 1 ml/min. As cerium(IV) was reduced the orange-yellow solution became discoloured; cerium(IV) was titrated by iodimetry in the effluent. As an example, a plot of the percentage of cerium(III) in the effluent against the

effluent volume is shown in Fig. 1. It appears from the plot that the column saturation is reached very steeply. The bed capacity proved to be 10.8 meq (1.59 meq/g).

Cycle 8. The column was washed with 6 *M* hydrochloric acid and a 0.1 *N* solution of cuprous chloride in 6 *M* hydrochloric acid was passed at 1 ml/min. The yellow (Cu+) solution turned to blue-green (Cu^{2+}) and the bed was reduced. The amount of copper(II) was determined by iodimetry and an oxidizing capacity of 12 meq was found. This result was higher than expected because some of the copper(I) had been spontaneously oxidized by air.

Cycle 9. The column was completely oxidized with an excess of a 0.1 *N* iron(III) solution and no evaluation of the reducing capacity was made.

Cycle 10. The column was washed with distilled water, and a 0.1 *N* solution of ascorbic acid at a flow-rate of 1 ml/min was used to reduce the bed, the ascorbic acid being oxidized to dehydroascorbic acid. The ascorbic acid in the effluent was determined by iodimetry and an oxidizing capacity of 10.9 meq (1.61 meq/g) was found.

Cycle 11. The bed was oxidized with a 0.1 *N* solution of iodine at pH 7.8 as in cycle 3. The capacity proved to be 10.7 meq.

Cycle 12. Reduction with potassium iodide as in the second cycle was carried out; the capacity was 10.5 meq.

Cycle 13. A final oxidation was carried out with a cerium(IV) solution (see cycle 7) and a capacity of 10.9 meq (1.61 meq/g) was found.

The experiments on column I were interrupted at this point because this column had proved to be sufficiently reversible, flexible and stable during all the numerous cycles in which acidic, neutral and slightly basic solutions had been used. The various oxidation-reduction reactions are listed in Table IV, together with the experimental values of the redox capacity. The average value, not considering those referred to in footnotes, is 10.8 meq, which corresponds to 1.59 meq/g dry material.

TABLE IV

REDOX REACTIONS OBTAINED WITH COLUMN I

	Reduced form			Oxidized form	
Cycle	Reaction	Bed capacity (meq)	Cycle	Reaction	Bed capacity (meq)
1	$Fe^{3+} \rightarrow Fe^{2+}$	9.80[a]	2	$I^- \rightarrow I$	9.60[b]
3	$I \rightarrow I^-$	10.96	4	$Sn^{2+} \rightarrow Sn^{4+}$	10.70
5	$V^{5+} \rightarrow V^{4+}$	—	6	$Sn^{2+} \rightarrow Sn^{4+}$	—
7	$Ce^{4+} \rightarrow Ce^{3+}$	10.80	8	$Cu^+ \rightarrow Cu^{2+}$	12.00[c]
9	$Fe^{3+} \rightarrow Fe^{2+}$	—	10	Ascorbic ac. $\rightarrow$ dehydroasc. ac.	10.90
11	$I \rightarrow I^-$	10.70	12	$I^- \rightarrow I$	10.50
13	$Ce^{4+} \rightarrow Ce^{3+}$	11.00			

[a] Incomplete saturation of the bed.
[b] The previous oxidation was incomplete.
[c] Cu+ partially oxidized to Cu^{2+} by atmospheric oxygen.

Column II

The column II was prepared by the same procedure as column I, but after the last addition of the organic solution to the Kel-F powder the ethyl ether solvent was

not removed and 2 M hydrochloric acid was immediately added to the mixture. This slight variation was made in order to check if the presence of the organic solvent would increase the exchange rate. The bed of column II had the same size as that of column I. With column II several redox cycles were again carried out; in some of them the redox capacity was determined. The experiments are summarized as follows:

Cycle 1. Oxidation of the bed with 0.1 N ceric sulphate.

Cycle 2. Reduction with 1 N stannous chloride in 2 M hydrochloric acid.

Cycle 3. Oxidation with 0.1 N iron(III) in 0.03 M hydrochloric acid at a flow-rate of 0.5 ml/min. The reaction rate was not higher than with column I.

Cycle 4. Reduction with 2.5% potassium iodide in 8 M hydrochloric acid and iodine formation. The total capacity proved to be 11.3 meq.

Cycle 5. Oxidation with cerium(IV); the total capacity was 10.9 meq.

Cycle 6. Reduction with 0.1 N ferrous sulphate in 8 M hydrochloric acid at 1 ml/min. The total capacity was 10.8 meq.

Cycle 7. After washing the bed with 2 M hydrochloric acid, a 1 N solution of potassium dichromate in 2 M hydrochloric acid was passed at a flow-rate of 0.5 ml/min. The orange-yellow solution (Cr^{6+}) turned violet (Cr^{3+}) whilst the bed turned from white to yellow. The total capacity was 11.3 meq.

Cycle 8. Reduction with potassium iodide solution.

Cycle 9. The column was washed with 2 M hydrochloric acid and a 1 N potassium iodate solution in 2 M hydrochloric acid was passed at 1 ml/min. Thus the bed was rapidly oxidized.

Cycle 10. After washing with distilled water, a 0.1 N solution of ascorbic acid was passed through the bed at 1 ml/min. The plot of the percentage of ascorbic acid in the effluent against the effluent volume is shown in Fig. 2. It can be seen that the front of the ascorbic acid is sharp enough to reveal that the reduction of the bed was quite rapid. In this last cycle the total capacity of the bed was 11.1 meq.

From the results of the ten cycles described above it was concluded that both columns operated very similarly as far as capacity and reaction rate were concerned.
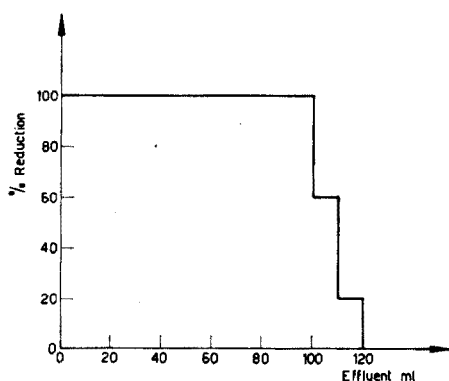

Fig. 1. Reduction curve of cerium(IV) on column I (reduced form) as a function of effluent volume. Feed solution: 0.1 N Ce(SO$_4$)$_2$ at 1 ml/min.
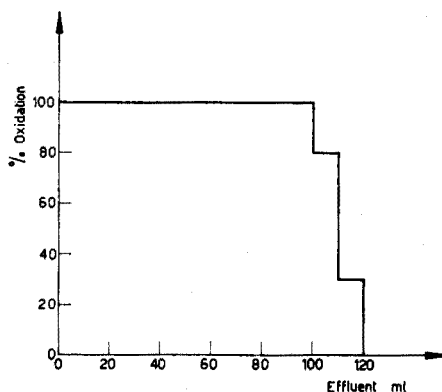
Fig. 2. Oxidation curve of ascorbic acid on column II (oxidized form) as a function of effluent volume. Feed solution: 0.1 N ascorbic acid at 1 ml/min.

In addition to those already tested with column I, three other processes were considered with column II; these were the reduction of dichromate and iodate and the oxidation of iron(II).

Influence of the hydrogen ion concentration on redox reactions

It is well known that the pH value of a system affects the redox potentials of the various redox components. In the above experiments, the oxidation of iron(II) to iron(III) or of iodide to iodine occurred when the organic matter in the quinone form was treated with a strongly acidic solution of these ions. Conversely, reduction of iron(III) to iron(II) and of iodine to iodide occurred when the hydroquinone form was treated with a weakly acidic solution (iron) or with a slightly alkaline solution (iodine).

To determine the extent of such effects, some simple experiments were carried out. A small redox column (column III) was prepared with only 2 g of 100–170-mesh Kel-F powder and 10 ml of a saturated solution of tetrachlorohydroquinone in hexone, added in 2.5 ml aliquots; the solvent was removed each time except for the last aliquot and 2 M hydrochloric acid was added. The size of the bed formed in column III was 7 mm × 125 mm. The redox capacity, determined by oxidation with cerium-(IV), was about 6 meq.

Finally, the oxidation of iron(II) to iron(III) through this bed was determined as a function of the acidity of the solution. Several solutions, each with a volume of 5 ml, were prepared by dissolving 0.5 meq of iron(II) in hydrochloric acid of strength 0.5 M to 8 M. After the bed had been conditioned with hydrochloric acid of the pertinent molarity, the 5 ml of solution were passed through the bed at a flow-rate of 0.2 ml/min. After washing with the same hydrochloric acid solution, the amount of iron(III) was determined iodimetrically in the effluent. The plot of the percentage of iron(II) oxidized is reported in Fig. 3 as a function of the acidity. It can be seen that the extent of reaction is negligible at low acidities and becomes appreciable as the molarity increases. Above 8 M hydrochloric acid it is practically 100%.

Analogously, the reverse reaction (reduction) was studied with solutions of iron(III) in hydrochloric acid of strength from 0 to 2 M using 5 ml aliquots. After each experi-
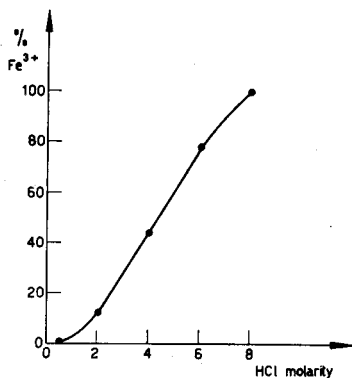
Fig. 3. Percentage oxidation of iron(II) as a function of HCl molarity in the feed solution (Column III in oxidized form).
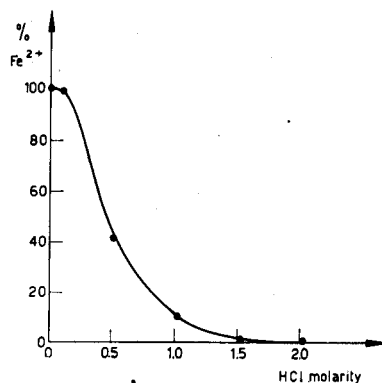
Fig. 4. Percentage reduction of iron(III) as a function of HCl molarity in the feed solution (Column III in reduced form).

ment, the bed was completely reduced with ascorbic acid. The flow-rate of the various solutions was 0.2 ml/min. The results given in Fig. 4 show that reduction occurs only when the acidity is low.

The effect of pH can be usefully exploited to carry out selective oxidations or reductions. For example: in 1.5–2 M hydrochloric acid it is possible to reduce chromium(VI) to chromium(III) or cerium(IV) to cerium(III) without reduction of iron(III) to iron(II). It is also possible to oxidize tin(II) to tin(IV), ascorbic acid to dehydroascorbic acid and copper(I) to copper(II) in 0.1–0.5 M hydrochloric acid without oxidizing iron(II) to iron(III).

The redox column used for indirect redox titrations

In some cases the direct titrimetric determination of an ion is not possible because of several interfering or disturbing effects. For example, the colour of the solution could hinder the correct use of an indicator or the presence of reagents or reaction products in the solution after titration could be undesirable from the point of view of further processing. In these cases, owing to the proved stability of the redox columns prepared as described above, it is possible to use such a column for indirect redox titrations. The column is used as an intermediate agent which can be regarded as holding a quantitative "memory" of the redox capacity of the substance under investigation. By means of the procedures described below no reagent is added to the original solution either before or after the treatment on the column.

(a) Determination of the reduction equivalent of a substance

A column in the oxidized form is required with an oxidation capacity in excess of the equivalent to be determined. The substance to be oxidized is dissolved in an aqueous solution of the appropriate acidity and passed through the bed; the bed is partially converted from the oxidized form (yellow) to the reduced form (white), whilst the substance is completely oxidized. The bed is accurately washed and, if necessary, all the effluents are collected. If the total capacity of the bed is known, the height of the reduced band gives a rough indication of the reduction equivalent of the substance. Anyway, a precise determination can be easily performed by passing an excess (two or three times the required amount) of an oxidizing solution (say cerium(IV)) which completely restores the oxidized form of the bed (yellow). The bed is washed and the washings are added to the cerium-containing effluent. Then the reduction equivalent is determined in this solution by titrating the residual cerium(IV). In this case the initial amount of cerium(IV) fed to the column must be known. In principle, depending on the type of oxidizing ion used, the determination could be made by directly titrating the amount of reduced ion in the effluent by means of a standard oxidizing solution.

(b) Determination of the oxidation equivalent of a substance

For this purpose an analogous procedure is followed. The bed is initially in the reduced form (white) and is partially oxidized by the solution to be analyzed. After washing, the bed is again completely reduced with a standard reducing solution and the effluent is titrated either for the oxidized portion of the reagent or for the residual reducing portion.

The experiments described in the following paragraphs have shown that in spite of the multi-stage procedure of the indirect titration, such substances can be determined with only a little loss in accuracy. A peculiar advantage of this use of redox columns lies in the possibility of selectively determining the amount of a given reduced or oxidized ion in the presence of foreign oxidizable or reducible ions or of a different valency state of the same ion (*e.g.* iron(III) in the presence of iron(II), etc.).

Indirect titration of iron(III) by reduction to iron(II)

A volume of 5 ml of a solution containing 0.490 meq of iron(III) in 0.05 M hydrochloric acid was slowly passed through the column III in the reduced form (about 6 meq), which had been previously treated with 0.05 M hydrochloric acid. The column was washed with the same acid and then 10 ml of freshly prepared 0.1 N ascorbic acid (1 meq) was passed through the bed. After washing with distilled water, the residual ascorbic acid in the effluent was determined by titration with a 0.1 N solution of iodine. The residual ascorbic acid was found to be 0.525 meq, hence the portion of the bed oxidized by iron(III) was 1.000 − 0.525 = 0.475 meq (compared with 0.490 meq of iron(III) initially in the solution). Thus the error was −3%. A second experiment with the same bed gave 0.495 meq, *i.e.* an error of +1%.

Indirect determination of iron(III) in the presence of iron(II)

A solution containing 0.45 meq of iron(III) and 1 meq of iron(II) was prepared in 0.05 M hydrochloric acid. Obviously iron(II) is not affected by the column and iron(III) can be determined by the above procedure. The results gave 0.44 meq of iron(III) with an error of about −2%.

Indirect determination of chromium(VI) by reduction to chromium(III)

A solution containing 0.445 meq of chromium(VI) in 2 M hydrochloric acid was prepared with a volume of 5 ml, and passed through column III (reduced form) at a flow-rate of 0.5 ml/min. After washing with 2 M hydrochloric acid, 10 ml of 0.1 M ascorbic acid were passed at 0.5 ml/min. The residual ascorbic acid in the effluent was determined with a 0.1 N iodine solution. By this method 0.450 meq of chromium(VI) were determined, the error being about +1%. Obviously chromium(VI) can be determined in the presence of chromium(III) or any other non-reducible ion.

The indirect determination of chromium(VI) in the presence of iron(III) is possible if the acidity of the solution is adjusted to a value which does not allow reduction of iron(III). The solution (5 ml) tested contained 0.455 meq of chromium(VI) and 0.50 meq of iron(III) in 2 M hydrochloric acid. Column III was used in the reduced form. When the solution was completely passed through and the bed was washed, only chromium(VI) was reduced. Ascorbic acid solution was used to reduce the bed again; titration of the effluent gave 0.448 meq of chromium(VI) (error +0.7%).

Indirect determination of cerium(IV)

Column III was treated with 5 ml of a solution containing 0.5 meq of ceric sulphate in 0.1 N sulphuric acid. After washing, ascorbic acid solution was passed through; titration of the effluent gave 0.5 meq of cerium(IV); errors were negligible. For the determination of cerium(IV) in the presence of cerium(III), column III was treated

with 5 ml of a solution containing 0.48 meq of cerium(IV) and 1.00 meq of cerium(III); the above method gave results of 0.495 meq (error −1%).

Indirect determination of iron(II) by oxidation to iron(III)

Column III was used in the oxidized form and pre-treated with 8 M hydrochloric acid; 10 ml of a 8 M hydrochloric acid solution containing 1 meq of iron(II) was passed at a flow-rate of 0.5 ml/min. After washing the bed with the 8 M acid, the column was eluted with 20 ml of a 0.1 N ceric sulphate solution (2 meq of cerium(IV)). Then the unreacted cerium(IV) was determined in the effluent by iodimetry, the result corresponding to 1.005 meq of iron(II) (error +0.5%).

For the determination of iron(II) in the presence of iron(III), column III in the oxidized form was treated with 5 ml of a solution containing 0.475 meq of iron(II) and 0.5 meq of iron(III) in 8 M hydrochloric acid. Then titration was carried out as above; 0.480 meq of iron(II) were found (error +1%).

Indirect determination of ascorbic acid in the presence of glucose

An aqueous solution was prepared containing 0.40 meq of ascorbic acid and 1 mmole of glucose in a total volume of 5 ml. The solution was passed through the oxidized bed of column III at a flow-rate of 1 ml/min. Glucose remained unaffected, and ascorbic acid was oxidized. After washing the bed with distilled water, 10 ml of a 0.1 N ceric sulphate solution were passed through the column and the excess cerium(IV) determined in the effluent in the usual way; 0.39 meq of ascorbic acid was found (error −2.5%).

Indirect determination of tin(II) in the presence of tin(IV) or iron(II)

A solution containing 0.860 meq of tin(II) and 2 meq of tin(IV) in 2 M hydrochloric acid (10 ml total volume) was passed through column III. The usual method gave a result of 0.845 meq (error −2%).

Owing to the fact that iron(II) is not oxidized to iron(III) at low acidities whereas tin(II) is oxidized, a 0.2 M hydrochloric acid solution was used; 10 ml of such a solution was prepared containing 0.510 meq of tin(II) and 1 meq of iron(II). The solution was passed through column III in the oxidized form. The determination gave a value of 0.510 meq of tin(II), *i.e.* no appreciable error.

CONCLUSIONS

From the experiments described above the following conclusions can be drawn.

(*a*) The columns prepared with Kel-F powder as a support for tetrachlorohydroquinone are suitable for oxidation-reduction reactions through a mechanism usually termed "electron exchange".

(*b*) The redox capacity of the substance is sufficiently high (*i.e.* 1.59 meq/g dry material) and the reaction rate is satisfactory.

(*c*) The colour changes of the two forms (yellow, oxidized; white, reduced) are useful for judging the extent of reaction within the column.

(*d*) Owing to the dependence of the redox potentials on pH, selective oxidations or reductions can be obtained.

(*e*) Without the addition of reagents to the solutions under examination, it is possible to carry out redox titrations by an indirect method.

SUMMARY

The preparation of simple electron-exchange columns is reported. An organic porous material (Kel-F powder) is used to support a water-insoluble redox reagent. Of the organic compounds tested, tetrachlorohydroquinone was best. Very stable columns were obtained with a sufficiently high redox capacity (1.59 meq/g dry material) and a satisfactory reaction rate.

The following oxidation reactions were carried out: $Fe^{2+} \rightarrow Fe^{3+}$, $Cu^{+} \rightarrow Cu^{2+}$, $Sn^{2+} \rightarrow Sn^{4+}$, $I^{-} \rightarrow I$, ascorbic acid $\rightarrow$ dehydroascorbic acid, as well as the following reduction reactions: $Fe^{3+} \rightarrow Fe^{2+}$, $I \rightarrow I^{-}$, $Ce^{4+} \rightarrow Ce^{3+}$, $V^{5+} \rightarrow V^{4+}$, $Cr^{6+} \rightarrow Cr^{3+}$. The effect of hydrogen ion concentration on the redox reactions was also studied.

The Kel-F–tetrachlorohydroquinone columns can be used for indirect titration of redox systems and for selective oxidations or reductions, *e.g.* Fe^{3+} in presence of Fe^{2+} and vice versa, Cr^{6+} in presence of Fe^{3+}, Ce^{4+} in presence of Ce^{3+}, ascorbic acid in the presence of glucose, and Sn^{2+} in presence of Sn^{4+} or Fe^{2+}.

RÉSUMÉ

Des colonnes de Kel-F (polytrifluorochloroéthylène), traitées par un réactif redox, la tétrachloro-hydroquinone, sont proposées comme échangeurs d'électrons ($Fe^{2+} \rightarrow Fe^{3+}$; $Cu^{+} \rightarrow Cu^{2+}$; $Sn^{2+} \rightarrow Sn^{4+}$; $I^{-} \rightarrow I$; acide ascorbique $\rightarrow$ acide déhydroascorbique; de même que $Fe^{3+} \rightarrow Fe^{2+}$; $I \rightarrow I^{-}$; $Ce^{4+} \rightarrow Ce^{3+}$; $V^{5+} \rightarrow V^{4+}$; $Cr^{6+} \rightarrow Cr^{3+}$). De telles colonnes ont été utilisées pour le titrage indirect de systèmes redox, ainsi que pour des oxydations et des réductions sélectives.

ZUSAMMENFASSUNG

Beschreibung einer einfachen Elektronen-Austauscherkolonne aus Kel-F (Polytrifluorochloro-äthylen) mit Tetrachlorohydrochinon als Redox-Reagenz. Die mit dieser Kolonne untersuchten Oxydations- und Reduktionsreaktionen sowie die Anwendung zur Titration von Redox-Systemen werden angegeben.

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THE APPLICATION OF MICROCHEMICAL METHODS TO RADIOCHEMICAL ANALYSIS

PART III.* SOLVENT EXTRACTION OF DIETHYLDITHIOCARBAMATES AND THE RADIOCHEMICAL SEPARATION AND PURIFICATION OF COBALT, NICKEL, PALLADIUM, SILVER AND CADMIUM

R. G. MONK

Atomic Weapons Research Establishment, U.K.A.E.A., Aldermaston, Berks (Great Britain)

In recent years solvent extraction has played an increasing role in separation procedures in analytical chemistry. It has proved particularly valuable in radiochemical work because it frequently effects greater decontamination in a single step than is possible in precipitation reactions. Normally, unwanted activities adsorbed on a precipitate cannot be removed by washing; however, dissolving the precipitate in an organic solvent, if possible, will return the impurities to the aqueous phase. COOK AND DUNCAN[1] give, as an example, the adsorption of ^{90}Sr on molybdenum 8-hydroxyquinolate which may be purified by dissolution in chloroform and washing with water.

In Part I[2] of this series the particular value of solvent extraction and ion-exchange processes for separations using 1 mg or smaller amounts of carrier was mentioned. The present paper is concerned with the uses of solvent extraction, particularly of diethyldithiocarbamates, in the separation and purification of cobalt, nickel, palladium, silver and cadmium from complex mixtures of radioactive elements consisting mainly of fission products a few hours old.

The use of diethyldithiocarbamate extractions for separating metals has been systematically studied by BODE[3] and it has been shown that the selectivity may be improved by such devices as pH adjustment and the use of masking reagents, *e.g.* cyanide and ethylenediaminetetraacetic acid. In fact it appears that separations normally using dithizone can also be carried out with diethyldithiocarbamate, possibly with slight alterations in reagent concentrations. However, considered purely as a separating agent, the latter reagent has considerable advantages over dithizone. These arise from the much higher solubilities of the reagent in water and of the corresponding chelates in organic solvents; consequently chelate formation and precipitation take place rapidly when an aqueous solution of sodium diethyldithiocarbamate is added to a solution of a metal ion, and the complex produced can be dissolved in a very small volume of solvent. Thus several mg of a metal as its diethyldithiocarbamate can be readily extracted by 1 ml of chloroform whereas the extraction of the corresponding dithizonate would probably need several hundred ml; in

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* Part II. *Anal. Chim. Acta*, 26 (1962) 305.

practice 100 μg is about the maximum weight of element for which dithizone is normally used and this involves a rather slow heterogeneous reaction between a dilute dithizone solution in chloroform or carbon tetrachloride and the aqueous solution containing the metal ions. For radiochemical separations, therefore, diethyldithiocarbamate extractions are much to be preferred and give quick and clean separations.

In the separation scheme to be described, extraction with chloroform of the diethyldithiocarbamates of one or more of the five elements, cobalt, nickel, palladium, silver and cadmium, is used for four distinct purposes which are enumerated below:

(*1*) Separation of the five elements as a group from the main solution of fission products and heavy elements is very useful. Radioactive isotopes of palladium, silver and cadmium are produced in relatively low yield in fission and the mixtures of interest contained even smaller amounts of cobalt and nickel activities. Consequently a very high degree of decontamination was needed for all five elements, particularly from the high-yield fission products, strontium, yttrium, zirconium, molybdenum, tellurium, iodine, barium and rare earths, whose activities preponderate heavily. Good separation was also needed from the heavy elements, thorium, protactinium, uranium, neptunium and plutonium, which could also be present in varying proportions and in different isotopic forms; [239]Np in particular was generally a significant contributor to the total β-activity. To reduce the need for lengthy purification of individual elements the first step in the scheme was designed to separate the five elements quantitatively as a group from the major fission products and heavy elements. This step consists in extracting the diethyldithiocarbamate with chloroform from ammoniacal solution containing citrate, under which conditions the only fission elements which are extracted, besides those required, are zinc, indium and antimony. Several quick washes with water are all that is then necessary to remove mechanically retained aqueous phase and the last traces of the major contaminants.

(*2*) Diethyldithiocarbamate extraction is used throughout the scheme as a quick method of recovering one or more elements from aqueous solution. The complexes are quickly destroyed by nitric acid or aqua regia and the small volume of chloroform needed for extraction is easily removed by evaporation. This method of recovery is cleaner and quicker than sulphide precipitation, particularly for the removal of nickel from ammoniacal solution because nickel sulphide tends to remain in colloidal suspension.

(*3*) Extraction of diethyldithiocarbamates from 2 M hydrochloric acid solution is used following solvent extraction of pyridine thiocyanates and α-furildioxime complexes. Recovery of elements is quicker and cleaner in this way and the necessity for the wet oxidation of pyridine and α-furildioxime is avoided.

(*4*) Diethyldithiocarbamate extraction is used for the separation of cobalt and nickel. In ammoniacal solution cobalt is oxidised to a trivalent complex by warming with hydrogen peroxide. On cooling and adding sodium diethyldithiocarbamate the yellow nickel complex alone is precipitated and extracted with chloroform. On warming the aqueous phase cobalt is reduced to the divalent state and green cobaltous diethyldithiocarbamate precipitates; after cooling this is also extracted with chloroform.

Other solvent extraction processes used in the scheme involve chloroform extraction of (*a*) pyridine–thiocyanate complexes of cobalt and nickel and (*b*) α-furildioxime complexes of palladium and nickel. The pyridine–thiocyanate complexes

were introduced as a recovery step involving some diversification of the procedure. α-Furildioxime is used for the individual purification of palladium and nickel and is specific for palladium in acid solution. It is preferred to dimethylglyoxime on account of the greater solubility of its metal chelates in chloroform, 1 mg of the dimethyl-glyoxime complexes of palladium or nickel requiring inconveniently large volumes of solvent.

Most of the remaining steps in the purification of palladium, silver and cadmium are conventional, involving precipitation reactions; these, however, are reduced to one of each type on account of the purification effected in the initial diethyldithio-carbamate extraction. After the sulphide precipitation the cobalt and nickel solution in 0.3 M hydrochloric acid is passed through an anion-exchange column as a final scavenging operation; this column is also an effective filter and retains traces of any finely divided sulphide which may escape centrifugation. Anion exchange is also the final step in the purification of cobalt which is adsorbed from 9 M, and eluted with 6 M, hydrobromic acid.

After the initial diethyldithiocarbamate extraction the aqueous phase may conveniently be used for determinations of other fission products. As a relatively large sample is needed for determining the minor activities only small portions of the solution are needed for the major fission products such as ^{99}Mo, ^{95}Zr and ^{97}Zr, and the higher-yield rare earths. A useful procedure is to add large measured amounts (10–20 mg) of the appropriate carriers at the beginning of the analysis and to carry out individual determinations on portions of the aqueous phase which need not be measured accurately but which contain about 1 mg carrier. This avoids the necessity for undesirably large dilution before source preparation.

<div align="center">EXPERIMENTAL</div>

The main experimental work involved testing likely procedures for separating and purifying cobalt and nickel on samples of slow neutron irradiated uranium to which cobalt and nickel carriers had been added. As these two elements do not occur in fission, a perfect procedure would have yielded completely inactive products; the total β-activity of the cobalt and nickel at any point in the procedure was therefore a measure of the contamination still present.

Purity of the separated sources of palladium, silver and cadmium was checked by observations of decay and indicated by the absence of extraneous half-lives.

Fission products. Portions (0.4 g) of natural uranium in the form of U_3O_8 were irradiated in B.E.P.O. at the Atomic Energy Research Establishment, Harwell, for 2 h at a flux of about 10^{12} neutrons/cm²/sec. These irradiations provided samples of the products of about $3 \cdot 10^{13}$ fissions; work was generally started about 2 h after removal from the reactor, at which time the total activity of the sample was about 40 mc, including about 1 mc of ^{239}Np.

Procedure. The irradiated U_3O_8 was dissolved in a little concentrated nitric acid and 1 mg each of carriers for cobalt, nickel, palladium, silver and cadmium, 10 mg each of molybdenum and zirconium and 25 mg of lanthanum were added; molybdenum carrier was added as ammonium molybdate and the other elements as nitrates. One ml of perchloric acid was added, and the solution evaporated to fumes and then nearly to dryness under a lamp. The residue was diluted somewhat, 4 ml of 10% tartaric acid were added, the solution was made alkaline to cresol red by the addition of 14 M

ammonia solution and 0.5 ml of ammonia was added in excess. The next part of the procedure consisted in the extraction with chloroform of the diethyldithiocarbamates, the precipitation of palladium, silver and cadmium sulphides from 0.3 M hydrochloric acid, the passage of the supernate containing cobalt and nickel through XE-119 anion resin and the chloroform extraction of the pyridine thiocyanates of cobalt and nickel. These operations were carried out as described below in the complete separation procedure and will be referred to as the "preliminary separation"; this was carried out on all samples.

Subsequent treatment varied with sample. At appropriate stages in the procedures the residual β-activities of the cobalt and nickel were determined by evaporating the solutions as nitrates on 1″ watch glasses and counting by means of a type EHM2 Geiger-Müller counter tube and usual ancillary electronic equipment. Scavenging precipitates were similarly mounted and counted. The overall efficiency of the counting arrangement was about 20% for β-particles above 0.5 MeV energy and this figure has been assumed for all sources counted. Obviously no great accuracy is possible in such experiments but this is not necessary for the purpose in hand; the results quoted in terms of disintegrations per minute are probably accurate to $\pm$ 50%. Chemical yields were not determined in these experiments but were all visually assessed as ≮ 50%. The chemical yield of the complete procedure has been found to be normally at least 60% for both elements. A conservative figure of 50% has been used for calculating residual activities on cobalt and nickel after separation from each other; the steps up to this stage have been assumed 75% efficient.

Purification of cobalt and nickel before separation from each other

In one experiment the total residual β-activity of the cobalt and nickel after the preliminary separation was found to be 120,000 d.p.m. 4.5 h after irradiation. The total fission product activity at this time would have been $3.6 \cdot 10^{10}$ d.p.m., using the figures of HUNTER AND BALLOU[4], so that the preliminary separation gave a decontamination factor of $3 \cdot 10^5$. After dissolving the cobalt and nickel nitrates in water a portion of about 1/6 was evaporated on a watch glass and counted at about hourly intervals for a few hours, and again on the following day, to observe the decay. The main component had a half-life of about 2 h but there was also 5–10% of an activity with a half-life of 15–20 h.

The cobalt and nickel were then scavenged together by precipitating a mixture of ferric and neodymium hydroxides (0.1 mg each) with excess of ammonia. After centrifuging the precipitate it was slurried with a little water, transferred to a watch glass, dried and counted. This operation was not carried out in a quantitative manner but over 75% of the activity remaining with the cobalt and nickel after the preliminary separation was found on the hydroxide source. This consisted of the 2-h half-life material with less than 2% of the long-lived constituent, calculated at 4.5 h after irradiation. The identity of the 2-h impurity will be discussed later.

Specific separations of cobalt and nickel

A number of methods for separating cobalt and nickel from each other and from residual active impurities were considered and briefly investigated. Thiocyanate and α-nitroso-β-naphthol extractions for cobalt were found to be insufficiently specific for the purpose and the procedures finally selected were anion exchange for cobalt,

α-furildioxime extraction for nickel and diethyldithiocarbamate extraction from an ammoniacal solution of cobalt(III) for separation of cobalt and nickel.

Anion-exchange separation of cobalt

Hydrochloric acid media are usually used for adsorbing cobalt on an anion resin but in the present work hydrobromic acid was used. No very strong reasons can be adduced for this; at one stage of the investigation evaporation with hydrobromic acid was used to remove possible traces of tin and antimony and it was convenient to carry out the exchange step with the same acid immediately afterwards. It was also observed that cobalt is adsorbed somewhat more strongly from hydrobromic than from hydrochloric acid. Consequently the same system was used throughout but doubtless the use of hydrochloric acid, perhaps at slightly different concentrations, would serve equally well. With hydrobromic acid, cobalt is adsorbed at 9 M concentration, the column washed with 2 or 3 column volumes of the same acid and the cobalt subsequently eluted with 6 M acid.

An experiment was carried out using the above procedure on cobalt and nickel recovered from the preliminary separation stage. The cobalt fraction contained 800 d.p.m. of an impurity which did not decay appreciably over a few hours. Again calculating to 4.5 h after fission the decontamination factor of the cobalt was $4.5 \cdot 10^7$, that of the anion-exchange stage alone being about 150.

Extraction of nickel diethyldithiocarbamate from ammoniacal solutions of cobalt(III)

There is some tendency for cobalt(II) to be adsorbed on hydroxide precipitates from ammoniacal solution and to avoid this it was found desirable to oxidise the cobalt with hydrogen peroxide to a trivalent complex before carrying out the ferric–neodymium hydroxide scavenge. Consequently it was convenient to separate cobalt and nickel immediately after the scavenge by adding sodium diethyldithiocarbamate. From such a solution only nickel is precipitated and, after extraction with chloroform, heating results in reduction of cobalt(III) by excess reagent and precipitation of cobalt(II) diethyldithiocarbamate.

Complete procedure for purification of cobalt and nickel

The overall procedure for the radiochemical separation and purification of cobalt and nickel comprises the following steps:

(1) Extraction with chloroform as diethyldithiocarbamates from ammoniacal citrate.

(2) Sulphide scavenge from 0.3 M hydrochloric acid.

(3) Anion-exchange resin scavenging column from 0.3 M hydrochloric acid.

(4) Extraction of pyridine thiocyanates with chloroform.

(5) Extraction of diethyldithiocarbamates from 2 M hydrochloric acid with chloroform.

(6) Iron and neodymium hydroxide scavenge from ammoniacal solution of nickel(II) and cobalt(III).

(7) Extraction of nickel diethyldithiocarbamate from solution containing cobalt(III).

(8) Extraction of nickel α-furildioxime complex with chloroform.

(9) Conversion to nickel diethyldithiocarbamate by treatment with 2 M hydrochloric acid and sodium diethyldithiocarbamate.

(10) Reduction of cobalt(III) to cobalt(II) and extraction as diethyldithiocarbamate.

(11) Adsorption of cobalt on anion-exchange column from 9 M hydrobromic acid and elution with 6 M acid.

The above procedure was carried out on the usual $3 \cdot 10^{13}$ fissions. The activities remaining in the cobalt and nickel fractions were respectively 1,200 d.p.m. at 7.5 h and 300 d.p.m. at 6.25 h after fission; the decontamination factors from total fission product activity were therefore about $2 \cdot 10^7$ and $8 \cdot 10^7$ respectively at these times.

Complete separation scheme for Co, Ni, Pd, Ag and Cd

To the sample add accurately weighed portions of carrier solutions (5–10 mg of element per ml) containing about 0.5 mg each of Co and Ni, 1 mg each of Pd, Ag and Cd and appropriate amounts of carriers for the isotopes of any other elements to be determined. Preliminary treatment depends on the nature of the sample but preferably should include heating with aqua regia followed by transfer to a platinum dish and fuming with hydrofluoric and perchloric acids to ensure interchange between carriers and active species; fuming with perchloric acid also eliminates ruthenium isotopes by volatilization as RuO_4. After fuming nearly dry, allow to cool, add 1 ml of 1 M hydrochloric acid and warm until the residue has dissolved, ignoring the silver chloride (and molybdenum trioxide if present). Transfer the solution to a 10-ml centrifuge tube, add 0.2 ml of 10% citric acid (or tartaric acid), make ammoniacal and add 1–2 ml of 6 M ammonia in excess. If zirconium, rare earth carriers or any other hydrolysable elements are present more citric acid may be needed to ensure complete dissolution at this stage. Add, without delay, 0.3 ml of a fresh 10% solution of sodium diethyldithiocarbamate and extract with 2×1 ml portions of chloroform using a transfer pipette to mix the phases. (Too long a delay between making ammoniacal and adding reagent might result in oxidation of some cobalt to an unreactive cobalt-(III) complex by dissolved oxygen.) Transfer the chloroform extracts to a clean 10-ml tube and retain the main aqueous phase for determinations of other constituents if required.

Chloroform extract of Co, Ni, Pd, Ag and Cd diethyldithiocarbamates. Wash quickly with 5 ml of a 1% solution of citric acid in 0.5 M ammonia and then with four successive 5 ml portions of water, rejecting all washings. Transfer to a 25-ml beaker, add 1 ml of aqua regia, cover with a watch glass and heat carefully under a lamp until the solvent has evaporated. Remove the glass and evaporate to dryness; add 0.2 ml of 6 M hydrochloric acid and again evaporate to dryness. Dissolve the residue in 0.3 M hydrochloric acid and transfer to a 3-ml tube with washes of the same acid, keeping the volume between 0.5 and 1 ml; retain the beaker (A) containing a little silver chloride. Heat in boiling water for a few minutes and saturate with hydrogen sulphide. Centrifuge, remove the supernate and wash the precipitate with two 0.5 ml portions of 0.3 M hydrochloric acid. Retain the precipitate of sulphides of Pd, Ag and Cd.

Aqueous solution of cobalt and nickel. Pass the solution and then the two washes in order through a column of Amberlite XE-119 or equivalent anion-exchange resin, 5 cm long and 3 mm in diameter, at a rate of about 0.2 ml/min. Discard the column and to the eluate add 0.2 ml of 10% ammonium thiocyanate and 0.5 ml of pyridine.

Centrifuge and reject the supernate; dissolve the precipitate in 0.5 ml of chloroform and wash the solvent layer quickly with two successive 2 ml portions of 1% ammonium thiocyanate solution, rejecting the washes. Extract the chloroform layer with 1 ml of 2 M hydrochloric acid, add 0.2 ml of 10% sodium diethyldithiocarbamate and back-extract the precipitate into the same chloroform. Reject the aqueous layer and wash the chloroform solution with 1 ml of 0.5 M hydrochloric acid; evaporate the chloroform layer to dryness with 1 ml of aqua regia as already described.

Dissolve the residue in 0.1 ml of 0.3 M hydrochloric acid and a little water and transfer to a 3-ml tube. Add 0.2 ml of 6 M ammonia and 0.1 ml of 20-vol. hydrogen peroxide and heat in boiling water for a few minutes to oxidise the cobalt(II) and decompose excess of peroxide. Dilute to about 1.5 ml, cool, add 0.1 ml of neodymium(III) carrier solution (1 mg Nd^{3+} per ml), centrifuge, add a further 0.1 ml of the same carrier and centrifuge again; reject the precipitate.

Cool the solution in ice water for a few minutes and add 0.3 ml of 2% sodium diethyldithiocarbamate solution; extract the nickel complex with 0.5 ml of chloroform, separate the organic phase and wash the aqueous layer with two further 0.25 ml portions of chloroform. Unite the chloroform layers and retain the aqueous phase for cobalt.

Chloroform solution of nickel diethyldithiocarbamate. Wash twice with water and destroy organic matter by evaporation with 0.5 ml of aqua regia. Dissolve the residue in water and transfer to a 50-ml centrifuge tube; add 0.2 ml of 10% citric acid, 0.5 ml of 1 M ammonia and 2 ml of an aqueous 1% solution of α-furildioxime. Dilute to 10 ml, allow to stand for 5 min and extract the nickel complex with 10 ml of chloroform. Wash the organic layer with two 10 ml portions of water and reject the original aqueous phase and washes. Add 5 ml of 1 M hydrochloric acid and 0.5 ml of 10% sodium diethyldithiocarbamate, and mix thoroughly without delay. The precipitated diethyldithiocarbamic acid is extracted by the chloroform and the colour of the organic phase changes from orange-yellow to greenish-yellow as the nickel complex with α-furildioxime is converted to the diethyldithiocarbamate. Reject the aqueous phase and wash the chloroform layer thoroughly with two 10 ml portions of water. Destroy organic matter by evaporation with aqua regia and dissolve the residue in 0.1 M hydrochloric acid.

Aqueous solution of cobalt. Add a further 0.1 ml of 2% sodium diethyldithiocarbamate and heat in boiling water for a few minutes to reduce cobalt(III) and precipitate the diethyldithiocarbamate. Cool, extract with 0.5 ml of chloroform, wash the organic phase with 1 ml of water and evaporate to dryness after adding 0.5 ml of aqua regia. Dissolve the residue in 0.2 ml of 9 M hydrobromic acid and transfer to a column of Amberlite XE-119 or equivalent anion-exchange resin, 5 cm long and 4 mm in diameter, previously conditioned by washing thoroughly with the same acid. Complete the transfer of the cobalt solution with further washings of 9 M hydrobromic acid, passing a total of about 3 ml through the column at a rate of about 0.5 ml per min. Reject the eluate up to this stage, elute the cobalt with 2 ml of 6 M hydrobromic acid and evaporate to dryness. Dissolve the residue in 0.1 M hydrochloric acid.

Precipitate of sulphides of Pd, Ag and Cd. Add 1 ml of 2 M hydrochloric acid and heat in boiling water for a few minutes to dissolve the cadmium sulphide; centrifuge and wash the precipitate with two successive 0.5 ml portions of water. Retain the insoluble residue of sulphides of Pd and Ag and add the washings to the main solution.

Solution of Cd in 1 M HCl. Add 0.2 mg of palladium carrier and pass hydrogen sulphide through the solution; centrifuge and reject the precipitate. Add 0.5 ml of 50% ammonium acetate to the supernate, centrifuge and wash the precipitate of cadmium sulphide once with water. Dissolve in 0.1 ml of 6 *M* hydrochloric acid and heat in boiling water for a few minutes to remove hydrogen sulphide. Add 0.2 mg of neodymium(III) carrier, dilute to 1.5 ml and add 0.2 ml of 6 *M* ammonia; centrifuge, add a further 0.1 mg of the same carrier and again centrifuge. Reject the precipitate and pass hydrogen sulphide through the supernate. Centrifuge and wash the precipitate of cadmium sulphide once with water and once with 0.1 *M* hydrochloric acid. Dissolve in 0.1 ml of 6 *M* hydrochloric acid, evaporate to dryness and dissolve the residue in 0.1 *M* hydrochloric acid.

Precipitate of sulphides of Pd and Ag. Add 0.5 ml of aqua regia, transfer the solution to the 25-ml beaker (A) and evaporate to dryness. Dissolve the residue in 0.2 ml of 1 *M* ammonia, dilute to 1.5 ml and reprecipitate silver chloride by adding 0.5 ml of 2 *M* hydrochloric acid, noting the time as zero for the separation of [112]Ag and [112]Pd. Centrifuge and wash the silver chloride twice with 1 ml portions of 0.5 *M* hydrochloric acid; retain the supernate and washings for palladium.

Precipitate of silver chloride. Dissolve in 0.5 ml of 2 *M* ammonia, dilute to 1.5 ml and scavenge with two successive portions of 0.1 mg of neodymium(III). To the supernate add 0.25 ml of 1 *M* hydrazine hydrate solution and heat in boiling water for a few minutes. Centrifuge and wash the precipitated silver twice with water. Dissolve the silver by warming with 0.1 ml of 6 *M* nitric acid and dilute to a suitable volume.

Solution of palladium. Transfer to a 50-ml centrifuge tube, add 1 ml of 6 *M* hydrochloric acid and 1 ml of a 1% solution of α-furildioxime and dilute to 15 ml. Stand for 5–10 min, extract the palladium complex with 15 ml of chloroform and reject the aqueous layer; wash the chloroform layer twice with 0.2 *M* nitric acid and once with water, noting the time of the last wash as zero for the growth of [112]Ag into [112]Pd. Add 5 ml of 1 *M* hydrochloric acid and 0.5 ml of 10% sodium diethyldithiocarbamate and mix thoroughly; reject the aqueous layer and wash the organic layer twice with water. Add 1 ml of aqua regia to the chloroform solution and evaporate to dryness. Dissolve the residue in 0.5 *M* hydrochloric acid.

After completing the purification of each element, transfer the final solution to a polythene ampoule and weigh out suitable quantities for preparing counting sources and determining chemical yield.

*Purity of separated palladium, silver and cadmium*

The radiochemical purity of the palladium, silver and cadmium separated by the above scheme was found to be as good as that given by standard methods. Palladium sources prepared a few hours after fission contain [109]Pd($t_{\frac{1}{2}}$ 13.5 h) and [112]Pd($t_{\frac{1}{2}}$ 21 h with 3.5 h [112]Ag growing in) while silver sources consist of [111]Ag($t_{\frac{1}{2}}$ 7.5 d), [112]Ag($t_{\frac{1}{2}}$ 3.5 h) and [113]Ag($t_{\frac{1}{2}}$ 5.3 h). No component has been observed in sources of these elements other than the above fission products. Similarly cadmium separated within 1–2 days contains only [115]Cd($t_{\frac{1}{2}}$ 2.3 d) and [115m]Cd($t_{\frac{1}{2}}$ 43 d).

DISCUSSION

The method described above for the separation and radiochemical purification of cobalt and nickel has been found to give adequate decontamination from fission

products, heavy elements, and other radioactive species occurring in the debris from the explosion of nuclear weapons. The small amounts of long-lived contamination found in the cobalt sources in the experiments described above with irradiated uranium were insignificant compared with the amounts of $^{58m}Co(t_{\frac{1}{2}}$ 9 h) and $^{58}Co(t_{\frac{1}{2}}$ 71 d) present in samples of weapon debris. The use of specific positron counting or γ-spectrometry also reduces interference from other emitters in the determination of both ^{58}Co and $^{57}Ni(t_{\frac{1}{2}}$ 37 h).

It was noted above that an impurity with a half-life of about 2 hours accompanied the cobalt and nickel through the preliminary separation and on chemical and nuclear grounds this can only have been ^{117m}In which has a half-life of 1.9 h. This nuclide grows into fission products through the following rather complex decay scheme:
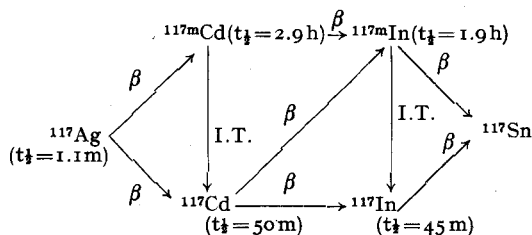
The details of the system have not been fully worked out and it is not known in what proportions ^{117m}Cd and ^{117}Cd disintegrate to ^{117m}In; it is not possible, therefore, to calculate accurately the amount of ^{117m}In present in a sample at any particular time. However, it is clear that less than 10% of the disintegrations of ^{117m}Cd give ^{117m}In and this mode of formation may therefore be neglected for the present purpose. The amount of ^{117m}In produced has been calculated on the assumption that all the ^{117}Cd atoms decay to this nuclide, thereby giving a maximum figure. As no 45-min component was observed in the decay of the sources concerned it appears that little ^{117}In is produced in the decay of ^{117}Cd and that the maximum figure for ^{117m}In calculated as above may not be very far out. It has also been assumed that the production of the $3 \cdot 10^{13}$ fissions in the irradiated uranium was instantaneous and occurred at the mid-time of the irradiation; errors arising from this assumption are also small compared with other uncertainties in the calculation.

Indium is extracted quantitatively as diethyldithiocarbamate by chloroform from ammoniacal citrate together with cadmium; the separation from cadmium, therefore, would be expected at the sulphide precipitation from 0.3 M hydrochloric acid, under which conditions indium is not normally precipitated. At this time, 4 h after zero (as defined above), the maximum number of ^{117m}In atoms which could have been present was calculated as $7 \cdot 10^8$. The number of atoms found with the cobalt and nickel calculated to the same time was only $2.6 \cdot 10^7$, about 4% of the maximum possible. Even taking into account the uncertainties in the calculation it is clear that most of the ^{117m}In present was removed in the preliminary separation. The distribution coefficient for indium between an anion-exchange resin and 0.3 M hydrochloric acid is low and under the conditions of the experiment indium should have been eluted virtually completely. Also a qualitative experiment with about 1 mg of indium showed that it was precipitated by thiocyanate and pyridine and that, while the precipitate was less soluble in chloroform than the pyridine thiocyanates of cobalt and nickel, the distribution between the aqueous and solvent phases was very much

in favour of the latter. Under tracer conditions, therefore, the indium would be very largely extracted into the chloroform phase. It appears, therefore, that the step in which a large fraction of the indium was removed must have been the sulphide precipitation and that, in the absence of hold-back carrier, tracer indium can be carried by a sulphide precipitate at an acidity as high as 0.3 M. In this connection HILLEBRAND AND LUNDELL[5] state that indium can be carried down by certain members of the hydrogen sulphide group in moderately acidic solution.

SUMMARY

The advantages of solvent extraction of diethyldithiocarbamates in radiochemical separations are discussed. The development of a procedure for the separation and purification of cobalt and nickel from mixtures containing fission products is described; diethyldithiocarbamate extraction is used extensively. A scheme incorporating this procedure is also described whereby the fission products palladium, cadmium and silver are also determined on the same sample.

RÉSUMÉ

L'extraction dans un solvant de diéthyldithiocarbamates a permis de mettre au point une méthode de séparation et de purification du cobalt et du nickel dans des produits de fission. Un procédé est également décrit pour doser le palladium, le cadmium et l'argent dans le même échantillon.

ZUSAMMENFASSUNG

Die Vorteile der Lösungsmittelextraktion von Diäthyldithiocarbamaten bei Trennungen von radioaktiven Spaltprodukten werden diskutiert und ein Verfahren zur Trennung und Reinigung von Kobalt, Nickel, Palladium, Silber und Cadmium beschrieben.

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SYSTEMATIC STUDY OF THE SOLVENT EXTRACTION OF METAL β-DIKETONATES

JIŘÍ STARÝ AND EDUARD HLADKÝ

Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Praha 1, Břehová 7

(Czechoslovakia)

β-Diketones are very widely used for the solvent extraction of many metals. Until the present time acetylacetone and thenoyltrifluoroacetone have been most widely applied[1]; benzoylacetone and dibenzoylmethane have been used in only a few cases[2,3].

The work described in the present paper was intended to find the general relationship between the extractability of metal β-diketonates and the properties of the β-diketones used. A systematic investigation of the extraction of 30 metals by acetylacetone, benzoylacetone and dibenzoylmethane solutions in benzene was therefore undertaken. From the results obtained the extraction constants were calculated and these can be used to predict the optimum conditions for the separation of many metals.

The present paper is a continuation of the systematic studies on the solvent extraction of metal chelates carried out in our laboratory. General theoretical considerations of the extraction procedures were described in the previous papers[4,5].

EXPERIMENTAL

Reagents

All reagents used were of A.R. quality. Benzene (A.R.) was not further purified. The radioisotopes used were of radiochemical purity.

Procedures

The procedures and distribution measurements used were described previously[5]. In addition to radiometric and spectrophotometric determinations, compleximetric and extractive microtitrations were used. A survey of the analytical methods employed is given in Table I.

In general 10^{-3}–10^{-4} M metal solutions were used; the ionic strength was 0.1 ($HClO_4$, $NaClO_4$, $NaOH$). The pH values were measured after equilibration and extraction. Solutions of the β-diketones in benzene were used throughout.

All distribution measurements were carried out at 20°.

With acetylacetone solutions, the extraction equilibrium is usually reached within a few minutes. Magnesium, molybdenum, cobalt and nickel are only the exceptions — attainment of equilibrium requires several hours. Equilibrium in the extraction of a metal by benzoylacetone solution is usually achieved on shaking for less than

TABLE I

THE ANALYTICAL METHODS USED FOR DETERMINATIONS OF DISTRIBUTION RATIO OR PERCENTAGE EXTRACTION

Metal	Method	Metal	Method
Be	Spectrophotometric as oxinate (380 mμ)	Ni	Spectrophotometric with dimethyl-glyoxime (450 mμ)
	spectrophotometric with eriochrome cyanine R (500 mμ)	Pd	Spectrophotometric with dithizonate (640 mμ)
Mg	Compleximetric		spectrophotometric with dimethyl-glyoxime (390 mμ)
Ca	Compleximetric radiometric (^{45}Ca)	Cu	Spectrophotometric as oxinate (400 mμ)
Sr	Radiometric (^{89}Sr)		radiometric (^{64}Cu)
Ba	Spectrophotometric as oxinate (380 mμ)	Ag	Radiometric (^{110}Ag)
	radiometric (^{140}Ba)	Zn	Compleximetric radiometric (^{65}Zn)
Sc	Spectrophotometric as oxinate (380 mμ)	Cd	Compleximetric radiometric (^{115}Cd)
	radiometric (^{46}Sc)	Hg	Extractive titration with dithizone radiometric (^{203}Hg)
La	Compleximetric radiometric (^{140}La)	Al	Spectrophotometric as oxinate (390 mμ)
Ti	Spectrophotometric as oxinate (380 mμ)	Ga	Spectrophotometric as oxinate (395 mμ)
Zr	Spectrophotometric with xylenol orange (530 mμ)	In	Spectrophotometric as oxinate (400 mμ)
Th	Compleximetric radiometric (^{234}Th)		radiometric (^{114}In)
Cr	Compleximetric	Tl	Spectrophotometric as oxinate (400 mμ)
Mo	Radiometric (^{99}Mo)		spectrophotometric with diethyl-di-thiocarbamate (430 mμ)
U	Spectrophotometric as β-diketonates (390–400 mμ)	Sn	Radiometric (^{123}Sn + ^{113}Sn)
Mn	Compleximetric	Pb	Compleximetric radiometric (^{210}Pb)
Fe	Spectrophotometric as β-diketonates (420–450 mμ)	Bi	Radiometric (^{210}Bi)
	radiometric (^{59}Fe)		
Co	Compleximetric radiometric (^{60}Co)		

1 h; but beryllium, magnesium, molybdenum, nickel and mercury are extracted slowly (during several days). The establishment of the extraction equilibrium for most metals by dibenzoylmethane solution is slow (4–5 h). Iron, uranium and copper are extracted comparatively quickly but in the case of beryllium, molybdenum, nickel, palladium, mercury and aluminium shaking for several days is required before the equilibrium is established.

RESULTS

Beryllium, magnesium, calcium, strontium and barium

The extraction of Be, Mg, Ca, Sr and Ba by 0.100 M acetylacetone, benzoylacetone and dibenzoylmethane solutions in benzene as a function of pH is shown in Figs. 1–3. Only beryllium, and partially magnesium, are extracted by acetylacetone solution; calcium, strontium and barium remain quantitatively in the aqueous phase. Dibenzoylmethane solution in benzene allows extraction of all the metals investigated (see Fig. 3).
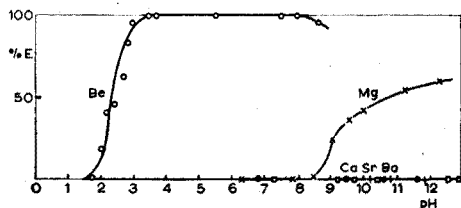
Fig. 1. Extraction of Be(II), Mg(II), Ca(II), Sr(II) and Ba(II) by 0.100 M acetylacetone $vs.$ the pH value of the aqueous phase. ○ Be, × Mg, □ Ca, ● Sr, + Ba.
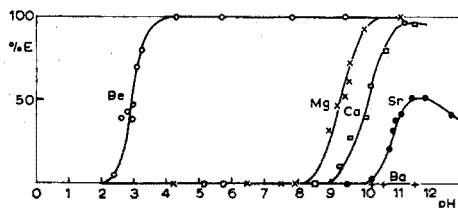

Fig. 2. Extraction of Be(II), Mg(II), Ca(II), Sr(II) and Ba(II) by 0.100 M benzoylacetone $vs.$ the pH value of the aqueous phase. ○ Be, × Mg, □ Ca, ● Sr, + Ba.
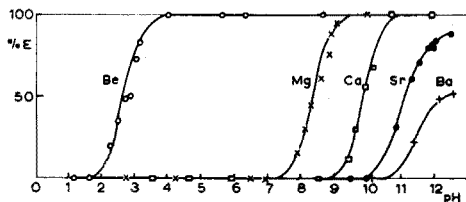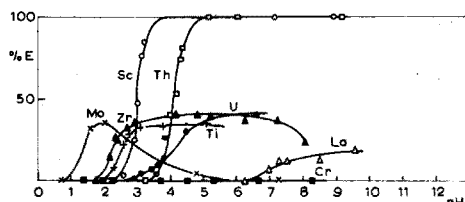

Fig. 3. Extraction of Be(II), Mg(II), Ca(II), Sr(II) and Ba(II) by 0.100 M dibenzoylmethane $vs.$ the pH value of the aqueous phase. ○ Be, × Mg, □ Ca, ● Sr, + Ba.

Fig. 4. Extraction of Sc(III), La(III), Ti(IV), Zr(IV), Th(IV), Cr(III), Mo(VI) and U(VI) by 0.100 M acetylacetone $vs.$ the pH value of the aqueous phase. ○ Sc, △ La, + Ti, ▲ Zr, □ Th, ■ Cr, × Mo, ● U.
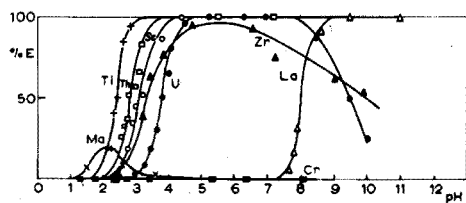
Fig. 5. Extraction of Sc(III), La(III), Ti(IV), Zr(IV), Th(IV), Cr(III), Mo(VI) and U(VI) by 0.100 M benzoylacetone $vs.$ the pH value of the aqueous phase. ○ Sc, △ La, + Ti, ▲ Zr, □ Th, ■ Cr, × Mo, ● U.

Fig. 6. Extraction of Sc(III), La(III), Ti(IV), Zr(IV), Th(IV), Cr(III), Mo(VI) and U(VI) by 0.100 M dibenzoylmethane $vs.$ the pH value of the aqueous phase. ○ Sc, △ La, + Ti, ▲ Zr, □ Th, ■ Cr, × Mo, ● U.
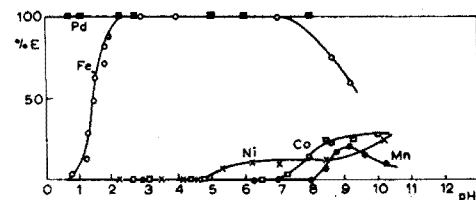
Fig. 7. Extraction of Mn(II), Fe(III), Co(II), Ni(II) and Pd(II) by 0.100 M acetylacetone $vs.$ the pH value of the aqueous phase. ● Mn, ○ Fe, □ Co, × Ni, ■ Pd.
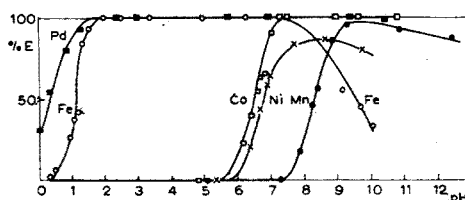

Fig. 8. Extraction of Mn(II), Fe(III), Co(II), Ni(II) and Pd(II) by 0.100 M benzoylacetone $vs.$ the pH value of the aqueous phase. ● Mn, ○ Fe, □ Co, × Ni, ■ Pd.

The present results for the extraction of beryllium are in agreement with previous data[6,7]. SHIGEMATSU AND TABUSHI[7] found that magnesium was not extracted by acetylacetone (1%) in chloroform. This discrepancy can be easily explained by the fact that shaking for 24 h is necessary to establish the extraction equilibrium. Under the present conditions, it was shown by the analysis of both phases that magnesium can be quantitatively extracted by benzoylacetone and dibenzoylmethane but calcium only by dibenzoylmethane. Strontium and barium cannot be quantitatively extracted.

Scandium, lanthanum, titanium, zirconium, thorium, chromium, molybdenum and uranium

The extraction curves of Sc, La, Ti, Zr, Th, Cr(III), Mo(VI) and U(VI) are shown in Figs. 4–6. Only scandium and thorium are extracted completely by 0.100 M solutions of the β-diketones used. The extraction of the acetylacetonates of lanthanum, titanium and uranium(VI) is incomplete whereas the benzoylacetonates and dibenzoylmethanates of these metals are extracted almost quantitatively. The incomplete extraction of zirconium even by benzoylacetone and dibenzoylmethane solutions is caused by hydrolysis. Chromium(III) does not react at room temperature with β-diketones and remains quantitatively in the aqueous phase. The extraction of molybdenum(VI) by 0.100 M solutions of the β-diketone decreases in the following order: acetylacetone, benzoylacetone and dibenzoylmethane. Our results for the extraction of lanthanum, uranium(VI) and thorium by acetylacetone solutions agree with the values of RYDBERG[8]. The extraction of titanium, zirconium and molybdenum(VI) by acetylacetone–chloroform solution (1 : 1) has been investigated by FREISER et al.[9,10]. When concentrated acetylacetone solutions are used, metals can generally be extracted in more acidic medium, so that the influence of hydrolysis is smaller and the extraction of these three metals is more quantitative.

Manganese, iron, cobalt, nickel and palladium

As can be seen from Figs. 7–9, only iron(III) and palladium(II) are completely extracted by 0.100 M solutions of all the β-diketones used. The extraction of cobalt-(II), nickel(II) and manganese(II) is incomplete with acetylacetone solution, but the use of dibenzoylmethane solutions allowed complete extraction of these metals.

McKAVENEY AND FREISER[10] found that neither cobalt(II) nor nickel(II) formed extractable acetylacetonates. The same results were obtained by SHIGEMATSU AND TABUSHI[7]. Our experiments carried out under equilibrium conditions (10 h in the case of cobalt(II), and 3 days in the case of nickel(II)) showed that some cobalt and nickel can be extracted into organic phase. The present results for the extraction of the acetylacetonates of iron(III) and manganese(II) are in agreement with previous data[7,10].

Copper, silver, zinc, cadmium and mercury

Copper, mercury(II) and zinc are extracted incompletely by 0.100 M acetylacetone solution in benzene (see Fig. 10), while cadmium and silver are not extracted at all. When benzoylacetone and dibenzoylmethane solutions are used, the percentage extraction increases in all cases (Figs. 11 and 12). The extraction behaviour of mercury-(II) and silver is affected by hydrolysis and by strong adsorption of mercury(II) and silver ions on glass vessels.
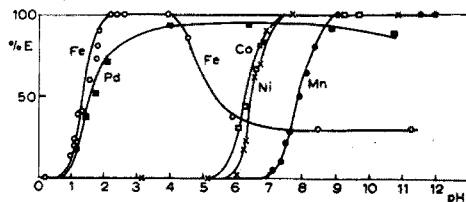
Fig. 9. Extraction of Mn(II), Fe(III), Co(II), Ni(II) and Pd(II) by 0.100 M dibenzoylmethane $vs.$ the pH value of the aqueous phase. ● Mn, ○ Fe, □ Co, × Ni, ■ Pd.
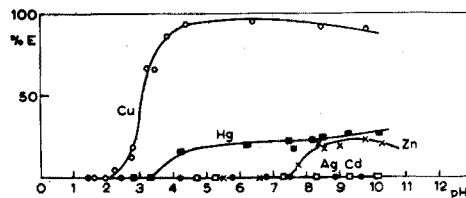
Fig. 10. Extraction of Cu(II), Ag(I), Zn(II), Cd(II) and Hg(II) by 0.100 M acetylacetone $vs.$ the pH value of the aqueous phase. ○ Cu, ● Ag, × Zn, □ Cd, ■ Hg.
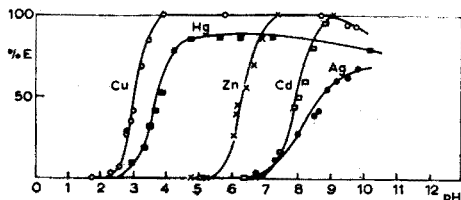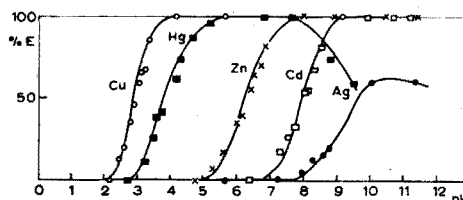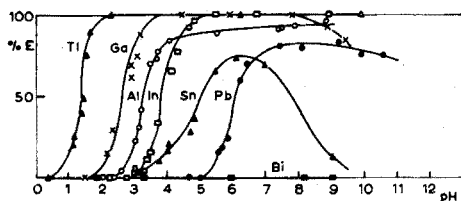
Fig. 11. Extraction of Cu(II), Ag(I), Zn(II), Cd(II) and Hg(II) by 0.100 M benzoylacetone $vs.$ the pH value of the aqueous phase. ○ Cu, ● Ag, × Zn, □ Cd, ■ Hg.

Fig. 12. Extraction of Cu(II), Ag(I), Zn(II), Cd(II) and Hg(II) by 0.100 M dibenzoylmethane $vs.$ the pH value of the aqueous phase. ○ Cu, ● Ag, × Zn, □ Cd, ■ Hg.

Fig. 13. Extraction of Al(III), Ga(III), In(III), Tl(III), Sn(II), Pb(II) and Bi(III) by 0.100 M acetylacetone $vs.$ the pH value of the aqueous phase. ○ Al, × Ga, □ In, △ Tl, ▲ Sn, ● Pb, ■ Bi.
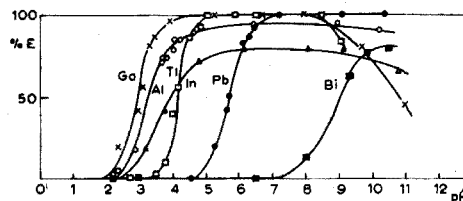
Fig. 14. Extraction of Al(III), Ga(III), In(III), Tl(III), Pb(II) and Bi(III) by 0.100 M benzoylacetone $vs.$ the pH value of the aqueous phase. ○ Al, × Ga, □ In, △ Tl, ● Pb, ■ Bi.
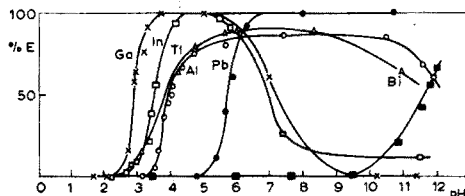
Fig. 15. Extraction of Al(III), Ga(III), In(III), Tl(III), Pb(II) and Bi(III) by 0.100 M dibenzoylmethane $vs.$ the pH value of the aqueous phase. ○ Al, × Ga, □ In, △ Tl, ● Pb, ■ Bi.

STEINBACH AND FREISER[11] reported that 90% of copper and 60% of zinc is extracted by pure acetylacetone (*i.e.* 10 M solution). Similar results were obtained by SHIGEMATSU AND TABUSHI[7] with 1% (*i.e.* 0.1 M) acetylacetone solution in chloroform. These authors found, also in agreement with our data, that silver and cadmium are not extracted by acetylacetone solutions at any pH value.

Aluminium, gallium, indium, thallium, tin, lead and bismuth

Trivalent gallium, indium and thallium are quantitatively extracted by 0.100 M acetylacetone solution in benzene (Fig. 13); the extraction of aluminium(III), tin(II) and lead(II) is incomplete, while bismuth is not extracted at all.

With 0.100 M solutions of benzoylacetone and dibenzoylmethane, gallium, indium and lead are completely extracted (Figs. 14 and 15). Thallium(III) is extracted by these solutions in more alkaline medium than in the case of acetylacetone, so that the decrease in percentage extraction can be explained by hydrolysis of thallic ions.

Our experimental data for the extraction of the acetylacetonates of aluminium, indium, lead and bismuth are in agreement with previous data[7,9,11]. The extraction of thallium(III) and tin(II) has not been investigated before.

DISCUSSION

From the distribution data of the metals investigated, the composition of the extractable complexes and the extraction constants were calculated. It was found that in general, β-diketones form complexes of the type MKe_N (where N is the charge of the metal ion); only uranium(VI) forms the additive complex UO_2Ke_2HKe (where HKe denotes the β-diketone molecule). Molybdenum(VI) is probably extracted as MoO_2Ke_2.

For calculations of the two-phase stability constant $K_N \cdot Q_N$ (K_N and Q_N are respectively the stability constant and the distribution coefficient of the metal complexes MKe_N), the following values of the dissociation constants (K_{HKe}) and the distribution coefficients (q_{HKe}) of the β-diketones were used:

Acetylacetone	pK_{HKe} 8.82[12]	$\log q_{HKe}$	0.77[13]
Benzoylacetone	pK_{HKe} 8.73[14]	$\log q_{HKe}$	3.14[14]
Dibenzoylmethane	pK_{HKe} 9.35[3]	$\log q_{HKe}$	5.35[3]

Values for the extraction constants K_0, the two-phase stability constants K_NQ_N, and the $(pH_{1/2})_{0.1}$ values (*i.e.* the pH value at which 50% of the metal is extracted by 0.100 M β-diketone in benzene) are summarized in Table II.

As can be seen from this Table, the extractability of metals with acetylacetone in benzene decreases in the following order: Pd^{2+}, Tl^{3+}, Fe^{3+}, Be^{2+}, Ga^{3+} and Cu^{2+}, Sc^{3+}, Al^{3+}, In^{3+}, UO_2^{2+}, Th^{4+}, Pb^{2+}, Ni^{2+}, La^{3+}, Co^{2+} and Zn^{2+}, Mn^{2+}, Mg^{2+}. Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Cd^{2+} and Bi^{3+} are not extracted at any pH value investigated. The stability constants of metal acetylacetonates decrease in a similar order[15]: Pd^{2+}, Fe^{3+}, Ga^{3+}, Be^{2+}, Cu^{2+}, In^{3+} and Sc^{3+}, Al^{3+}, UO_2^{2+}, Th^{4+}, Ni^{2+}, Co^{2+}, Zn^{2+}, La^{3+}, Mn^{2+}, Mg^{2+}.

When benzoylacetone solutions were used, the following order of extractability was obtained: Pd^{2+}, Fe^{3+}, Tl^{3+}, Th^{4+}, Be^{2+}, Cu^{2+}, Ga^{3+} and Sc^{3+}, Al^{3+}, UO_2^{2+}, In^{3+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, La^{3+}, Cd^{2+}, Mn^{2+}, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}. When dibenzoylmethane

TABLE II

EXTRACTION DATA FOR METAL β-DIKETONATES

Metal ion	$-\log K_0$			$\log K_N Q_N$			$(pH_{1/2})_{0.1}$		
	AA [a]	BA [a]	DM [a]	AA	BA	DM	AA	BA	DM
Be^{2+}	2.79	3.88	3.46	16.42	19.86	25.94	2.45	2.94	2.73
Mg^{2+}		16.65	14.72		7.10	14.68	9.4	9.38	8.50
Ca^{2+}		18.28	18.00		5.46	11.40		10.1	9.9
Sr^{2+}		~20.0	~20.9		~3.7	~8.4 ·		11.5	11.1
Ba^{2+}									~12
Sc^{3+}	5.83	5.99	6.04	22.89	29.64	38.07	2.95	3.10	3.05
La^{3+}		20.46	19.46		15.2	25.4		7.89	7.42
TiO^{2+}								2.4	2.5
ZrO^{2+}(?)								3.4	3.3
Th^{4+}	12.16	7.68	6.38	26.24	39.80	52.52	4.10	2.90	2.60
UO$_2{}^{2+}$ [b]		4.68	4.12		22.20	30.63		3.82	3.56
Mn^{2+}		14.63	13.71		9.12	15.71		8.30	7.80
Fe^{3+}	1.39	0.50	1.93	27.42	35.13	42.18	1.60	1.20	1.70
Co^{2+}		11.11	10.78		12.64	18.61		6.60	6.40
Ni^{2+}		12.12	11.02		11.62	18.38		6.90	6.40
Pd^{2+}	< −2	−1.2		> 21	~25		<0	0.4	1.8
Cu^{2+}	3.93	4.17	3.80	15.28	19.58	25.6	2.90	3.00	2.90
Zn^{2+}		10.79	10.67		12.96	18.74		6.50	6.40
Cd^{2+}		14.11	13.98		9.64	15.42		8.10	8.00
Ag$^+$		7.81	8.58		4.06	6.12		8.9	9.9
Hg^{2+}								3.7	3.9
Al^{3+}	6.48	7.60	8.92	22.32	28.02	35.19	3.30	3.60	4.00
Ga^{3+}	5.51	6.34	5.76	23.31	29.28	38.34	2.90	3.10	2.90
In^{3+}	7.20	9.30	7.61	21.60	26.19	36.60	3.40	4.10	3.60
Tl^{3+}							1.3	4.0	3.8
Sn^{2+}							~5	~5	
Pb^{2+}	10.15	9.61	9.45	9.06	14.14	19.96	6.2	5.7	5.6
Bi^{3+}								9.2	10.5

[a] AA = acetylacetone, BA = benzoylacetone, DM = dibenzoylmethane.
[b] Additive complex UO$_2$Ke$_2$HKe is formed.

solutions were used, the order of extractability was Fe^{3+}, Pd^{2+}, Th^{4+}, Be^{2+}, Cu^{2+}, Ga^{3+}, Sc^{3+}, UO$_2{}^{2+}$, In^{3+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+}, La^{3+}, Mn^{2+}, Cd^{2+}, Mg^{2+}, Ag$^+$, Ca^{2+}, Sr^{2+}, Ba^{2+}.

As is well established[16,17], the relation between the stability constants K_N and the dissociation constants K_{HKe} of related organic reagents can be expressed as follows:

$$\log K_N = N \cdot pK_{HKe} + u$$

and the linear relationship between the distribution coefficient of a metal complex Q_N and the distribution coefficient of an organic reagent q_{HKe} can be expressed as follows:

$$\log Q_N = N \cdot \log q_{HKe} + v$$

Thus,

$$\log K_N \cdot Q_N = N(pK_{HKe} + \log q_{HKe}) + z$$

where u, v, z are constants.

The difference between the log $K_N Q_N$ values for metal complexes with closely related β-diketones is

$$\Delta \log K_N \cdot Q_N = N \Delta(pK_{HKe} + \log q_{HKe}) + \Delta z$$

For closely related compounds Δz is approximately zero and it is therefore possible to calculate from this equation the conditions suitable for the extraction of a certain metal with various chelating agents.

The values of log $K_N \cdot Q_N$ which are given in Table II, conform approximately to the above equation; steric hindrance and changes in solubility may have caused some differences.

From the values of the dissociation constants of the β-diketones investigated and from potentiometric investigations of the corresponding β-diketonates[15], it follows that the stabilities of the complexes formed by certain metals with acetylacetone, benzoylacetone and dibenzoylmethane do not differ substantially. The increase of the log $K_N \cdot Q_N$ values in the order acetylacetonate, benzoylacetonate and dibenzoyl-methanate (see Table II) is therefore caused by the increase in the distribution coefficient of the metal complexes Q_N.

The linear relationship between log Q_N and log q_{HKe} is also confirmed by the fact that the $(pH_{1/2})_{0.1}$ values found for extraction with benzoylacetone agree quite well with the predicted values[18]. These values were calculated by assuming this linear relationship. The above relationship has also been confirmed by SKYTTE JENSEN[19].

ANALYTICAL APPLICATION

Of all the β-diketonates investigated only the iron(III) and uranium(VI) complexes absorb strongly in the visible region, hence spectrophotometric methods can be used only for the determination of these metals. A very selective determination of iron(III) can be readily accomplished by extracting iron(III) from an aqueous phase at about pH 2.5 into 0.100 M acetylacetone, benzoylacetone or dibenzoylmethane in benzene and measuring the absorbance at 430, 450 or 420 mμ respectively; at pH < 2.5 uranium(VI) is practically not extracted into these solutions. Uranium(VI) can be selectively determined by extraction from an aqueous phase at pH 5.5–6.0 containing 1,2-diaminocyclohexanetetraacetic acid (0.005 M) as a masking agent, with a solution of 0.200 M benzoylacetone or dibenzoylmethane in benzene; the absorbance is measured at 380 or 400 mμ respectively.

The extraction constants determined in the present paper can be used for the prediction of the optimum conditions for the separation of many metals[5]. Thus palladium can be selectively separated from all the other metals investigated by extraction with 0.100 M acetylacetone in benzene at approximately pH 0 (halides must be absent); likewise, beryllium can be selectively extracted with the same solution at pH 6–8 in the presence of ethylenediaminetetraacetic acid (0.010 M), etc. If the known values of the stability constants[15] of metal complexes with masking agents are utilized, many other separations can be carried out.

In conclusion, it may be said that all the β-diketones investigated and especially benzoylacetone, can successfully replace the widely used thenoyltrifluoroacetone for many analytical and radiochemical separations.

SUMMARY

The extraction of 30 metals (Be, Mg, Ca, Sr, Ba, Sc, La, Ti, Zr, Th, Cr, Mo, U, Mn, Co, Fe, Ni, Pd, Cu, Ag, Zn, Cd, Hg, Al, Ga, In, Tl, Sn, Pb and Bi) by solutions of acetylacetone, benzoylacetone and dibenzoylmethane in benzene has been studied in relation to the pH values for extraction. The extraction constants and two-phase stability constants of the β-diketonates were calculated; these can be used to determine the optimum conditions for the separation of many metals. The linear relationship between the distribution coefficients of β-diketones and their corresponding β-diketonates has been confirmed.

RÉSUMÉ

Une étude systématique a été effectuée sur l'extraction par solvant de 30 métaux, au moyen de solutions d'acétylacétone, de benzylacétone et de dibenzoylméthane. Cette étude permet de déterminer les conditions optimales pour la séparation de plusieurs métaux.

ZUSAMMENFASSUNG

Das Verhalten von 30 Metallen bei der Extraktion mit Lösungen von Acetylaceton, Benzoylaceton und Dibenzoylmethan in Abhängigkeit vom pH und anderen Faktoren wurde systematisch untersucht. Mit Hilfe der angegebenen Konstanten können die optimalen Bedingungen für Trennungen vieler Metalle bestimmt werden.

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TEMPERATURE CHANGES IN SOLVENT EXTRACTIONS OF CADMIUM OXINATE

HERBERT E. HELLWEGE AND GEORGE K. SCHWEITZER

Departments of Chemistry, Rollins College, Winter Park, Florida, and The University of Tennessee, Knoxville 16, Tennessee (U.S.A.)

In recent years several investigations have been reported concerning the solvent extraction of metal ions from aqueous solutions into organic phases containing oxine (8-hydroxyquinoline or 8-quinolinol). These include studies with over thirty metals[1]. Several general treatments applicable to the various equilibria involved have appeared in the literature[2].

Recently DYER AND SCHWEITZER[3] investigated the effects of temperature change on extractions of silver as the dithizonate into several non-aqueous solvents. After obtaining values of the extraction constant K as a function of temperature, they were able to calculate values of the free energy, enthalpy, and entropy changes for extractions into chloroform and carbon tetrachloride. A few other scattered and incomplete studies have been carried out including the one by SCHWEITZER AND COE[4] on the extraction of indium oxinate.

Extraction equations

If one considers the extraction of the cadmium ion from an aqueous phase into a chloroform phase containing oxine, HR, the following equation has been shown to be applicable:

$$\frac{1}{D} = \frac{1}{P_c} + \frac{P_r{}^4 K_r{}^2 (H)^2 Q}{P_c K_c (HR)_0{}^4} \tag{1}$$

In this relation the extracting species is assumed to be predominantly $CdR_2(HR)_2$ (as has been demonstrated in this study), D is the organic–aqueous distribution ratio of the total metal concentration in the organic phase to that of the aqueous phase, P_c is the organic–aqueous distribution coefficient of the $CdR_2(HR)_2$, P_r is the organic–aqueous distribution coefficient of the HR, K_r is the association constant of the HR, K_c is the association constant of the $CdR_2(HR)_2$, (H) is the hydrogen ion concentration in the aqueous phase, $(HR)_0$ is the equilibrium concentration of HR in the organic phase, and Q is a term known as the complexing term. This term Q accounts for complexation in the aqueous phase. In the absence of any added masking agents, that is, in perchlorate solutions, one possible form it might take would be

$$Q = 1 + k_1(OH) + k_2(OH)^2 + k_3(OH)^3 + \text{etc.}$$
$$+ K_b(R) + K_d(R)^3 + K_e(R)^4 + \text{etc.} \tag{2}$$

In this exemplary equation, k_1, k_2, k_3, etc. are the successive cumulative association constants for complexes between the cadmium ion and the hydroxide ion; (OH) is the equilibrium concentration of the hydroxide ion; K_b, K_d, K_e, etc. are the successive cumulative association constants for chelates between the cadmium ion and the oxinate ion; and (R) is the equilibrium concentration of the oxinate ion.

By using values for k_1, k_2, k_3, etc., K_b, K_d, K_e, etc., from the literature, it can be shown that Q is very nearly unity for pH values below 7.0[5]. In the specific form of Q as given above, all mixed complexes are ignored and no species other than $CdR_2(HR)_2$ is considered as extracting appreciably into the organic phase.

When Q is unity and P_c is large (as was the case in this study), equation (1) may be made to read

$$D \cong \frac{P_c K_e (HR)_o^4}{P_r^4 K_r^2 (H)^2} = \frac{K(HR)_o^4}{(H)^2} \tag{3}$$

with

$$K = \frac{P_c K_e}{P_r^4 K_r^2} \tag{4}$$

Taking logarithms of (3), one arrives at

$$\log D \cong \log P_c + \log K_e - 4 \log P_r - 2 \log K_r + 4 \log (HR)_o + 2\,pH$$
$$\cong \log K + 4 \log(HR)_o + 2\,pH \tag{5}$$

The pH value observed at 50% extraction when equal phase volumes are employed is termed the $pH_{1/2}$. At this point, $D = 1$, $\log D = 0$, and equation (5) changes into

$$2\,pH_{1/2} \cong 4 \log P_r + 2 \log K_r - \log P_c - \log K_e - 4 \log (HR)_o$$
$$\cong - \log K - 4 \log (HR)_o \tag{6}$$

The constant K in the above equations approximates closely the equilibrium constant for the simple extraction reaction expressed as follows:

$$Cd^{2+} (aq.) + 4HR (org.) \rightleftharpoons CdR_2(HR)_2 (org.) + 2H^+ (aq.) \tag{7}$$
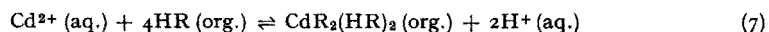
Present problem

In this study an investigation was made at several temperatures of the extraction of the cadmium ion from aqueous solutions into chloroform containing oxine. Values of P_r, K_r, and P_c were also determined at these temperatures, allowing values of K_e to be calculated. These were sought in order to estimate the values of several thermodynamic functions for the total extraction and for its several component equilibria.

EXPERIMENTAL

The chemicals, apparatus, and general experimental approach for P_r and K_r determinations were essentially the same as described in previous work[6].

Oxine

Samples consisting of 10 ml of 0.1 M sodium perchlorate solution were equilibrated at 0°, 18°, 30°, 40°, and 50° for 12 h with 10 ml of 0.1 M oxine in chloroform at pH values from 2.0 to 13.0. Each solvent had been previously saturated with the other. Adjustments in pH were made with concentrated solutions of sodium hydroxide and

perchloric acid. The percentage extraction of oxine, E, in each sample was determined by evaporating and weighing aliquots of the chloroform phase after equilibration. Results of approximately 30 samples at each temperature were plotted on a curve of E against pH. At all temperatures 100% extraction was shown between pH values of 2 and 9.

Values of P_r were determined by equilibrating 1 l of chloroform-saturated 0.1 M sodium perchlorate solution with 50 ml of water-saturated chloroform 0.5 M in oxine for 12 h at 0°, 18°, 30°, 40°, and 50° and a pH of 7.0. The phases were separated and the aqueous phase was equilibrated for 12 h at the proper temperature and a pH of 7.0 with 25 ml of water-saturated chloroform. Twenty ml of this chloroform was evaporated to dryness and weighed. The distribution of oxine between the organic and aqueous phase was calculated from a relationship used by RANDOLPH[7]. The organic–aqueous distribution coefficient of oxine d is given by the following equation:

$$d = \frac{-V_1 V'_2 T_f + V_2 V'_1 T_f - V_2 V'_2 T_o}{2 V_2 V_1 T_f}$$

$$\pm \frac{\sqrt{(V_1 V'_2 T_f + V_2 V'_1 T_f - V_2 V'_2 T_o)^2 - 4 V_1 V_2 V'_1 V'_2 T_f^2}}{2 V_2 V_1 T_f} \tag{8}$$

In this equation T_o is the original amount of HR in the original organic phase of volume V_1, V'_1 is the volume of the original aqueous phase, V_2 is the volume of the organic phase used in the second extraction which will contain the amount T_f of oxine, and V'_2 is the volume of the aqueous phase used in the second extraction.

In a typical run, 50.0 ml of chloroform containing 3.568 g of oxine (V_1 containing T_o) was equilibrated with 1000.0 ml of 0.1 M aqueous sodium perchlorate solution (V'_1) for 12 h at a pH of 7.0. After separation of the two phases, 993.2 ml of the aqueous phase (V'_2) was equilibrated with 25.0 ml of water-saturated chloroform (V_2) for 12 h at the same pH. Twenty ml of this chloroform was evaporated to dryness and weighed, giving 0.1083 g of oxine. Corrected to 25 ml, this yields 0.1354 g of oxine (T_f). This d value is identical with P_r.

Using the values of P_r obtained as above, plus values of (H) and the distribution coefficient d at pH values between 9.0 and 11.0, K_r values were calculated from the equation:

$$\frac{1}{d} = \frac{1}{P_r} + \frac{1}{K_r P_r (\mathrm{H})} \tag{9}$$

Cadmium oxinate·di(oxine)

Samples consisting of 10 ml of chloroform-saturated aqueous phase, 10^{-1} M in sodium perchlorate and $10^{-5.1}$ M in radio-labelled (^{115m} Cd) cadmium perchlorate were equilibrated for 12 h at 0°, 18°, 30°, 40°, and 50° with 10 ml of water-saturated chloroform 10^{-1} M in oxine at pH values from 2.0 to 12.0. The results of at least 30 samples studied at each temperature were plotted as E against pH, and the usual sigmoid-shaped curves resulted in all cases. The error in each experimental point ran about ± 0.1 pH unit and ± 2% extraction. The temperature was maintained within ± 0.5°. Values of $pH_{1/2}$ were determined from these plots.

To ascertain the effect of $(HR)_0$ on the $pH_{1/2}$, about 30 extractions were run at

$30°$ with various pH values using each of the following $(HR)_o$ concentrations: $10^{0.0}$, $10^{-0.4}$, $10^{-1.0}$, and $10^{-1.3}$ M. These data were plotted as E against pH; sigmoid-shaped curves resulted, and $pH_{1/2}$ values were read.

Values of P_c were obtained by equilibrating a 20 ml portion of chloroform containing the cadmium chelate with 1 l of 10^{-1} M sodium perchlorate solution at a proper pH value (around 7.0) for 24 h. After equilibration, aliquots of each phase were evaporated to dryness, counted, and the P_c value was calculated. Each value was determined at least three times.

<div align="center">RESULTS</div>

The following results were obtained at $30°$ in the experiments designed to ascertain the effect of $(HR)_o$ on $pH_{1/2}$. In each series of values the pH value appears first and the % extraction follows in parentheses. At $10^{0.0}$ M oxine: 2.3 (5), 2.8 (20), 3.1 (36), 3.2 (58), 3.3 (71), 3.4 (82), 3.5 (86), 3.6 (87), 4.0 (97), 4.2 (98), 4.3 (98), 4.5 (98). Many of these values represent two, three, or even more determinations. At $10^{-0.4}$ M oxine: 3.6 (7), 3.8 (14), 4.0 (24), 4.1 (33), 4.4 (58), 4.5 (69), 4.7 (81), 5.0 (90), 5.2 (95). At $10^{-1.0}$ M oxine: 4.2 (2), 4.4 (3), 4.8 (7), 4.9 (9), 5.0 (21), 5.1 (31), 5.2 (43), 5.9 (88), 6.0 (89), 6.6 (99), 7.0 (99). At $10^{-1.3}$ M oxine: 4.4 (1), 4.5 (2), 5.0 (11), 5.2 (17), 5.4 (25), 5.6 (59), 5.7 (60), 6.6 (76), 6.8 (83). From the E vs. pH curves the $pH_{1/2}$ values of 3.2, 4.4, 5.2, and 5.8 were read for the $10^{0.0}$, $10^{-0.4}$, $10^{-1.0}$, and $10^{-1.3}$ M oxine systems. When $pH_{1/2}$ was plotted against log $(HR)_o$ a curve with a slope of -2 and an intercept of $-1/2$ log K equal to 3.2 was obtained. These results are compatible with equation (6) and therefore the assumption of $CdR_2(HR)_2$ as the dominant extracting species is validated.

These results were obtained using $10^{-1.0}$ M oxine solutions at various temperatures. At $0°$: 3.4 (6), 3.5 (12), 3.7 (18), 4.0 (31), 4.1 (34), 4.3 (60), 4.4 (67), 4.5 (77), 4.7 (86), 5.0 (95), 5.4 (97). At $18°$: 3.6 (2), 3.9 (5), 4.0 (6), 4.1 (12), 4.4 (23), 4.5 (32), 4.8 (52), 4.9 (59), 5.2 (92), 5.7 (92), 6.3 (94), 6.5 (96), 7.0 (97). At $30°$: 4.2 (2), 4.4 (3), 4.8 (7), 4.9 (9), 5.0 (21), 5.1 (31), 5.2 (43), 5.9 (88), 6.0 (89), 6.6 (99), 7.0 (99). At $40°$: 4.1 (1), 4.7 (3), 5.0 (9), 5.3 (18), 5.4 (34), 5.5 (47), 5.8 (73), 6.1 (85), 6.3 (91), 6.4 (95), 6.6 (96), 7.3 (98). At $50°$: 4.7 (4), 5.1 (10), 5.3 (16), 5.6 (31), 5.8 (48), 5.9 (62), 6.1 (84), 6.6 (95), 6.9 (96), 7.0 (97), 7.3 (98). Plotting of the values as E against pH again yielded the typical sigmoid curves. Values of $pH_{1/2}$ were then read; they are listed in column 2 of Table I. Through the use of equation (6) values of log K were calculated; these appear in column 3 of Table I.

<div align="center">TABLE I</div>

<div align="center">FUNDAMENTAL CONSTANTS FOR CADMIUM EXTRACTIONS[a]</div>

Temperature (°)	$pH_{1/2}$	log K	log P_r	log K_r	log P_c	log K_c
0	4.2	(-4.4)[b]	2.7	9.9	4.9	(21.2)
18	4.8	(-5.6)	2.7	9.8	4.5	(20.1)
25	(5.0)[b]	(-6.1)	2.6	9.7	4.1	(19.5)
30	5.2	(-6.4)	2.6	9.7	3.9	(19.4)
40	5.6	(-7.2)	2.5	9.6	3.7	(18.6)
50	5.8	(-7.6)	2.5	9.5	3.0	(18.1)

[a] All values were obtained by extraction into chloroform containing 0.1 M oxine.
[b] All values in parentheses were calculated; all others were measured.

Values of log P_r and log K_r ascertained by equations (8) and (9) are listed in columns 4 and 5 of Table I. Values of log P_c as measured at the various temperatures appear in column 6 of Table I. The values of log K_c which are included in Table I have been calculated by means of equation (4). In order to ascertain values of the variables at 25°, each column of values was plotted against the reciprocal of absolute temperature and straight lines were obtained. The equations corresponding to these lines were:

$$pH_{1/2} = 14.7 - 2900\, T^{-1}$$

$$\log K = -24.6 + 5500\, T^{-1}$$

$$\log P_r = 1.35 + 370\, T^{-1}$$

$$\log K_r = 7.30 + 710\, T^{-1}$$

$$\log P_c = -6.70 + 3200\, T^{-1}$$

$$\log K_c = 1.10 + 5500\, T^{-1}$$

All of these equations were determined by the method of least squares.

Using the values of Table I and the following equations, standard free energy, enthalpy, and entropy changes of the reactions represented by K, P_r, K_r, P_c, and K_c were calculated.

$$\triangle H° = \left(\frac{\partial \log k}{\partial T}\right) 2.3RT^2 \tag{10}$$

$$\triangle F° = -2.3RT \log k \tag{11}$$

$$\triangle S° = \frac{\triangle H° - \triangle F°}{T} \tag{12}$$

In these three equations k represents the appropriate equilibrium constant (K, P_r, K_r, P_c, or K_c). The thermodynamic values so obtained are recorded in Table II.

TABLE II

THERMODYNAMIC VALUES

k	Reaction	$\triangle H°$ (kcal/mole)	$\triangle F°$	$\triangle S°$ (e.u.)
K	$Cd^{2+} + 4HR_{(o)} \rightleftharpoons CdR_2(HR)_{2(o)} + 2H^+$	-25	$+8$	-110
P_r	$HR \rightleftharpoons HR_{(o)}$	-2	-4	$+6$
K_r	$H^+ + R^- \rightleftharpoons HR$	-3	-13	$+34$
P_c	$CdR_2(HR)_2 \rightleftharpoons CdR_2(HR)_{2(o)}$	-15	-6	-31
K_c	$Cd^{2+} + 2R^- + 2HR \rightleftharpoons CdR_2(HR)_2$	-25	-27	$+7$

DISCUSSION

The values of P_r obtained in this study agree quite favorably with those found in the literature. LACROIX[8] found log P_r to be 2.9 at 18°, and DYRSSEN[2] determined log P_r to be 2.61 for $(HR)_0$ of 10^{-1} M at 25°. Likewise the value of log K_r agrees with the values given by HOLLINGSHEAD[9] (9.9), NASANEN, LUMME AND MUKULA[10] (9.8), and DYRSSEN[2] (9.66), all at 25°. SCHWEITZER AND RANDOLPH[11] have reported a log P_c value of 4.0 and a $pH_{1/2}$ of 5.2 with $10^{-1.0}$ M oxine at 30°.

To our knowledge, no chelate extraction system has been investigated in thermo-

dynamic detail previously. However, some few other data are available for rough comparisons. SCHWEITZER AND BRAMLITT[12] show a free energy change of 8 kcal/mole, an enthalpy change of -17 kcal/mole, and an entropy change of -84 e.u. for the extraction of silver into chloroform containing 10^{-1} M oxine. The orders of magnitude of these are very similar to those in this work.

SUMMARY

The extraction of $10^{-5.1}$ M cadmium ion from aqueous solution into chloroform containing oxine has been investigated and the effects caused by changing the temperature were studied. Values of equilibrium constants for all reactions participating in the extraction have been obtained as a function of temperature. Plots of the logarithms of the constants vs. the reciprocal of the absolute temperature gave straight lines. Thermodynamic functions for all reactions involved have been calculated.

RÉSUMÉ

Une étude a été effectuée sur l'extraction du cadmium au moyen d'oxine, dans le chloroforme. Les valeurs des constantes d'équilibre pour toutes les réactions participant à l'extraction ont été obtenues en fonction de la température et les fonctions thermodynamiques de chacune des réactions ont été calculées.

ZUSAMMENFASSUNG

Es wird eine Untersuchung über die Extraktion von Cadmium aus wässriger Lösung mit Chloroform-Oxin Lösung beschrieben und die Temperaturabhängigkeit des Systems untersucht. Die Gleichgewichtskonstanten der Extraktionsreaktionen zeigen eine lineare Abhängigkeit gegenüber der reziproken absoluten Temperatur. Die thermodynamischen Werte dieser Reaktionen wurden berechnet.

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COCRYSTALLIZATION OF ULTRAMICRO QUANTITIES OF ELEMENTS WITH 2-MERCAPTOBENZIMIDAZOLE

DETERMINATION OF GOLD IN SEAWATER

HERBERT V. WEISS AND MING-GON LAI

Nuclear Chemistry Branch, U. S. Naval Radiological Defense Laboratory,
San Francisco 24, California (U.S.A.)

In this laboratory the concentration of ultramicro quantities of elements from solution by cocrystallization with organic agents has been investigated[1]. The process has been applied to the collection of radioelements as well as the characterization of the trace element abundance in seawater.

Cocrystallization of various elements with 2-mercaptobenzimidazole is described in this report. This reagent has limited solubility, is readily crystallized from aqueous solution, and forms highly insoluble complexes with certain metals. These properties usually favor effective cocrystallization.

The influence of pH upon the cocrystallization of 25 diverse elements was studied. To permit the quantitative measurement of trace quantities of these elements, radioactive tracers were used. The distribution of gold between the mother liquor and solid phase was determined by the crystallization of different quantities of carrier from solution. Finally, the system was applied in a determination of the natural abundance of gold in seawater.

EXPERIMENTAL

Reagents

2-Mercaptobenzimidazole solution. A weighed quantity of 2-mercaptobenzimidazole (K & K Laboratories, Jamaica, N.Y.) was dissolved in absolute ethanol at a concentration ranging from 0.3 to 1.5%.

Solutions of different hydrogen ion concentration. Solutions of pH 1 through 3 consisted of hydrochloric acid of the appropriate normality. Solutions of pH 4 and 5 were mixtures of acetic acid (AR) and sodium acetate (AR) each about 0.1 M.

Tracers

The following radioactive tracers were furnished by Oak Ridge National Laboratory:

In hydrochloric acid solution: [144]Ce(III), [46]Sc(III), [114]In(III), [91]Y(III), [113]Sn(II), [124]Sb(III), [59]Fe(III), [65]Zn(II), [51]Cr(III), [137]Cs(I), [192]Ir(IV), [60]Co(II), [181]Hf(IV), [75]Se(IV), [106]Ru(III).

In oxalic acid: [95]Zr(IV). (This radioelement was separated from [95]Nb just before use[2].)

In nitric acid: $^{85}Sr(II)$, $^{110}Ag(I)$, $^{204}Tl(I)$, $^{203}Hg(II)$.

In potassium hydroxide: $^{182}Ta(V)$, $^{185}W(VI)$.

Supplied by Nuclear Science and Engineering Corporation were $^{54}Mn(II)$ and $^{195}Au(III)$ each in hydrochloric acid. Prepared in the laboratory by the reaction $^{236}U(n,\gamma)$ ^{237}U was $^{237}U(VI)$ in nitric acid.

The purity of the gamma-ray emitters was established by gamma-ray pulse-height analysis. Some of the tracers contained inert carrier. In such cases the quantity of tracer introduced into the test solution was limited so that the final concentration of the element was 10^{-8} g/ml or less.

Method

The influence of hydrogen ion concentration upon the cocrystallization of various radioelements with 2-mercaptobenzimidazole was studied at pH 1, 3 and 5. (More alkaline media were not examined since the reagent becomes increasingly soluble as the pH is raised.) To 11 ml of the solution of definite pH containing the inorganic microcomponent was added 1 ml of a 1.5% solution of 2-mercaptobenzimidazole. The solution was cooled at 5° for 48 h. The crystals which formed were collected by filtration and dissolved in ethanol. The recovery of the radioelement in the solid phase was determined by measurement of the gamma-ray activity of the alcoholic solution in a well scintillation counter and by comparison of the count with a radioactivity control of the same volume. In a number of cases this solution was also submitted to spectro-photometric analysis to determine the fraction of organic reagent which crystallized.

The distribution of gold between solid phase and mother liquor was studied at different hydrogen ion concentrations by crystallizing different fractions of the organic carrier from solution. The procedure was the same as described above except that, to effect variable yields of crystallized carrier, the concentration of 2-mercapto-benzimidazole in alcoholic solution added to a sample varied from 0.3–1.5%.

Spectrophotometric determination of 2-mercaptobenzimidazole

The distribution of 2-mercaptobenzimidazole between solid phase and mother liquor was determined photometrically. With a Beckman spectrophotometer the maximum spectral absorption occurred at 327 mμ when the reagent was dissolved in absolute ethanol. At this wavelength the absorbancy of 0.98, 1.95, 3.90 and 5.85 p.p.m. was 0.151, 0.300, 0.584 and 0.905, respectively, with adherence to Beer's Law.

RESULTS AND DISCUSSION

The recovery of the tracer quantities of elements from solutions of different hydrogen ion concentration with crystallized 2-mercaptobenzimidazole is shown in Table I. (Under the conditions of crystallization, 97% of the reagent was recovered at pH 1 and 3, and 93% at pH 5.) Tin (pH 5), mercury (pH 1 through 5), silver (pH 1 through 5), tantalum (pH 1 through 3) and gold (pH 1) were recovered with high yield.

With several exceptions the other elements were carried only minimally. However, it is clear that the cocrystallization process is useful primarily as a mechanism of concentration rather than a method for purification.

The relation of the logarithmic (λ) and homogeneous (D) distribution coefficients[3,4] for gold to the carrier recovery and hydrogen ion concentration is shown in Table II.

TABLE I

THE RECOVERY OF VARIOUS ELEMENTS WITH 2-MERCAPTOBENZIMIDAZOLE UPON CRYSTALLIZATION FROM SOLUTIONS OF DIFFERENT pH

Element	Recovery (%)		
	pH 1	pH 3	pH 5
Cs	0.6	5.9	0.8
Sr	3.4	1.5	1.6
Se	29.8	14.6	16.2
Sb	2.2	6.9	4.9
Sn	92.3	91.2	99.8
In	4.8	8.6	6.6
Tl	5.1	7.3	17.5
Zn	2.9	3.1	2.0
Hg	98.7	98.8	98.7
Ag	99.0	99.0	99.5
Co	0.6	1.7	2.0
Ir	3.1	1.4	3.7
Fe	2.8	3.7	7.0
Ru	29.1	35.1	41.7
Mn	2.5	0.9	2.0
Cr	3.5	5.8	5.9
W	1.1	4.3	3.5
Ta	97.8	98.1	95.4
Zr	1.3	4.8	28.7
Hf	66.8	71.8	80.2
Au	99.4	93.5	81.5
Sc	5.5	6.5	7.3
Y	3.5	6.8	3.7
Ce	2.7	3.0	3.1
U	14.9	13.7	13.8

TABLE II

LOGARITHMIC (λ) AND HOMOGENEOUS (D) DISTRIBUTION COEFFICIENTS FOR THE COCRYSTALLIZATION OF GOLD WITH 2-MERCAPTOBENZIMIDAZOLE FROM SOLUTIONS OF DIFFERENT pH

Crystal recovered (%)	Distribution coefficients							
	pH 1		pH 2		pH 4		pH 5	
	λ	D	λ	D	λ	D	λ	D
2.3	22.1	23.3						
5.0	14.2	20.1						
18.2	7.2	10.0						
48.5			2.7	5.4				
50.0					2.0	2.9	1.2	1.2
54.0	3.4	10.0						
62.8	3.3	15.3						
66.8			1.9	4.2				
68.8							1.1	1.2
73.4	2.8	13.2						
75.0	2.8	14.7						
77.7			1.8	3.8				
78.1					1.4	2.0		
81.0			1.7	3.2				
81.5							1.1	1.1
84.4					1.4	2.4		

The coefficients were calculated according to the equations:

$$\log \frac{M_i}{M_f} = \lambda \log \frac{C_i}{C_f}$$

$$\frac{M_i - M_f}{M_f} = D \frac{C_i - C_f}{C_f}$$

where M and C represent the microcomponent and carrier, i and f initial and final quantities in solution. At a constant hydrogen ion concentration the distribution coefficient, as calculated by either equation, is in general inversely related to the degree of crystallization. The inconstancy of the homogeneous distribution coefficient indicates that redistribution of the microcomponent by diffusion and recrystallization was at best incomplete. Furthermore, the relationship between the distribution coefficients and the degree of crystallization, as was previously observed[5], is probably attributable to a disproportionate concentration of gold in the solid phase during the nucleation process, compared with that accumulated during crystal growth after supersaturation is relieved. Also, for any degree of crystallization the distribution coefficient is inversely related to the pH. To account for this observation, solubility relationships between the organic reagent and its gold chelate were determined under the experimental conditions.

The reagent and the gold compound of known specific radioactivity each were stirred separately for 8 h at 5° in solutions of specified pH containing 8.3% ethanol (v/v). The solubility of the gold compound was determined by radiometrically measuring the inorganic component in the saturated solution, while the solubility of 2-mercaptobenzimidazole was estimated spectrophotometrically. Over the range of hydrogen ion concentrations studied the solubility of the organic compound increased slightly as the pH was raised (Table III). While the metallic compound showed the same relationship, the effect was markedly more pronounced. According to FAJANS' Rule[6] the differential effect of pH upon the respective solubilities would manifest itself by greater enrichment in more acid systems, and in fact precisely this result was observed.

TABLE III

THE SOLUBILITY OF 2-MERCAPTOBENZIMIDAZOLE AND ITS GOLD COMPOUND AT DIFFERENT HYDROGEN ION CONCENTRATIONS

pH	Solubility (moles/l)	
	2-Mercaptobenzimidazole	Gold mercaptobenzimidazolate
1.0	$2.48 \cdot 10^{-4}$	$4.2 \cdot 10^{-7}$
2.0	$2.52 \cdot 10^{-4}$	$1.1 \cdot 10^{-6}$
4.0	$2.6 \cdot 10^{-4}$	$2.1 \cdot 10^{-6}$
5.0	$2.7 \cdot 10^{-4}$	$2.9 \cdot 10^{-6}$

DETERMINATION OF GOLD IN SEAWATER

The abundance of gold in seawater has been extensively studied since the work of SONSTADT in 1872[7]. Most of the analytical procedures depend upon the separation of gold from the salt medium by coprecipitation with lead or iron compounds. A radio-

activation method recently described[8] does not depend upon a preliminary separation. However, the variability of results in all these procedures indicates a requirement for improvement.

The cocrystallization of gold with 2-mercaptobenzimidazole was applied to the development of a reliable analytical method. A preliminary experiment was performed in seawater containing [195]Au tracer to determine the quantity of reagent required for effective cocrystallization.

Different volumes of ethanol, which contained the organic reagent at a concentration of 50 mg/ml, were added to 200 ml of seawater adjusted to pH 1 with hydrochloric acid. The sample was maintained at 5° for 48 h. Crystals which formed were collected on sintered glass and solubilized with nitric acid. The recovery of gold was determined by comparing the gamma-ray count of this sample with a radioactive control diluted to the same volume. Gold cocrystallized to the extent of 65.6, 97.2, 98.8 and 99.0% when 0.6, 0.8, 1.0 and 1.6 ml of organic reagent were used, respectively.

Procedure

Surface seawater was collected in 20-l polyethylene bottles 40 miles due west of San Francisco. Each bottle was acidified with 200 ml of concentrated hydrochloric acid to pH 1 at the time of collection. (Studies with tracer show that under such acid conditions gold is not adsorbed by the walls of the container.) To correct for chemical yield a measured quantity of [195]Au was added 16 h after collection and the bottles were stored for 3 weeks. Then 5 g of 2-mercaptobenzimidazole in 100 ml of ethanol were added slowly to each of six 20-l containers; the bottles were placed in a cold room (0 to 5°) for two days. Crystals were collected by filtration, combined, and dissolved with 300 ml of concentrated nitric acid.

Organic matter was removed by acid oxidation steps as follows. The nitric acid solution was boiled gently for several hours. After partial oxidation the sample was cooled in an ice-bath and the insoluble degradation products were removed by filtration through sintered glass. To the clear solution were added 100 ml of concentrated nitric acid and 20 ml of concentrated sulfuric acid and the solution was boiled vigorously until sulfur trioxide fumes evolved and it appeared colorless.

The completely oxidized solution was separated into three unequal portions and each was treated individually as follows. To prepare for purification of gold by solvent extraction, 200 ml of distilled water and 50 ml of concentrated hydrochloric acid were added to the sulfuric acid solution. The solution was shaken twice with 200 ml portions of ethyl ether. The ether extracts were combined and evaporated to dryness at room temperature.

Further purification was effected by co-precipitating the gold with tellurium. The residue, after ether evaporation, was dissolved in 10 ml of concentrated hydrochloric acid and 40 ml of distilled water were added. Tellurium tetrachloride (0.2 mg) was introduced and the tellurium metal was precipitated by treatment with stannous chloride according to the method of SANDELL[9]. The tellurium precipitate was dissolved in 2–3 ml of hot aqua regia and the solution was evaporated to near-dryness. Aqua regia (0.5 ml) was again added and then completely evaporated in vacuo in a desiccator at room temperature.

A colorimetric method was adapted[10] to the quantitative assay of gold in the sample aliquot. To the residue were added 2.5 ml of water, 1 ml of a solution consisting of 9%

sodium bisulfite (anhydrous) and 20% sodium sulfite (anhydrous), 0.25 ml of 1% sodium fluoride solution, 0.3 g of sucrose, 0.30 ml of acetone, and 0.250 ml of p-dimethylaminobenzalrhodanine (9 mg/100 ml ethanol). The solution was diluted to 5 ml with distilled water in a volumetric flask. One ml of this solution was removed to determine radiometrically the quantity of seawater represented by the same aliquot. The absorbancy of the remaining solution was measured in a Beckman spectrophotometer at 470 mμ. With the use of the absorbancy values 0.028, 0.053 and 0.109 for gold solutions at concentrations of 0.23, 0.45 and 0.90 p.p.m. respectively, the concentration of gold in the sample was determined.

Results

The results of the determinations of the three aliquots are shown in Table IV. The average concentration of gold was 0.068 $\pm$ 0.003 μg/l, a value within the normal range for seawater[11]. A blank analysis was performed on all the materials that entered the analysis for a sample volume of 25 l. The assay indicated that the quantity of gold introduced by way of reagents was within the indicated experimental error of the gold determinations; therefore, its effect upon the seawater determinations was disregarded.

TABLE IV

THE GOLD CONTENT OF SEAWATER

Seawater sample volume (l)	Gold content (μg/l)
23.1	0.069
30.6	0.065
36.1	0.070
average 0.068 $\pm$ 0.003	

Discussion

With regard to the reliability of these measurements, palladium and platinum metals which interfere with color development in the quantitative method are completely eliminated by ether extraction[12]. Other interfering elements such as copper, iron and lead are removed from the system in the tellurium precipitation step. Moreover, spectrographic analysis of the combined aliquots after the colorimetric determination revealed besides gold, detectable quantities of magnesium only as an extraneous contaminant. This element is without influence in the colorimetric determination of gold.

Another consideration of importance involves the radiometrically determined chemical yield correction. The validity of this correction presumes that the natural gold in seawater and the radioactive tracer introduced are chemically identical. The probable chemical form of gold in the acidified seawater samples was determined from the pertinent equilibrium constants (20°, zero activity)[13].

$$AuCl_2^- + e^- \rightleftharpoons Au(s) + 2\ Cl^- \quad \log K = 19.2$$
$$AuCl_4^- + 3e^- \rightleftharpoons Au(s) + 4\ Cl^- \quad \log K = 51.3$$
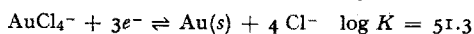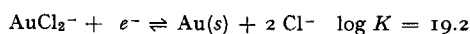
By substitution of the appropriate values for the pH-adjusted seawater: $pE = 19.6*$, and log $[Cl^-] = $ log [0.55 (natural to seawater) + 0.1 (from hydrochloric acid added)] $= -0.19$, and neglecting the activity coefficients, the log $[AuCl_2^-] = -0.2$ and log $[AuCl_4^-] = 6.7$. Clearly $AuCl_4^-$ predominates at equilibrium. The radiometric correction appears valid since the radioactivity was introduced in this chemical form.

The separation of gold from seawater by cocrystallization with 2-mercaptobenzimidazole provides several important advantages over the usual coprecipitation methods with inorganic carriers. The crystallization is performed at pH 1, a condition which completely obviates the difficulties which arise from wall-adsorption of gold at higher pH. Further, more than 95% of the gold is carried by the crystalline phase. The method of crystallization is simple and the crystals are easily separated from the mother liquor. Since the major constituents in seawater are not cocrystallizable, this first step in the process eliminates the large bulk of salts. Finally the ability to remove the organic carrier by acid oxidation facilitates the ultimate isolation.

SUMMARY

The cocrystallization of ultramicro quantities of 25 diverse elements with 2-mercaptobenzimidazole was investigated with the aid of radiotracers. Under optimum conditions Sn, Hg, Ag, Ta and Au were recovered in high yield. Distribution coefficients between mother liquor and solid phase were calculated for gold and were found to vary inversely with the degree of crystallization and the hydrogen ion concentration. The cocrystallization process was applied to the isolation and subsequent determination of the natural gold abundance in seawater. After radiometric correction for chemical yield, the concentration of gold was calculated to be 0.068 ± 0.003 μg/l.

RÉSUMÉ

Les auteurs ont examiné la cocristallisation de 25 éléments différents (en ultramicroquantités) avec le mercapto-2-benzimidazole, au moyen de radiotraceurs. Cette méthode par cocristallisation a été appliquée à la séparation et au dosage de l'or dans l'eau de mer.

ZUSAMMENFASSUNG

Die Co-Kristallisation von 25 verschiedenen Elementen mit 2-Mercaptobenzimidazol wurde mit Hilfe von Tracern untersucht. Nach diesem Verfahren lässt sich auch der Goldgehalt des Meerwassers bestimmen.

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* $pE = $ –log e^-. As described by SILLEN[13] in seawater the pE is determined by the equilibrium with atmospheric oxygen and is 19.6 for seawater adjusted to pH 1.

AMPEROMETRIC TITRATION OF COPPER WITH DIALLYLDITHIO-CARBAMIDOHYDRAZINE

E. JACOBSEN AND C. HANSTEEN

University of Oslo, Chemical Institute A, Blindern (Norway)

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Certain metals such as mercury, copper, lead, palladium, nickel and zinc form 1:1 complexes with diallyldithiocarbamidohydrazine ("Dalzin") which are slightly soluble in water, the solubility products depending on the pH of the solution. DUTT and coworkers have recommended this reagent for the gravimetric determination of the above metals alone and in some two-component mixtures[1-3]. The gravimetric procedures described are tedious and several hours are needed for complete precipitation and drying of the precipitates. The present work was carried out in order to ascertain whether the metals could be titrated with Dalzin using amperometric endpoint detection, thus making the method more suitable for routine analysis.

EXPERIMENTAL

Apparatus

A Tast Polarograph, Selector D (Atlas Werken, Bremen, Germany) was used for recording polarograms and for amperometric titration. The conventional types of dropping mercury electrode (D.M.E.) and of electrolysis cell were used. An external saturated calomel electrode (S.C.E.) connected to the cell by means of an agar bridge, served as reference electrode. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min. The pH of the solutions was measured with a Beckman Zeromatic pH meter. Some amperometric titrations were performed by short-circuiting the dropping mercury electrode with the reference electrode and measuring the current with a Radiometer spotlight galvanometer, type G.M.V. 23a. A 2,000 μF condenser was included in the circuit for damping the galvanometer oscillations. These titrations were performed in an open beaker in the presence of air.

Reagents

Diallyldithiocarbamidohydrazine was prepared from hydrazine sulphate and allyl-isothiocyanate according to FREUND AND WISCHEWIANSKY[4]. The product (about 40% yield) was recrystallized three times from 96% ethanol and dried in a vacuum desiccator (m.p. 186°). The pure and dry Dalzin was found to be stable for several months. Dalzin is very slightly soluble in water and a 0.010 M solution of the reagent was prepared by dissolving 2.302 g of Dalzin in 100 ml of 0.1 M sodium hydroxide and diluting to 1 l. The titer was checked by amperometric titration of a standard

copper solution following the procedure given below. The titration gave theoretical results for the first 24 h after the solution had been prepared but the results decreased slowly afterwards. This is probably due to decomposition of Dalzin in the alkaline medium and the reagent solution was consequently prepared or standardized every day.

Standard copper(II) solution was prepared by dissolving an accurately weighed amount of electrolytic copper in nitric acid. Part of the excess acid was evaporated, and the residue diluted to an appropriate volume. The remaining chemicals were of reagent grade and used without further purification. 0.2 M Acetic acid–ammonium acetate buffer of pH 4.60 was used as supporting electrolyte in the amperometric titrations.

Preliminary investigations

Current–voltage curves of Dalzin in acetic acid buffers showed that the reagent was not reduced at the D.M.E., but a drawn out anodic wave, probably due to oxidation of mercury to a mercury–Dalzin complex, was observed on the polarograms. In the potential range +0.1–0 V *vs.* S.C.E. the limiting current was fairly constant, and, at Dalzin concentrations less than $4 \cdot 10^{-4}$ M, proportional to the concentration. This anodic wave was found useful as an indicator of excess reagent in amperometric titrations, because the titration could be performed at a potential more positive than the reduction of oxygen and most metal ions. When the titration was performed at these positive potentials, the current remained zero until the equivalence point was reached and then increased proportionately to the amount of excess reagent added.

Preliminary experiments indicated that the reaction rate between Dalzin and mercury, nickel, zinc and palladium ions was very slow at room temperature. In the case of copper(II) and lead(II), however, the reaction rate was sufficiently fast for a titration. The effect of pH on the precipitation of the copper complex was investigated in acetic acid buffers. Equivalent amounts of copper(II) and the reagent were added to acetic acid and the pH of the solution was adjusted by addition of ammonia. The concentration of copper(II) in the pH range where the precipitate was formed, was determined by running polarograms of the mixtures. The results are shown in Fig. 1, and indicate that copper is quantitatively precipitated by an equivalent amount of Dalzin at pH values above 4.
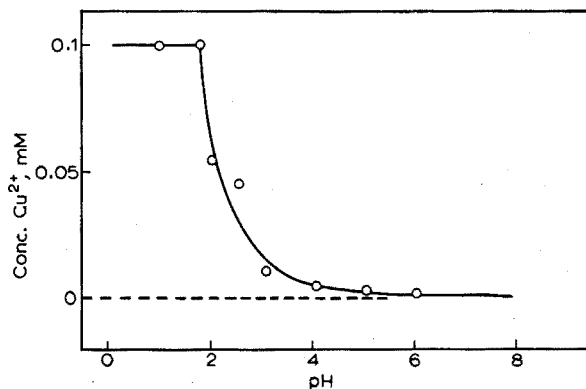
Fig. 1. Effect of pH on the precipitation of the copper–Dalzin complex (10^{-4} M copper(II) and 10^{-4} M Dalzin in acetic acid–ammonium acetate buffers).

Similar experiments with lead(II) showed that this complex was quantitatively precipitated at pH values above 7. No suitable supporting electrolyte was, however, found for the titration of lead. In most media the pH had to be carefully adjusted during the titration in order to avoid co-precipitation of lead hydroxide, and in complex-forming electrolytes (citrate, tartrate, etc.) the reaction rate between the lead complex and Dalzin was too slow for a titration. Consequently, copper is the only metal which can be readily titrated amperometrically with Dalzin. Based upon the above results the following procedure for the determination of copper is suggested.

Procedure

Mix the sample solution with 25 ml of 0.2 M acetic acid–ammonium acetate buffer of pH 4.6 and titrate with a Dalzin solution using an applied potential of +0.1 V *vs.* S.C.E. Allow an interval of 1 min after each addition of reagent for mixing the solution and for the attainment of equilibrium. Plot the titration results graphically and determine the equivalence point from the reversed L-shaped graph.

RESULTS AND DISCUSSION

The results of some titrations of various amounts of copper following the above procedure are reported in Table I. Some of these titrations were repeated using a simpler apparatus; in these experiments the titrations were performed by short-circuiting the dropping mercury electrode with the reference electrode and measuring

TABLE I

TITRATION OF COPPER IN 0.2 M ACETIC ACID–AMMONIUM ACETATE BUFFER (pH 4.6) WITH DALZIN AT +0.1 V *vs.* S.C.E.

Copper taken (mg)	Added species (mg)	Copper found (mg)	Error (%)
0.0630		0.0637	+1.0
0.1580		0.1600	+1.3
1.575		1.575	0
1.575		1.568	—0.4
1.575	$\{$ 15 Cr^{3+} 15 Mn^{2+}	1.580	+0.3
1.575	$\{$ 14 Fe^{2+} 15 Co^{2+} 15 Ni^{2+}	1.562	—0.8
1.575	$\{$ 16 Zn^{2+} 13 Cd^{2+}	1.593	+1.1
1.575	52 Pb^{2+}	1.556	—1.2
1.575	2500 SO_4^{2-}	1.613	+2.4
1.575	100 Cl^-	1.460	—7.3

the current after the end-point with a high sensitivity galvanometer. An accuracy of ± 1% was obtained also in these determinations. A 0.1 M KCl/calomel electrode was advantageous as reference electrode in this method, because the sharpest end-point was obtained at that potential (*i.e.* +0.09 V *vs.* S.C.E.) when the pH of the supporting electrolyte was 4.6.

Interfering ions

In the titration of copper at pH 4.6 it was found that the results were not affected by large excesses of Al^{3+}, As^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Cr^{3+}, Co^{2+}, In^{3+}, Mg^{2+}, Mn^{2+}, MoO_4^{2-}, Ni^{2+}, Pb^{2+}, Sr^{2+}, VO^{2+}, Zn^{2+} and Zr^{4+}. Mercury, bismuth and silver formed precipitates with Dalzin at pH 4.6 and interfered with the titration. The solubility product of the bismuth complex is much greater than that of the copper complex and concentrations of bismuth up to $3 \cdot 10^{-5}$ M did not interfere. Iron(III) and noble metals which are reduced at $+0.1$ V *vs.* S.C.E. interfered with the titration when present in amounts equal to or greater than that of copper.

In the presence of chloride and large amounts of sulphate the dissolution of mercury occurred at more negative potentials and interfered when the titration was performed at $+0.1$ V *vs.* S.C.E. Hence, the sample should be dissolved in nitric or perchloric acid and the pH adjusted with acetate buffer. Anions forming stable complexes with copper(II) (oxalate, citrate, etc.) should not be present, because the reaction rate between these copper complexes and Dalzin is very slow.

Conclusions

Dalzin is a selective reagent for copper(II). The reagent is easy to prepare in a pure and weighable form and has the advantage of a large equivalent weight (230.2); moreover, the reagent solution need not be standardized if used shortly after preparation. The suggested method for the titration of copper with Dalzin is very fast. Dissolved air need not be removed from the solution, no maximum suppressor is needed and the titration may be performed with very simple apparatus.

SUMMARY

Small amounts of copper(II) can be titrated with diallyldithiocarbamidohydrazine using ampero-metric end-point detection. The titration may be performed in the presence of air by short-circuiting the dropping mercury electrode with the reference electrode and measuring the limiting current of excess reagent after the end-point with a galvanometer. Few metals interfere. The time required for one determination is 10–15 min.

RÉSUMÉ

Le cuivre (en faible quantité) peut être titré ampérométriquement au moyen de la diallyldithio-carbamidohydrazine. Le titrage peut s'effectuer en présence d'air, en court-circuitant l'électrode à gouttes de mercure avec l'électrode de référence, et en mesurant le courant limite du réactif en excès.

ZUSAMMENFASSUNG

Kleine Mengen Kupfer können amperometrisch mit Diallyldithiocarbamidohydrazin titriert werden.

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THE OSCILLOGRAPHIC POLAROGRAPHY OF NOBLE METAL COMPLEXES

R. J. MAGEE AND I. A. BEATTIE

Department of Chemistry, Queen's University, Belfast (Northern Ireland)

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Of the noble metals copper, silver and gold, copper has been the subject of numerous investigations, polarographic and otherwise[1]. However, for both silver and gold, the literature indicates that polarographic studies or polarographic methods of determination are very few. Because of this situation, it was the intention in the present work to carry out a complete survey of these noble metals by oscillographic polarography with the aim of developing simple methods for their determination. In this investigation an approach was made through a study of the polarographic behaviour of different complexes of the metals formed by different ligands and, to put the investigation on a sounder basis, recourse was made to the ligand field theory[2]. This theory[3,4] deals with the relation of the behaviour of non-bonding electrons in the valency shell of an atom to the symmetry and strength of the electric field arising from the attached ligands. The basic physical idea is that the electrons of the central metal ion tend to avoid those regions where the field due to the attached negative ions is largest. This tendency results in the removal of the degeneracy of the ground state of transition metal ions. Thus, in the case where six cyanide ligands are brought up to the iron(III) ion to form the complex $[Fe(CN)_6]^{3-}$, a set of d_ε orbitals of lower energy, and a set of d_γ orbitals of higher energy are produced. The energy of separation (ΔE) between these two levels, where the central metal atom is the same, will depend on the strength of the applied field, *i.e.* on the ligand.

From observations of absorption spectra of metal ions, the size of ΔE for almost any metal and set of ligands can be determined. With metal ions in their normal valency states the following series for increasing ΔE arises[5]: I^-, Br^-, Cl^-, F^-, H_2O, oxalate, pyridine, NH_3, NO_2^-, CN^-.

Up to the present most of the work carried out in the study of this effect has been done by means of absorption spectra. It is, however, a basic fact of polarography that half-wave potentials of simple ions shift to more negative values on complexing, *i.e.* on introducing a ligand[5]. It would appear reasonable, therefore, to assume that, if the shift in $E_{1/2}$ follows the same pattern as ΔE in absorption spectra, then by choice of ligands for the different metals, the polarography might be markedly simplified. This paper represents results obtained in investigations with the noble metals.

EXPERIMENTAL

A K 1000 Cathode Ray Polarograph supplied by Southern Instruments, England, was used. The ligands used in the investigation were chloride, thiocyanate, water,

TABLE I

STUDY OF COPPER(II) IN VARIOUS SUPPORTING ELECTROLYTES

Exp. no.	Supporting electrolyte	$E_{1/2}$	Maximum	Colour	Reaction
1	0.1 M HCl	-0.24	885 mμ 13,000 cm^{-1}	Green	$Cu^{2+} \rightarrow Cu^{0}$
2	0.2 M EDTA	-0.363	725 mμ 39,000 cm^{-1}	Blue	ditto
3	0.2 M Triethanolamine + 0.2 M Na$_2$SO$_4$	-0.41	650 mμ 54,000 cm^{-1}	Blue	ditto
4	0.2 M Urea + 0.2 M NaOH	-0.495	560 mμ 79,000 cm^{-1}	Violet	ditto
5	0.2 M Ethylenediamine tartrate + 0.2 M NaOH	-0.515	550 mμ 82,000 cm^{-1}	Violet	ditto
6	0.2 M Ethylenediamine + 0.2 M Na$_2$SO$_4$	-0.585	557 mμ	Violet	ditto
7	0.2 M Ethanolamine + 0.2 M Na$_2$SO$_4$	-0.42	595 mμ 68,000 cm^{-1}	Violet	ditto
8	0.2 M NH$_3$ + 0.2 M NH$_4$Cl	-0.16 -0.445	605 mμ	Blue	$Cu^{2+} \rightarrow Cu^{+}$ $Cu^{+} \rightarrow Cu^{0}$
9	0.2 M Pyridine + 0.2 M Na$_2$SO$_4$	-0.29	610 mμ	Blue	ditto
10	0.2 M Ethylamine + 0.2 M Na$_2$SO$_4$	-0.255 -0.445	580 mμ	Violet	ditto
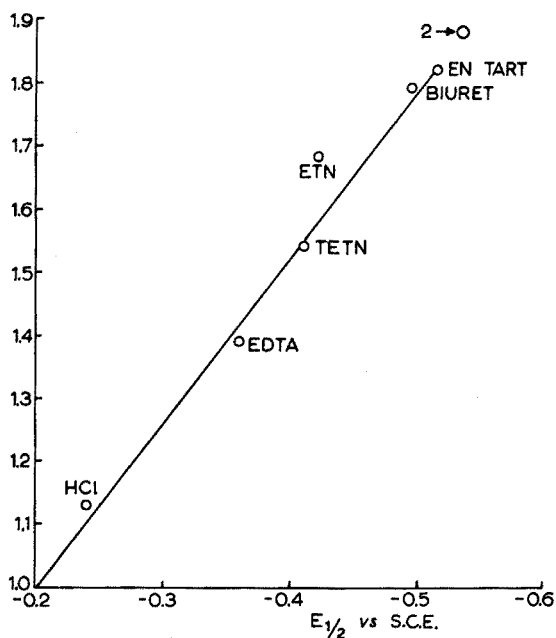
Fig. 1. Plot of absorption maxima vs. $E_{1/2}$ values for different complexes.

ammonia, pyridine, ethylamine, ethanolamine (ETN), triethanolamine (TETN), EDTA, biuret, piperidine and ethylenediamine tartrate (EN TART).

For each cation the above ligand series was investigated, and, on the same solution, the polarographic reduction wave and the absorption spectrum were determined, where possible. In general no special conditions were necessary to form a complex with the different ligands. The position of the absorption maximum was plotted against $E_{1/2}$ for each complex obtained; a reasonable straight line was obtained, as expected (Fig. 1). The results obtained for copper are shown in Table I; in all cases the concentration of the copper(II) was 10^{-3} M.

In all cases gelatine was added to the solutions to prevent the occurrence of absorption maxima which are inclined to blot out reduction peaks, and nitrogen was bubbled through the solution for at least 5 min to remove oxygen. With ammonia, pyridine, and ethylamine distinct double waves were obtained. Piperidine did not give complexes with copper(II) ion. With these reagents the hydroxide of copper was precipitated. With ethanolamine, triethanolamine, ethylamine and diethylamine complexes were formed and good reducible polarographic waves obtained. While ethylamine gave a double wave, ethanolamine showed only a single wave. It would appear, therefore, that copper(II) is stabilised by the latter probably by chelation.

Silver and gold

Following the procedure outlined above for copper, silver and gold were examined using ligands from the weak chloride through to the strongest. In all cases the concentration of metal ion was 10^{-3} M, the salts used being silver nitrate and chloro-auric acid. If the ligand was not itself a conductor of current, 0.2 M sodium sulphate was added.

Investigations with silver were beset with a number of difficulties. In the first instance, the complexes formed were colourless which made detection of complex formation difficult by the simple visual methods which were used for copper and later gold. Secondly, complexes were formed which showed no reduction waves at all; this is confirmed by the literature[6]. However, in analytical applications it was possible to make use of this property of silver.

TABLE II

STUDY OF GOLD(III) IN VARIOUS SUPPORTING ELECTROLYTES

Exp. no.	Supporting electrolyte	$E_{1/2}$	Peak height
1	0.2 M NaOH	−0.685	4.8 × 4
2	0.2 M piperidine + 0.2 M Na₂SO₄	−0.375	3.3 × 6
3	0.2 M ethylamine + 0.2 M Na₂SO₄	−0.215	4.15 × 6
4	0.2 M ethylenediamine + 0.2 M Na₂SO₄	−0.35	3.65 × 6
5	0.2 M ethanolamine + 0.2 M Na₂SO₄	−0.19	4.3 × 6

With gold the best complexes polarographically were those formed between gold(III) ions and the ligands: ethanolamine, ethylamine, piperidine and ethylenediamine. Results with these are shown in Table II.

Although the literature claims that complexes are formed with thiourea, examina-

tion of the reaction between these ligands and gold(III) both polarographically and spectrophotometrically confirmed the suspicion that complexes were not formed. Fig. 2 shows the wave for gold with ethanolamine as complexing agent.

Analytical applications

In looking for a possible analytical procedure for copper and gold, those ligands which formed reducible complexes with gold(III) were the limiting factor. The ligands are shown in Table II and the corresponding results for copper(II) in Table I.

The hydroxy complex was not considered satisfactory for, although in the literature[7] it has been recommended for the polarographic determination of gold(III), in the present work it was not suitable. The ethylamine ligand gave two reduction waves with copper, but the first coincided with that for gold. With piperidine, copper(II) gave a hydroxide precipitate, but a satisfactory reduction wave was obtained for gold. This reaction has possibilities.

Ethylenediamine gave with copper a good wave at -0.585 V; with gold a wave was obtained at -0.35 V. These waves were well separated but the gold(III) wave was a little too close to the larger oxidation wave for mercury which appeared to shift to more negative values with time.

Ethanolamine gave a very satisfactory wave with copper(II) at -0.42 V, the corresponding wave for gold(III) occurring at -0.19 V (Fig. 3). With this ligand the waves for both ions were well separated and the waves were well suited for analytical development.
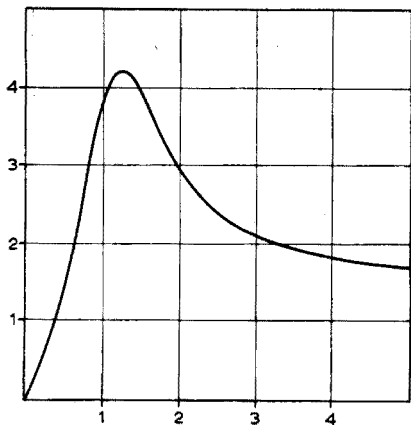
Fig. 2. Polarographic wave for gold with ethanolamine as ligand.
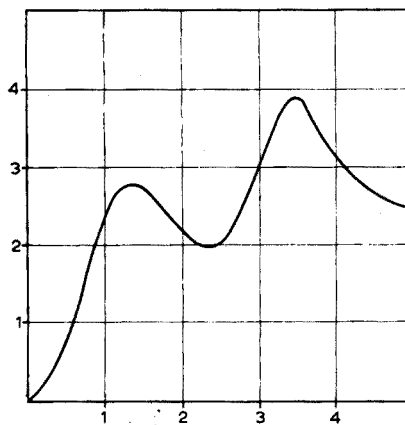
Fig. 3. Polarographic waves for copper and gold with ethanolamine as ligand.

Different concentrations were prepared for each cation and the peak height was determined at each concentration. Calibration curves of concentration *vs.* peak height were prepared. For both metals good straight lines were obtained. The concentration range used in each case was 10^{-4} *M* to $2 \cdot 10^{-3}$ *M*.

Silver was now fitted into the scheme. It was indicated above that no reduction waves were found with any of the ligands. It was further found that silver, when added to mixtures containing gold and copper, did not interfere in any way with the determination of these two elements, regardless of the amount of silver added.

When silver was present with gold in the form of $HAuCl_4$, a precipitate of silver chloride was obtained. However, this caused no trouble because the silver chloride was rapidly converted into a water-soluble complex on the addition of ethanolamine.

To test the effectiveness of the procedure, synthetic "unknowns" were analysed by one of us (I.A.B.). The results are shown in Table III. As can be seen, these results are highly satisfactory. Some of the error involved is attributed not to the method, but to the measuring of the very small volumes in making up the "unknowns".

TABLE III

RESULTS FOR COPPER AND GOLD

Metal+	Actual concn. (M)	Peak height found	Concn. found (M)
Cu	10^{-3}	3.8×6	$1.06 \cdot 10^{-3}$
Au	$1.27 \cdot 10^{-3}$	4.3×6	$1.27 \cdot 10^{-3}$
Cu	$0.5 \cdot 10^{-3}$	4.7×2.5	$0.54 \cdot 10^{-3}$
Au	$1.27 \cdot 10^{-3}$	4.3×6	$1.27 \cdot 10^{-3}$
Ag	$0.5 \cdot 10^{-3}$		
Cu	$2 \cdot 10^{-3}$	42.5	$1.98 \cdot 10^{-3}$
Au	$0.508 \cdot 10^{-3}$	10	$0.48 \cdot 10^{-3}$
Cu	$0.5 \cdot 10^{-4}$	2	10^{-4}
Au	$2.54 \cdot 10^{-3}$	54.8	$2.54 \cdot 10^{-3}$
Cu	0	0.11	0
Au	$1.016 \cdot 10^{-4}$	3.15	$1.56 \cdot 10^{-4}$
Cu	$2 \cdot 10^{-4}$	4.9	$2.29 \cdot 10^{-4}$
Au	0	0.6	0
Cu	$0.4 \cdot 10^{-3}$	9.35	$0.43 \cdot 10^{-3}$
Au	$0.508 \cdot 10^{-3}$	10.8	$0.51 \cdot 10^{-3}$
Ag	$0.4 \cdot 10^{-3}$		
Cu	$2 \cdot 10^{-3}$	43	$2 \cdot 10^{-3}$
Au	$3 \cdot 10^{-4}$	5.6	$2.8 \cdot 10^{-4}$
Ag	10^{-3}		

Analysis of alloys

The combination of noble metals occurs in dental alloys. The method was, therefore, applied to the analysis of these alloys.

The alloy, usually about 20 mg, was dissolved in either hot concentrated nitric acid or hot aqua regia, evaporated to dryness, taken up in complexing agent and diluted to 25 or 50 ml after addition of sodium sulphate and gelatine. The results for two dental alloys are shown in Table IV.

TABLE IV

ANALYSIS OF DENTAL ALLOYS

Alloy	Cu		Ag	Au	
	Present	Found	Present	Present	Found
I	7.5%	7.63%	92.5%	—	—
2	3.0%	3.0%	—	75.0%	74%

Inclusion of palladium in the analytical scheme

The dental alloys examined contained palladium in addition to the elements determined. It was considered that the scheme would be even more useful, if this element could be included. Accordingly, a stock solution of palladium nitrate was prepared and samples 10^{-3} M in the ion were mixed with the same electrolyte as used for the other metals, *i.e.*, 0.2 M sodium sulphate and ethanolamine. It was found that palladium gave a well-formed wave at -0.78 V. The calibration graph proved to be linear for the concentration range examined, 10^{-4} M to $2 \cdot 10^{-3}$ M.

Synthetic "unknowns" containing gold, silver, copper and palladium were analysed by one of us (I.A.B.). The results are shown in Table V.

TABLE V

ANALYSIS OF SYNTHETIC MIXTURES

	Au	*Cu*	*Pd*	*Ag*
$E_{1/2}$ (V)	-0.2	-0.42	-0.78	No wave
Peak height	25.2	11.5	3.7	—
Concn. found (M)	$1.25 \cdot 10^{-3}$	$0.53 \cdot 10^{-2}$	$2.2 \cdot 10^{-4}$	10^{-3}
Actual concn. (M)	$1.27 \cdot 10^{-3}$	$0.5 \cdot 10^{-3}$	$2.0 \cdot 10^{-4}$	—

In this mixture the ratio of Pd : Cu : Au was 1 : 2.5 : 6.4. It can be seen that, once again, silver did not interfere with the determination of the other three constituents. Nickel does not give a polarographic wave under the conditions described above, so it may also be present in the mixture.

SUMMARY

The polarographic behaviour of complexes of the noble metals was studied by oscillographic polarography. A method was developed for the polarographic determination of copper, gold and palladium; silver and nickel do not interfere. Applications to the analysis of dental alloys proved successful.

RÉSUMÉ

Les auteurs ont examiné le comportement polarographique des complexes des métaux nobles au moyen d'un polarographe oscillographique. Une méthode est proposée pour le dosage du cuivre, de l'or et du palladium; l'argent et le nickel ne gènent pas. Application à l'analyse d'alliages dentaires.

ZUSAMMENFASSUNG

Es wird das polarographische Verhalten einer Anzahl von Edelmetall-Komplexverbindungen mit Hilfe eines Oscillationspolarographen untersucht und eine Methode zur Bestimmung von Kupfer, Gold und Palladium beschrieben, bei welcher Silber und Nickel nicht stören. Die Methode eignet sich zur Analyse von Dentallegierungen.

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SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF PALLADIUM AFTER COPRECIPITATION WITH TELLURIUM

ELIOT R. R. MARHENKE AND E. B. SANDELL

School of Chemistry, University of Minnesota, Minneapolis 14, Minn. (U.S.A.)

Preliminary work twenty years ago showed the feasibility of determining microgram quantities of palladium colorimetrically with *p*-nitrosodiphenylamine after isolation by coprecipitation with tellurium precipitated with stannous chloride[1]. This method has now been investigated in greater detail and some modifications have been introduced. The palladium–nitrosodiphenylamine complex is extracted into an immiscible organic solvent (diethyl oxalate) for absorbance measurement, without removal of tellurium. Coprecipitation of palladium with tellurium provides an effective separation from much iron, copper, nickel and cobalt, *i.e.*, from metals making up the bulk of such samples as sulfides and meteorites in which the determination of traces of palladium is of interest.

Many colorimetric reagents for the determination of palladium are available. We have preferred to retain the use of *p*-nitrosodiphenylamine because of its excellent sensitivity, which is about three times that provided by α-furildioxime, a reagent which otherwise has some advantages: the acidity need not be closely controlled and gold does not interfere in milligram quantities.

The procedure given below should be applicable with little modification to meteorites, containing more than 0.1 p.p.m. Pd. It appears possible that refinement of the procedure will permit its use for the determination of palladium in subsilicic rocks. Sparse data obtained by neutron activation indicate palladium contents of ~0.01 p.p.m. in basalts and gabbros and as much as 0.1 p.p.m. in dunites[2]. By reducing the volume of organic solvent extractant to 1 ml and measuring the absorbance in a spectrophotometer affording a precision of 0.001 in the value of log I_0/I, 0.01 p.p.m. palladium should be determinable to 20% in a 2 g sample of rock, barring unforeseen difficulties. Rocks are favorable samples because they are not likely to contain interfering elements in sufficient amounts to cause trouble. Presumably decomposition can be carried out with hydrofluoric acid in Teflon vessels.

DISCUSSION

Extraction of the palladium–nitrosodiphenylamine complex

The compound $Pd[NOC_6H_4N(CH_3)_2]_2Cl_2$ is only slightly soluble in water, but it dissolves in various organic solvents immiscible with water, such as chloroform, ether and ethyl acetate[3]. PRZHEVAL'SKIĬ and coworkers[4] used *n*-butanol to extract the palladium complex in their analytical method. We tested chloroform, butyl and

amyl alcohols, butyl and amyl acetates, butyl propionate, butyl butyrate, ethyl oxalate and isopropyl ether as extractants and found diethyl oxalate to be the most suitable. It is superior to *n*-butanol because it is less volatile (b.p. 185°) and less soluble in water and has a density (1.08) greater than that of water. It separates well from water and gives a clear phase. The palladium complex is stable in diethyl oxalate, *e.g.*, a solution showing an absorbance of 0.317 immediately after extraction showed 0.315 fifteen hours later.

Under the conditions of the *Procedure*, the acidity of the aqueous solution may vary from 0.005 to 0.015 *M* (in hydrochloric acid) without important effect on the color intensity of the palladium extract:

	Absorbance		
	0.005 M	0.010 M	0.015 M
0.25 μg Pd (5 ml diethyl oxalate)	0.029	0.031	0.030
5.0 μg Pd (10 ml diethyl oxalate)	0.311	0.316	0.319

At higher acidities the color intensity decreases. A standing period of 20 min before extraction suffices for full color development. The excess reagent is largely extracted by diethyl oxalate, but the resulting solution absorbs only slightly at 525 mμ (Fig. 1).
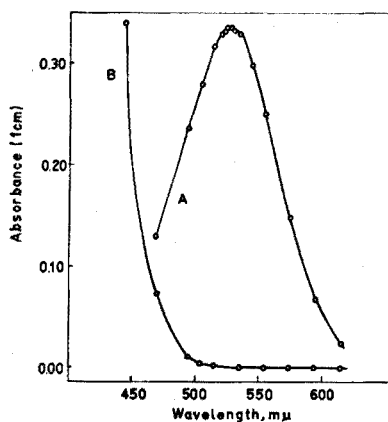
Fig. 1. (A) Absorbance curve of palladium(II)–*p*-nitrosodiphenylamine complex in ethyl oxalate *vs.* reagent blank. 10 ml of aqueous phase containing 5.0 μg of Pd and 50 μg *p*-nitrosodiphenylamine shaken with 10 ml diethyl oxalate. Beckman Model B spectrophotometer. (B) Blank absorbance curve.

With 0.05 mg of reagent, which suffices for as much as 5 μg of Pd, the blank absorbance is approximately 0.002. Small amounts of sodium chloride (10 mg) do not affect the color intensity significantly, but large amounts decrease it (0.5 g NaCl cuts the color given by 5 μg Pd by about 50%).

The absorbance of the extract is proportional to the palladium concentration up to at least 1 μg Pd per ml of diethyl oxalate.

Limitations of the method

The recovery of palladium averages ~90% for 0.2–0.5 μg Pd, and higher for larger amounts (Table I). There is little reason to doubt the quantitative coprecipitation of palladium with tellurium. The small losses may arise from retention of a little

palladium by minute amounts of metastannic acid resulting from carrying down of tin compounds by tellurium. Large amounts (0.5 g) of iron, copper, nickel, and cobalt, as well as other elements which are not precipitated by stannous chloride, are without effect. Milligram amounts, at least, of Ti, Zr, V, As, Sb, and Bi may be present.

TABLE I

DETERMINATION OF PALLADIUM FOLLOWING COPRECIPITATION WITH TELLURIUM

Foreign elements	Pd taken (μg)	Pd found (μg)
	0.20	0.18, 0.17
	0.50	0.51, 0.48, 0.42, 0.50, 0.41 (avg. 0.46)
	1.00	0.94, 0.91, 0.95, 0.96, 0.97 (avg. 0.95)
	1.5	1.4, 1.4, 1.4, 1.5
	2.5	2.4, 2.4, 2.4, 2.3, 2.4
	10.0	9.8, 9.7[a]
0.5 g each Fe(III), Ni, Co	0.0	0.0
0.5 g each Fe(III), Ni, Co	0.20	0.19, 0.18
0.5 g Fe(III)	1.5	1.4, 1.5
0.5 g Cu(II)	0.20	0.21, 0.18
0.5 g Cu(II)	1.5	1.4, 1.5
5 mg each Ti, V(V), Mn, Cr(III)	2.5	2.4, 2.3
1.0 mg each W and Mo	2.5	1.9, 1.6, 2.1, 2.0
0.1 mg each W and Mo	2.5	2.2, 2.4, 2.3
1.0 mg Zr	2.5	2.4
1 mg each As, Sb, Bi, Ge	0.50	0.43, 0.46
50 mg Pb, 1 mg Tl	0.50	0.43
50 mg Pb, 1 mg Tl	2.5	2.3
1 mg Hg	0.50	0.42
0.01 mg Ag	1.0	0.96, 0.97
0.1 mg Ag	1.0	0.95, 0.96
1.0 mg Ag	1.0	0.74, 0.84
0.01 mg Au	0.50	0.57, 0.64
0.01 mg Au	2.5	2.6, 2.7
0.75 mg Au	0.50	10.4
0.10 mg each Pt, Rh, Ir	0.50	0.51, 0.49
0.10 mg each Ru, Os	1.0	1.0, 0.98
1.0 mg Se	2.5	1.6[b]
0.1 mg Se	2.5	2.3
1.0 mg Re	2.5	2.3

[a] Filtrates contained 0.00 and 0.01 μg Pd.
[b] After evaporation of HNO_3-HCl solution of Te, residue treated with 3 ml of 0.1 M HCl and solution diluted to 30 ml, but some insoluble material remained.

Elements that are reduced to slightly soluble products, or otherwise precipitated with stannous chloride, may cause trouble. Chief among these are silver and gold. Both are completely precipitated by stannous chloride. Treatment of the tellurium precipitate with nitric and hydrochloric acids forms silver chloride which retains palladium. The amount of silver in the sample should not exceed 0.1 mg. This amount still allows 95% recovery of 1 μg of palladium; with 1 mg of silver the recovery drops to

roughly 75%. Gold causes high results by giving a color with the reagent; the absorbance is about 0.01 of that produced by an equal weight of palladium, judging from the errors in Table I. This means that the ratio of gold to palladium in the sample should not exceed 10 if the error in palladium is to be kept below 10%. When appreciable amounts of gold are present, α-furildioxime is a more suitable spectrophotometric reagent, although at the cost of decreased sensitivity. Gold can always be removed by ether or ethyl acetate extraction of chloroauric acid from 1 : 1 hydrochloric acid. This separation step can be introduced after elemental tellurium has been brought into solution, without complicating the procedure unduly. Alternatively, the ether extraction can be carried out on the original sample, most of the iron(III) being removed at the same time.

The platinum metals in small amounts (100 μg Pt, Rh, Ir, Os, and Ru) do not interfere, even though platinum is completely coprecipitated and rhodium is partly coprecipitated with tellurium. Mercury, which is also carried down with tellurium, does not cause trouble. Selenium, which is completely precipitated, should not exceed 0.1 mg, else it will be difficult to bring into solution and low results will be obtained for palladium. Tungsten may be present in small amounts only (0.1 mg W and a like amount of Mo) because tungstic acid retains palladium.

<div align="center">EXPERIMENTAL</div>

Reagents

Tellurite solution (0.8 mg Te per ml). Prepare by dissolving tellurous oxide or sodium or potassium tellurite (K_2TeO_3/Te = 2.0) in concentrated hydrochloric acid and diluting tenfold with water.

Stannous chloride solution (20% $SnCl_2 \cdot 2H_2O$ in 2 M HCl). Filter if not clear. Prepare fresh weekly.

p-Nitrosodiphenylamine (0.005% in 50% ethyl alcohol).

Diethyl oxalate. A product of good purity need not be distilled.

Standard palladium solution (5 μg Pd per ml). Dissolve 50 mg of palladium metal in a few ml of aqua regia and evaporate to dryness. Take up the residue in a ml of concentrated hydrochloric acid and evaporate to dryness; repeat the addition and evaporation of hydrochloric acid. Dissolve the residue in 1.0 M hydrochloric acid and dilute to 100 ml in a volumetric flask with the same acid. Dilute 5.0 ml of this solution to 500 ml with water to obtain a standard solution containing 5.0 μg Pd per ml in 0.01 M hydrochloric acid.

Procedure

Isolation of palladium. If the sample has been brought into solution with nitric acid, aqua regia or other volatile oxidizing agents, evaporate to dryness several times with concentrated hydrochloric acid to remove them. If significant amounts of gold are present, this element should be removed in the usual way by extraction with ethyl or isopropyl ether, or ethyl acetate, from 1 : 1 hydrochloric acid.

Dilute the sample solution (0.2–5 μg Pd) to make its hydrochloric acid concentration about 3 M (volume conveniently 25–50 ml) and add 0.5 ml of tellurite solution. Add stannous chloride solution with stirring until a precipitate of tellurium appears, and then an excess of 3–5 ml. Heat the solution to boiling and keep near the boiling point until the precipitate is well coagulated (15–30 min). Collect the precipitate in

a small (7 ml) porous porcelain filter crucible and wash the beaker and crucible well with 1 M hydrochloric acid ($\sim$ 25 ml).

Dissolve the tellurium precipitate in the beaker and in the crucible by adding 0.5–1 ml of warm concentrated nitric acid, followed by 1 ml of concentrated hydrochloric acid. Allow the acid mixture to remain in the crucible for a few minutes before drawing it through into a small (25 ml) suction flask. Wash the precipitation beaker and crucible well with small portions of hot water. Add 5 mg of sodium chloride to the combined filtrate and washings, and evaporate to dryness on the steam bath. Add 0.25 ml of concentrated hydrochloric acid and evaporate to dryness. Repeat the addition and evaporation of hydrochloric acid four times. In the last evaporation make sure that all acid has been removed and no droplets are left on the sides of the vessel.

Dissolve the residue in 1.00 ml of 0.10 M hydrochloric acid and transfer the solution with 9 ml of water (thus obtaining a 0.01 M hydrochloric acid solution) to a small separatory funnel.

Determination of palladium. Add 1.00 ml of p-nitrosodiphenylamine solution and allow to stand at room temperature for 20 min. Add 5.0 ml of diethyl oxalate and shake for 1 min to extract the palladium complex. Allow the phases to separate and remove any droplets of aqueous solution in the diethyl oxalate extract by filtration through a small plug of glass wool. Measure the absorbance at 525 mμ. Run a reagent blank through the procedure.

Establish the standard curve by taking 0, 0.5, 1–5 μg Pd in 10 ml of 0.01 M hydrochloric acid and extracting with 5 ml of diethyl oxalate.

SUMMARY

A spectrophotometric method for the determination of microgram amounts of palladium in the présence of much iron, copper, nickel, cobalt and other common elements ($\sim$ 0.5 g) is described. Palladium is separated by stannous chloride precipitation with tellurium as collector. p-Nitrosodiphenylamine is used as the colorimetric reagent, and diethyl oxalate as extractant for the palladium complex (sensitivity = 0.0015 μg Pd/cm^2 $\equiv$ log I_0/I = 0.001). Silver, selenium and tungsten lead to low results and should not exceed $\sim$ 0.1 mg. The weight ratio Au/Pd should not exceed 10, else results for palladium are high. For Pd > 1 μg, recoveries average 90% or better.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du palladium (en microquantités), en présence de fortes teneurs en fer, cuivre, nickel, cobalt et d'autres éléments courants. Le palladium est séparé par précipitation au moyen de chlorure stanneux, en présence de tellure comme collecteur. On utilise la p-nitrosodiphénylamine comme réactif colorimétrique et l'oxalate d'éthyle pour l'extraction du complexe formé.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur spektrophotometrische Bestimmung von Spuren von Palladium neben grossen Mengen Eisen, Kupfer, Nickel, etc. Palladium wird in Gegenwart von Tellur mit Zinnchlorür gefällt, in den p-Nitrosodiphenylamin-Komplex übergeführt und dieser mit Diäthyloxalat extrahiert.

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SPECTROPHOTOMETRIC DETERMINATION OF SCANDIUM WITH ANTHRARUFIN-2,6-DISULFONIC ACID (DISODIUM SALT)

JOHN C. MACDONALD AND JOHN H. YOE

Pratt Trace Analysis Laboratory, Department of Chemistry, University of Virginia, Charlottesville, Va. (U.S.A.)

There is no selective spectrophotometric reagent for the detection and determination of scandium. This lack of selectivity is due to the electronic structure of the Group III A ions which have no d electrons available for bond formation; hence, these ions do not react in an individualistic manner.

The spectrophotometric determination of an ion belonging to Group III A requires separation of the ion from all similar ones. Scandium in concentrated hydrochloric acid solution can be separated conveniently from similar ions by using Dowex-1X8 anion-exchange resin[1]. The scandium–chloride complex ion is weakly adsorbed by the resin and elutes later than the unadsorbed ions[2]. The other weakly adsorbed ions, *i.e.*, Cr^{3+}, Ti^{3+}, Tl^+ and V^{4+} can be separated from scandium by solvent extraction with thenoyltrifluoroacetone (TTA).

This paper describes a new spectrophotometric method for the determination of scandium based on a sensitive color reaction of scandium with anthrarufin-2,6-disulfonic acid (disodium salt). The scandium is separated from interfering ions by Dowex-1X8 exchange resin and by solvent extraction with TTA. The method has been applied successfully to a variety of salt solutions containing scandium.

EXPERIMENTAL

Apparatus

Beckman spectrophotometers, Models DK-2 and DU, with matched 1.000-cm Corex cells were used.

A Beckman pH meter, Model G, was employed for all pH measurements. It was calibrated with certified standard buffer solutions.

Reagents

Standard scandium solution. A solution containing 1 mg Sc per ml was prepared by dissolving 1.541 g of scandium oxide (Sc_2O_3 99.5%, A.D. Mackay, Inc., New York) in 1 N hydrochloric acid and diluting to 1 l with 1 N hydrochloric acid.

Anthrarufin-2,6-disulfonic acid (disodium salt) solution. A $1.0 \cdot 10^{-3}$ M solution of anthrarufin-2,6-disulfonic acid (disodium salt) was prepared by dissolving 11 mg of the compound in distilled water and diluting to 25 ml.

Thenoyltrifluoroacetone (TTA). A 0.1 M thenoyltrifluoroacetone solution was prepared by dissolving 2.2 g of the compound in 100 ml of redistilled cyclohexane.

Other reagents. All other reagents were analytical grade and were used without further purification.

<center>PRELIMINARY STUDIES</center>

Properties of the reagent

Anthrarufin-2,6-disulfonic acid (disodium salt) is an orange-red solid which dissolves readily in water to give a clear red solution. Its acid solution is yellow but changes to red over the pH range 7 to 12; the mid-point of the color change is at pH 9.2. The acid form has an absorbance maximum at 417 mμ, the base form at 515 mμ.

In order to obtain a low reagent blank and a useful range of scandium concentration, a $1.0 \cdot 10^{-4}$ M reagent solution is required. Its absorbance curve is shown in Fig. 1 (Curve I). The reagent solution is not very stable and a fresh one should be prepared daily.
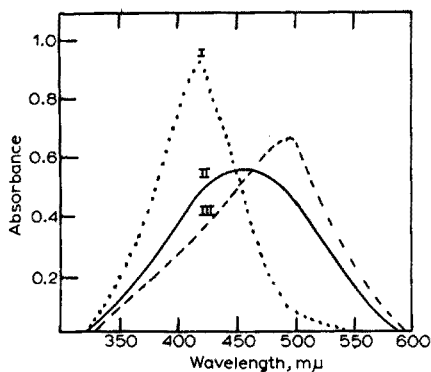
Fig. 1. Effect of scandium concentration on the spectrum of the complex. Curve I, reagent alone; Curve II, scandium plus excess reagent; Curve III, reagent plus excess scandium.
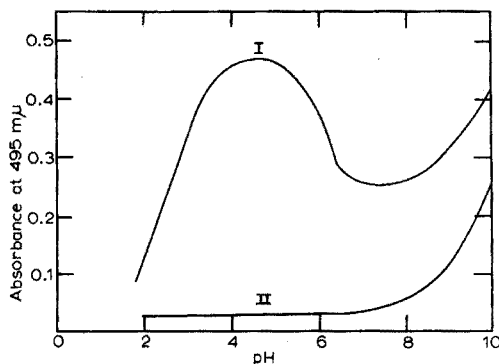
Fig. 2. Effect of pH. Curve I, scandium–reagent complex; Curve II, reagent alone.

Properties of complex

Color. In acid solution scandium forms a soluble red complex with the reagent. The absorbance of the complex in excess reagent is shown in Fig. 1 (Curve II). In excess reagent, the color of the complex is partially masked by the yellow color of the reagent and for this reason absorbance measurements are made at 495 mμ.

When scandium is in a two-fold excess, the absorbance maximum is at 498 mμ as shown in Fig. 1 (Curve III). Greater excesses cause a shift of the maximum to longer wavelengths.

Effect of pH. The effect of hydrogen-ion concentration on the reagent and the complex is shown in Fig. 2. The complex has maximum absorbance at pH 3.9 to 5.1. The use of buffers resulted in decreased sensitivity of the reaction and hence pH adjustments were made with a glass electrode.

Reaction rate and stability. Maximum absorbance of the complex is attained immediately and is constant for about 24 h; then the absorbance slowly decreases.

Order of addition of reagents. The order of addition of the reagents was found to have no effect upon the absorbance of the complex.

Effect of temperature. Absorbance measurements at 15°, 25°, and 35°, respectively, showed the complex to be independent of normal variations in laboratory temperature.
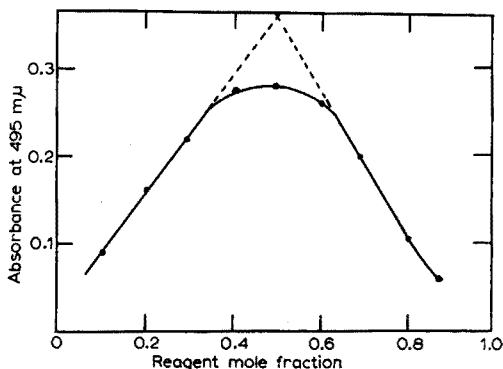
Fig. 3. Mole-ratio determination by the method of continuous variations.

Mole ratio studies. The ratio of scandium to organic ligand was measured by three techniques: the mole-ratio method of YOE AND JONES[3], the continuous variations method of JOB[4] as modified by VOSBURGH AND COOPER[5], and by the slope ratio method of HARVEY AND MANNING[6]. All three methods showed the complex to have a 1 : 1 ratio of scandium to the organic ligand. The graph for the continuous variations method is shown in Fig. 3.

Adherence to Beer's law. Beer's law is obeyed up to 2 p.p.m. scandium at 1.0 · 10^{-4} M reagent concentration. Above 2 p.p.m. there is a negative deviation as the scandium concentration approaches the reagent concentration.

Sensitivity. The sensitivity of the color reaction is 0.004 μg Sc per cm^2 for log I_0/I = 0.001, corresponding to 1 part of scandium in 250 million parts of solution. A more practical sensitivity, *i.e.*, an absorbance of 0.005 unit, is 0.020 p.p.m.

Effect of diverse ions. Interfering ions are arbitrarily defined as those which cause an absorbance change of $\pm$ 0.005 unit at a concentration of 100 p.p.m. or less. The following ions give no interference at the 1 p.p.m. scandium level: Ca^{2+}, Cd^{2+}, Hg^{2+}, Mg^{2+}, NH$_4^+$, Sr^{2+}, Zn^{2+}, Br$^-$, BrO$_3^-$, C$_2$H$_3$O$_2^-$, Cl$^-$, and I$^-$. Ions interfering at 1 p.p.m. for a scandium concentration of 1 p.p.m. are: Al^{3+}, Be^{2+}, Cu^{2+}, Fe^{3+}, rare earths, Sn^{4+}, Th^{4+}, Tl$^+$, VO^{2+}, Y^{3+}, Zr^{4+}, C$_2$O$_4^{2-}$, F$^-$, Fe(CN)$_6^{3-}$, MoO$_4^{2-}$, PO$_4^{3-}$, citrate, and

tartrate. The following ions interfere at the concentration in p.p.m. given in parentheses: $Ag^+(5)$, $Bi^{3+}(3)$, $Co^{2+}(20)$, $Cr^{3+}(50)$, $Ga^{3+}(2)$, $In^{3+}(3)$, $Mn^{2+}(20)$, $Ni^{2+}(40)$, $Pb^{2+}(100)$, $Sn^{3+}(3)$, $Ti^{4+}(6)$, $UO_2^{2+}(4)$, $BO_3^{3-}(100)$, $CO_3^{2-}(80)$, $Cr_2O_7^{2-}(50)$, $SCN^-(1)$, $SiO_3^{2-}(10)$, $SO_4^{2-}(50)$.

Separations

By extraction. Yttrium was selected as representative of the Group III A ions. Solutions containing both scandium and yttrium were prepared and the ions were then separated by using dibutylphosphate (DBP) and tributylphosphate (TBP) as extractants. Both scandium and yttrium are selectively extracted from 0.1 N hydrochloric acid by DBP[7]. Scandium is then separated from yttrium by equilibration of a concentrated hydrochloric acid solution with TBP which extracts the scandium only[7]. This part of our investigation was carried out at the University of Virginia reactor facility using scandium-46 and yttrium-90, employing a scintillation counter for [46]Sc and a Geiger-Müller counter for [90]Y.

Although quantitative separation of both scandium and yttrium was accomplished and also scandium from yttrium, as shown by radiochemical technique, low results were obtained for scandium using the anthrarufin-2,6-disulfonic acid (disodium salt) color reaction, perhaps due to a trace of phosphate from the slight hydrolysis of DBP and/or TBP. For this reason separation by solvent extraction was discarded in favor of separation by ion-exchange resin. Obviously a sensitive colorimetric reagent for scandium and/or yttrium which could be used in conjunction with the DBP and TBP separation technique is much desired.

By ion exchange. Dowex-1X8 anion-exchange resin adsorbs many of the interfering ions from concentrated hydrochloric acid[1]. The alkalis, alkaline earths, Y^{3+}, the lanthanides, actinides, Th^{4+}, Al^{3+} and Ni^{2+} pass through a Dowex-1X8 column unadsorbed from concentrated hydrochloric acid solution; Cr^{3+}, Sc^{3+}, Ti^{3+}, Tl^+ and V^{4+} are weakly adsorbed and pass through the resin column more slowly. For this selective separation of scandium a column of dimensions 23 cm × 0.50 cm² was used;
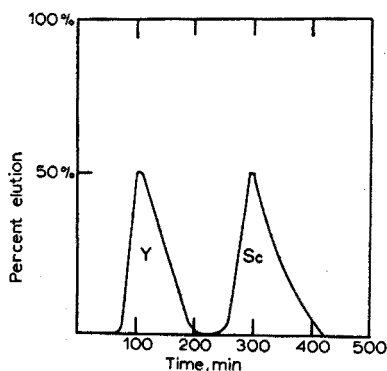
Fig. 4. Calibration of ion-exchange column.

shorter column lengths resulted in overlap of the strongly adsorbed and weakly adsorbed ions. Yttrium(III) was used to determine the elution time of the unadsorbed ions. A solution of scandium and yttrium in concentrated hydrochloric acid was

passed through the column and the eluate analyzed in 30-min portions. The calibration curve is shown in Fig. 4.

<div align="center">PROCEDURE</div>

Prepare an ion-exchange column of Dowex-1X8, 200–400 mesh, with dimensions 23 cm $\times$ 0.50 cm^2. Put the resin in the chloride form with concentrated hydrochloric acid. Allow the hydrostatic head to fall to the top level of the resin. Pipet a 1 ml aliquot of the concentrated hydrochloric acid solution containing 0.2–20 μg of scandium onto the column. Maintain a hydrostatic head of 0 to 1 ml with concentrated hydrochloric acid solution. Discard the effluent until scandium break-through, as indicated by the calibration curve. Collect the effluent containing the scandium in a Pyrex beaker and evaporate to dryness. Add 5 ml of 0.01 N hydrochloric acid to the beaker, cover with a Pyrex watch glass and heat in an oven at 105° for 1 h. Cool and quantitatively transfer the acid solution to a 10-ml volumetric flask. Pipet 1 ml of $1 \cdot 10^{-3}$ M reagent solution into the flask and adjust the pH to between 4 and 7 with 0.1 N sodium hydroxide. The reagent serves as a pH indicator to adjust the pH approximately. Dilute to volume with distilled water and make the final pH adjustment to 3.9 to 5.1 with the glass electrode, using 0.1 N hydrochloric acid and/or 0.1 N sodium hydroxide. Thoroughly mix and read the absorbance of the solution at 495 mμ. Read the scandium concentration from a Beer's law plot.

Separation of Sc from Cr, Tl and V

TTA is an effective solvent extractant[8] and was used to separate Sc^{3+} from Cr^{3+}, Tl$^+$ and V^{4+}. A 0.1 M TTA solution in cyclohexane was used to extract scandium from a solution of pH 2.0. The scandium was then stripped with 1 N hydrochloric acid.

<div align="center">TABLE I</div>

<div align="center">EFFECT OF HYDROCHLORIC ACID ON THE SEPARATION</div>

Volume, 1 N HCl (ml)	Sc recovered (p.p.m.)	Sc recovered (%)
0	1.95	98
0	2.00	100
1	1.93	97
1	1.91	91
5	1.45	73
5	1.53	77
10	1.19	60
10	1.10	55

Separation procedure. Adjust 10 ml of the solution (containing 0.2–20 μg Sc) to pH 2.0. Equilibrate the solution with 10 ml of 0.1 M TTA for 1 min in a separatory funnel. Discard the aqueous phase and backwash the organic phase twice with 10 ml of 0.01 N hydrochloric acid, discarding the washings. Strip the scandium by equilibrating 1 ml of 1 N hydrochloric acid with the organic phase for 1 min. Transfer the aqueous phase to a Pyrex beaker. Run 5 ml of 1 N hydrochloric acid down the inside of the separatory funnel and out the stem into the beaker. Repeat with second portions of 1 ml and 5 ml, respectively, of 1 N hydrochloric acid. Evaporate the combined portions to dryness and continue as directed in the PROCEDURE.

Separation interferences. Unexpected interferences in the separation procedure were observed but were eliminated by various techniques. (*1*) Fluoride interferes and is present in ordinary glass wool; hence, fluoride-free glass wool was used to support the ion-exchange column. (*2*) Phosphate interferes and is a common trace impurity in sodium hydroxide; hence the amount used in the procedure must be controlled. In this study 0.05 meq of phosphate was the maximum amount permissible in reagent grade sodium hydroxide. (*3*) Polyethylene containers were observed to decompose slightly and caused a decrease in the recovery of scandium; hence, Pyrex containers were employed. (*4*) In the TTA stripping process volumes greater than 1 ml of 1 N hydrochloric acid caused a decrease in the recovery of scandium; hence, the use of 1 ml of the acid. The effect of the acid is shown in Table I.

Analysis of salt solutions

A series of salt solutions in concentrated hydrochloric acid (5 containing 10 p.p.m. Sc and 1 containing 2 p.p.m. Sc) was prepared and analyzed for scandium. The results are summarized in Table II.

TABLE II

ANALYSIS OF SALT SOLUTIONS

Ions[a]	1	2	3	4	5	6
Sc^{3+}	10	10	10	10	10	2
Al^{3+}	10					40
Ca^{2+}		30		20		
Co^{2+}	10					
Cr^{3+}					10	
Cu^{2+}		30				
Eu^{3+}				10		
Fe^{3+}	10	30	30	20		100
Gd^{3+}			30	10		30
Mg^{2+}	10	30		30		30
Ni^{2+}	10	30				100
Nd^{3+}				10		
Tl^+					10	
VO^{2+}					10	
Y^{3+}	25	25	25	25	25	5
Zn^{2+}	10	30				30
Sc^{3+} found	10.1	9.7	10.2	9.9	9.5	1.86
Percent recovery	101	97	102	99	95	93

[a] All concentrations are in p.p.m.

SUMMARY

A new spectrophotometric method for the determination of scandium is described using anthrarufin-2,6-disulfonic acid (disodium salt) as a reagent. The color reaction has a sensitivity of 0.004 μg Sc per cm^2 for log I_0/I = 0.001 and obeys Beer's law up to 2 p.p.m. The effects of pH, time, order of addition of the reagents, temperature, and diverse ions were investigated. A separation procedure was developed and applied to six salt solutions containing scandium plus a variety of foreign ions.

RÉSUMÉ

Une nouvelle méthode spectrophotométrique est proposée pour le dosage du scandium, au moyen de l'acide anthrarufinedisulfonique. L'influence de divers facteurs a été examinée et une séparation d'avec des ions étrangers est donnée.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Scandium mit Hilfe von Anthrarufindisulfosäure. Der Einfluss verschiedener Faktoren wurde untersucht und ein Verfahren zur Abtrennung von den Fremdionen angegeben.

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SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM AFTER SEPARATION BY ANION EXCHANGE

J. KORKISCH*, G. ARRHENIUS AND D. P. KHARKAR**

University of California, Scripps Institution of Oceanography, La Jolla, California (U.S.A.)

Ascorbic acid as a reagent for the photometric determination of titanium was first described by HINES AND BOLTZ[1] and was used by KORKISCH AND FARAG[2] to determine titanium directly after fusion of mineral samples, or after a column operation in which the element was collected on the strongly basic anion exchanger Amberlite IRA-400 as the titanium ascorbate complex. Since not only titanium was retained by this procedure but also uranium, molybdenum, vanadium, tungsten and zirconium, most of them interfering seriously with the titanium determination, another method had to be developed to ensure the complete separation of these elements.

For this purpose we have adapted the method of KORKISCH AND FARAG[3] for the precise assay of zirconium in rocks and minerals by adsorption on strongly basic anion exchangers, to the determination of titanium in such materials.

The adaptation of this method for titanium assay is based on the fact that titanium is taken up quantitatively by strongly basic anion exchangers (sulfate form) from

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* Permanent address: University of Vienna, Analytical Institute, IX Waehringerstr. 38, Austria.
** Permanent address: Tata Institute of Fundamental Research, Bombay, India.

0.1 N sulfuric acid solution containing sodium fluoride. Titanium is adsorbed as a negatively charged fluoride complex, whereas most of the other elements pass into the effluent. Only the elements vanadium(V), molybdenum(VI), tungsten(VI), uranium(VI), zirconium(VI), tin(II and IV), and antimony (V) are adsorbed together with the titanium.

<div align="center">EXPERIMENTAL</div>

Reagents

Resins. The strongly basic anion exchangers Amberlite IRA-400, Dowex 1-X8 and 2 (100–200 mesh, chloride form) were transformed to their corresponding sulfate ·forms by treating them repeatedly with 6 N sulfuric acid until chloride ions could no longer be detected in the effluent by means of silver nitrate.

Titanium standard solutions. From a standard titanium solution (1 N sulfuric acid) which contained a photometrically determined[4] amount of 1 mg Ti/ml, diluted solutions were prepared which contained up to 100 μg Ti/ml in 0.1 N sulfuric acid.

Sodium fluoride solution. The sodium fluoride solution was prepared by dissolving an appropriate amount of reagent-grade sodium fluoride in 0.1 N sulfuric acid to give a solution containing 0.1 g NaF/ml. The solution must be kept in a polyethylene bottle.

Aluminium chloride solution. $AlCl_3 \cdot 6H_2O$ was dissolved in 1 N hydrochloric acid giving a solution containing 0.4 g/ml (44.7 mg Al/ml).

Ascorbic acid solution. 5 g of reagent-grade ascorbic acid (Wiener Heilmittelwerke) were dissolved in 60 ml of distilled water and the pH value adjusted to 3.8 by slowly adding 2.5 M sodium acetate solution. Afterwards the solution was diluted with water to 100 ml and thoroughly mixed. This solution should always be prepared fresh, *i.e.* no more than 2–3 h before use.

Apparatus

All photometric measurements were made with a Beckman Model B spectrophotometer using 1-cm cells and a blue-sensitive phototube.

The ion-exchange columns used for the adsorption of titanium were of the same type and dimensions as described previously[5,6]. In place of glass wool, which is severely attacked by acidic fluoride solutions, pure cotton was used.

(1) Adsorption of titanium

To 1 ml of the titanium solution containing 100 μg Ti/ml, were added 10 ml of the sodium fluoride solution and 90 ml of 0.1 N sulfuric acid. This sorption solution was passed through a column of Dowex 1 previously transformed into the sulfate form by treatment with 50 to 70 ml of 6 N sulfuric acid and washed first with 50 ml of water and then with 50 ml of 0.1 N sulfuric acid; the flow rate was 0.5 ml/min. After the passage of the sorption solution the resin was washed with 100 ml of 0.1 N sulfuric acid containing 10 ml of the sodium fluoride solution and subsequently with 20 to 30 ml of 0.1 N sulfuric acid to remove the sodium fluoride. Titanium was then eluted with 50 ml of 0.1 N sulfuric acid containing 5 ml of 30% hydrogen peroxide (perhydrol). The process could be visually controlled since the titanium was eluted as the yellow peroxy titanic acid complex. A series of experiments were carried out in this manner using amounts larger or smaller than 100 μg. The determination of

titanium in the eluate is described below. The breakthrough capacity of the columns used was reached with 10 mg of titanium under the above conditions.

(2) Spectrophotometric determination of titanium in the eluate

The 0.1 N sulfuric acid eluate containing the titanium and excess hydrogen peroxide (visibly yellow colored in the presence of much titanium) was transferred to a platinum dish, which was covered with a watch glass and heated on a water bath until no more effervescence of oxygen was observed. Subsequently, the watch glass was removed and the solution evaporated to a small volume. The sulfuric acid was then removed by careful fuming and the resulting residue of titanium sulfate was ignited for less than 1 min to form titanium dioxide. A few ml of concentrated hydrofluoric acid were then added to the dish and the solution was evaporated to dryness on the water bath. When much titanium was present this process was repeated. The residue consisting of titanium fluoride was dissolved portionwise in altogether 20 ml of 1 N hydrochloric acid and simultaneously transferred to a 50 ml measuring flask. (In those cases where very small amounts of titanium were expected the dilution was made in 10 ml measuring flasks. The amounts of reagents were correspondingly changed and the photometer readings divided by 5 in calculating the titanium concentration of the measuring solution from the calibration curve, shown in Fig. 1.) Five ml of the aluminium chloride solution were then added followed by 12.5 ml of 2 5 M sodium acetate solution (resultant pH 3.8) and the volume was diluted to 50 ml by addition of the buffered ascorbic acid solution. The absorbance of this solution was measured at a wavelength of 355 mμ against distilled water as a blank.
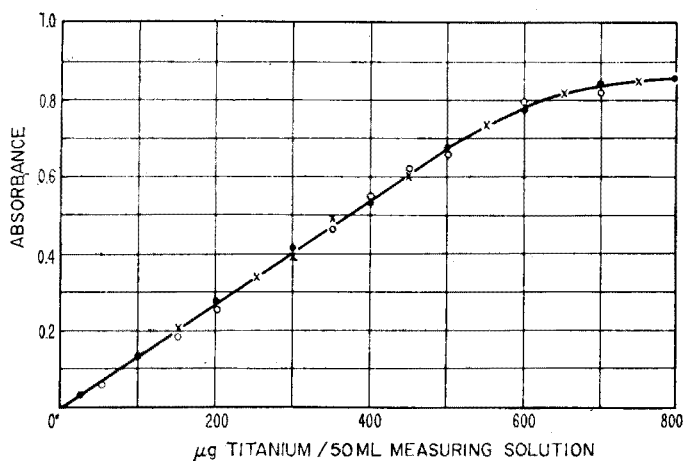
Fig. 1. Spectrophotometric measurements on the titanium solutions.

The results of a series of such ion-exchange experiments are shown in Fig. 1 (filled circles), which constitutes the calibration curve.

The crosses of the curve indicate the results obtained by measuring directly the titanium (without preliminary column operation but with the same treatment as described above). The open circles show the results obtained by directly measuring titanium standard solutions in absence of fluoride and aluminium ions.

From these experiments and measurements it is concluded that the adsorption of titanium on the ion exchanger is complete (all of the strongly basic resins used gave identical results), and its elution correspondingly quantitative. The evaporation procedure and the conversion to titanium fluoride appear to be highly satisfactory. Further, the masking of the fluoride ions is quantitative and the addition of aluminium ions does not interfere with the measurements.

(3) Separation of titanium from other elements

Since the procedure for titanium analysis described in this paper is similar to that previously described for zirconium analysis[3] all those elements which could be separated from zirconium can also be removed before the determination of titanium. Moreover, the separation from co-adsorbed elements (Zr, V, W, Mo, U, Sn and Sb), which are not eluted with 0.1 N sulfuric acid containing hydrogen peroxide, has been found to be quantitative.

Dissolution of the sample must be effected by means of sodium carbonate fusion and not by hydrofluoric-nitric acid treatment, as the organic compounds usually present in sediments might interfere with the adsorption of titanium due to the formation of titanium complexes which are not adsorbed. Consequently, low yields of titanium are usually obtained when dissolution by acid treatment is attempted. The addition of a large amount of aluminium ions (see below) prevents the adsorption of titanium on insoluble fluorides of the alkaline earth and rare earth elements. This effect has been studied in detail previously in connection with the assay of zirconium[3].

Interferences

Since extremely pure titanium is obtained after the column operation interferences with the spectrophotometric determination of the kind studied in detail previously[2] are entirely eliminated. The adsorption of titanium on the resin is only likely to be disturbed by the presence of very large amounts of the co-adsorbed elements, V, Mo, W, U, Zr, Sn and Sb, in the sorption solution. Since fusion of the sample and subsequent leaching of the melt remove V, Mo, W and U from titanium, no interference of the column operation by these elements is to be expected.

Procedure

Dissolution of the sample. An exactly weighed amount of the sample is placed in a platinum crucible. After addition of a ten-fold amount of anhydrous sodium carbonate and thorough mixing, the mixture is fused for 20 to 30 min. The hot platinum crucible is cooled in water, placed in a beaker, and sufficient distilled water is added to cover the entire crucible and its lid. The fused melt is leached for about 12 h whereafter the solution is filtered off. The insoluble residue (hydroxides, carbonates, etc.) contains the titanium as well as zirconium, iron, beryllium, nickel, cobalt, zinc, manganese, rare earths, alkaline earths and some of the thorium.

The clear filtrate, which is sometimes green owing to the presence of manganate ions, contains Mo, U, W, V, Cr, Al, P, Si, As, Sb, Ga, Ta and Cd and is discarded. If the filtrate is turbid, it is filtered either through a denser filter paper or once more through the same filter.

The precipitate must of course be transferred to the filter paper quantitatively. This is done by rinsing the beaker and the crucible with a 1% solution of sodium

carbonate; some residue usually sticks to the wall of the platinum crucible and is removed by successive treatment with a few ml of hot concentrated hydrochloric and hydrofluoric acid. These solutions are transferred to a platinum dish of appropriate size containing about 5 ml of the aluminium chloride solution. The presence of hydrochloric acid is advantageous since reduction of manganese dioxide is effected if the sample contains a large amount of manganese (*e.g.* in manganese nodules). In this case, however, it would also be advantageous to use a plastic dish in place of platinum since the chlorine evolved would attack the platinum too much.

To the hot solution in the platinum dish which is kept on a steam bath, is added the filter paper with the residue which has been washed several times with 1% sodium carbonate solution. After the addition of an excess of hydrofluoric acid the solution is kept on the water bath for 1 to 2 min. The filter paper is then cautiously removed during steady rinsing with distilled water and is finally discarded. The resulting solution containing the Ti, Zr, Fe, Ca, Mg, etc. as fluorides, is evaporated to dryness on the water bath. Another portion of hydrofluoric acid is added in excess and the solution is again evaporated to complete dryness. The residue of fluorides is taken up portionwise in altogether 100 ml of 0.1 N sulfuric acid containing 10 ml of the sodium fluoride solution (heating of the residue with the first portion of this mixture is preferable) and is at the same time transferred to a plastic beaker. This solution is filtered after standing overnight, and the residue (insoluble fluorides) is washed with 20 to 50 ml of 0.1 N sulfuric acid containing 2 to 5 ml of the sodium fluoride solution. The filtrate contains the titanium, zirconium, etc. as fluoride complexes.

Ion exchange operation. The clear filtrate is passed through the column which has been pretreated as previously described (see p. 271) at a flow rate of 0.5 ml/min. After sorption of the titanium the resin is washed with 50–100 ml of 0.1 N sulfuric acid containing 10 ml of the sodium fluoride solution and then with 20–30 ml of 0.1 N sulfuric acid to remove the fluoride ions. Thereafter the titanium is eluted by means of 50 ml of 0.1 N sulfuric acid containing 5 ml of 30% hydrogen peroxide. In order to avoid decomposition of hydrogen peroxide this elution should be performed at temperatures about or below room temperature. During washing the flow rate should be the same as during sorption.

Spectrophotometric determination of titanium. The eluate is prepared for spectrophotometric measurements as described earlier (see p. 272). The photometric readings are evaluated in terms of titanium concentration from the curve in Fig. 1.

<div align="center">RESULTS AND DISCUSSION</div>

In order to check the quantitative isolation of titanium employing the working procedure described above, four marine sediment samples were analyzed twice (125 mg amounts of each), once without addition of titanium and once after addition of 200 μg of titanium to each. The results of these experiments are given in Table I.

Since the difference, which ideally should be 200 μg of titanium, is practically always quantitatively found, this method can be considered reliable and accurate. Because zirconium is adsorbed on the resin together with the titanium and can be eluted after the titanium by means of 4 N hydrochloric acid[3] both elements can be determined quantitatively in the same sample.

Replicate analyses were performed on standard samples of the granite G1, and the diabase W1, which have been assayed by several workers[8–12,15,16]. The results given

TABLE I

TITANIUM DETERMINATION IN MARINE SEDIMENTS[a]

Sample no.	Ti yield (μg)	Ti yield after addition of 200 μg Ti (μg)	Yield difference (μg)
16406	115	315	200
16405	37	230	193
16407	70	260	190
16410	60	255	195

[a] The mineralogical composition of the samples and the geochemical importance of these data will be described elsewhere[7].

in Table II show a close agreement between the analyses obtained for W1 by the present method and the most probable value by previous estimates[12]. The three samples of W1 were submitted on the same occasion and analyzed together. The analyst was aware of the fact that the samples were duplicates, but was not informed about their identity or the results of previous assays. Of the granite standard G1, a total of nine samples were analyzed. Three of the samples were submitted under identical circumstances and gave the results listed in Table II under the designation "Occasion 1". The results show satisfactory agreement between each other, but deviate by 25% from the previously estimated most probable value[12]. In view of this discrepancy, three new samples were submitted for analysis, this time under a different number (but all three identically labelled), and together with 34 other rock samples (reported on elsewhere[7]), in order to exclude any subconscious special care in the analysis. The results are indicated as "Occasion 2" in Table II and fall 12% below the previous estimate and at the lower limit of its adopted limits of acceptability. The samples designated under "Occasion 3" were diluted with spectrally pure quartz (the samples 1, 2 and 3 contained 20%, 10% and 0% quartz respectively). The results (see Table II) calculated for undiluted samples show that the average value on this occasion is as low as 0.184 or 26.4% below the most probable value[12]. If it is assumed that all the data from the different occasions are randomly distributed, the average concentration value obtained here for G1 falls within 3% of the most probable value from the literature. The standard deviation of the present G1 data, however, is rather large and amounts to 28% of the mean.

Considerably better reproducibility was obtained from duplicate analysis of samples with smaller grain size. Two such pairs of analyses are reported at the bottom of Table II. Occasion 1 was in January and Occasion 2 in May 1961. It appears probable that the samples of G1 were inhomogeneous with regard to the distribution of titanium. A deviation of 28% from the mean would be caused by the addition or subtraction in a sample of a volume of rutile (TiO_2) corresponding to a cube with 600 μ side.

The source of the error at Occasion 1 is uncertain; however, a rather closely corresponding discrepancy in the assay of zirconium[3] carried out on the same aliquots of the dissolved sample as the titanium analyses, indicates that an error in the volumetric procedure may have been responsible. This suggestion is further corroborated by the fact that simultaneous analyses of uranium[13] and thorium[14] carried out on a different aliquot, showed good agreement between the two occasions. As to Occasion 3, the source of the error is unknown.

TABLE II

TITANIUM ANALYSES OF ROCK STANDARDS AND OTHER MATERIALS

Sample	Duplicate no.	Concentration of TiO_2 (%)		
		Present method	Previous estimate[12]	
Diabase W1	1	1.06		
	2	1.06		
	3	1.06		
		Average 1.06	Average 1.10	
Granite G1 (Occasion 1)	1	0.321		
	2	0.339		
	3	0.332		
		Average 0.332		
(Occasion 2)	1	0.215		
	2	0.209		
	3	0.216		
		Average 0.213		
(Occasion 3)	1	0.200		
	2	0.183		
	3	0.170		
		Average 0.184	Average 0.25	
		Average for occasions 1–3 = 0.243 ± 0.068		
			Analyst 1	Analyst 2
NBS Standard Sample No. 88 Dolomite (1928)		0.057	0.004	0.005
NBS Standard Sample No. 99 Soda Feldspar (1931)		0.094	0.014	0.019
Pelagic Clay Ch 21 Sample No. 17850 (Occasion 1)		0.319		
(Occasion 2)		0.310		
Pelagic Clay Ch 3 Sample No. 17825 (Occasion 1)		0.689		
(Occasion 2)		0.685		

In addition to the analyses of W1 and G1, assays of two National Bureau of Standards standard rock samples with a low titanium content are also reported in Table II. Considerably higher values are found by the present method than those reported in the standard sample certificates. This discrepancy might be due to incomplete fusion of the samples and by analysts 1 and 2 using gravimetric separation methods, not quite suitable for trace analysis.

SUMMARY

A method is outlined for separation of titanium by anion exchange and subsequent spectrophotometric determination. Titanium fluoride is adsorbed quantitatively on a column of strongly basic anion exchanger and thus separated from ions which would normally interfere. The spectrophotometric measurement is achieved by formation of the intensely yellow and stable titanium ascorbate complex which has a maximum absorbance at 355 mμ.

RÉSUMÉ

Une méthode est décrite pour la séparation du titane (sous forme de fluorure) d'avec des ions gênants, au moyen d'un échangeur d'anions. Le titane peut finalement être dosé spectrophotométriquement sous forme d'ascorbate.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Abtrennung von Titan (als Titanfluorid) durch Adsorption an stark basischen Austauscherharzen. Die Bestimmung erfolgt nach Ueberführung in den Ascorbinsäure-Komplex durch Spektrophotometrie.

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A COMBINED ANION EXCHANGE–SOLVENT EXTRACTION PROCEDURE FOR SEPARATING TRACE AMOUNTS OF Eu, Gd, Dy, Sm AND Er FROM THORIUM TETRAFLUORIDE

R. A. EDGE

Department of Geochemistry, University of Cape Town, Rondebosch, Cape (South Africa)

Because of their high thermal neutron absorption cross-sections, only trace amounts of Eu, Gd, Dy, Sm and Er can be tolerated in thorium compounds used in nuclear technology[1]. Although emission spectrographic methods possess the greatest general utility for the determination of trace amounts of rare earths, their spectrographic determination in thorium tetrafluoride would not be without difficulties. Firstly, the complex spectrum, together with the intense general background emitted by thorium[2], lowers sensitivity and causes interference. Secondly, the toxic thorium vapour evolved during the arcing process may present a considerable health hazard[3]. Separation of the rare earths from the thorium tetrafluoride would reduce the spectral difficulties and at the same time eliminate the health hazard. A combined anion exchange–solvent extraction procedure, shown schematically in Fig. 1 and discussed

ThF_4
|
hot 7 N Al(NO₃)₃ solution
|
adjust acidity to 8 N HNO₃ with conc. HNO₃
|
Y carrier
|
anion exchange
|
┌──────────────┴──────────────┐
resin   8 N HNO₃ effluent
| |
thorium   rare earths, yttrium and aluminium
                              |
                         evaporate off HNO₃ and
                         adjust the Al(NO₃)₃
                         concentration to 7 N by
                         the addition of water
                              |
                         TBP solvent extraction
                              |
                    ┌─────────┴─────────┐
              aqueous phase   organic phase
                    | |
               aluminium   rare earths and yttrium

Fig. 1. Schematic diagram of the proposed separation procedure.

more fully below, was developed for this purpose. Although the separation procedure is primarily considered in combination with emission spectrography, it could also be combined with other quantitative techniques, *e.g.* X-ray fluorescence.

The separation procedure was based on the following 4 facts:

(*1*) Hot concentrated (*ca.* 7 N) aluminium nitrate solution is an excellent solvent for thorium tetrafluoride[1,4] and rare earth fluorides[4].

(*2*) Determinative errors are practically eliminated if yttrium is used as a carrier for trace amounts of rare earths during separation procedures and as an internal standard in their subsequent spectrographic analysis[5-8].

(*3*) Thorium is separated from the rare earths, yttrium and aluminium by passing a solution of these elements in 7–9 N nitric acid through a column of strong base anion-exchange resin[9-11]. Thorium is retained on the resin and the rare earths, yttrium and aluminium pass through unadsorbed.

(*4*) Rare earths and yttrium are very efficiently extracted by undiluted tributyl phosphate (TBP) from a 7.2 N aluminium nitrate–0.2 N nitric acid solution[12].

<center>EXPERIMENTAL</center>

Apparatus and reagents

Ion-exchange columns 22 cm long and 1.9 cm in internal diameter were used. The resin was the strongly basic Deacidite FF 7-9X, 100–200 mesh, NO$_3$-form. A column of the above dimensions could handle 12 g of ThF$_4$ · 3 H$_2$O.

Commercial grade TBP was purified as described by PEPPARD *et al.*[12].

Rare earth-free ThF$_4$ · 3 H$_2$O was prepared from Th(NO$_3$)$_4$ (anion exchange in 8 N nitric acid was used to free the thorium nitrate of rare earth impurities[13,14]) by the procedure of D'EYE AND BOOTH[15].

National Carbon S.P.–2 graphite powder and Specpure Y$_2$O$_3$.

All other reagents were of analytical grade.

Procedure

Thorium fluoride trihydrate (1 g)* was dissolved in 10 ml of warm 7 N aluminium nitrate solution; 10 mg of yttrium oxide dissolved in 10 ml of concentrated nitric acid (s.g. 1.42) was added and the resultant solution was soaked into the top of an anion-exchange column at a flow rate not exceeding 0.25 ml/min. Before the sorption step, the column was washed with 2–3 column volumes of 8 N nitric acid at a flow rate of 2 ml/min. The column was eluted with 120 ml of 8 N nitric acid at a flow rate of 1 ml/min. The effluent containing the rare earths, yttrium and aluminium was evaporated just to dryness**. The residue was dissolved in 10 ml of deionised water and transferred together with two 1–2 ml of 7 N aluminium nitrate washings to a 100-ml separating funnel.

The aqueous phase (*ca.* 7 N aluminium nitrate solution) was extracted with two 10 ml portions of undiluted TBP pre-equilibrated with 7 N aluminium nitrate. A shaking time of 3 min was employed for each extraction. After extraction the layers were allowed to settle and the TBP layer was carefully withdrawn. The combined

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* It should be borne in mind that rare earth detection limits can be increased by using a larger thorium tetrafluoride sample.
** Complete removal of nitric acid was unnecessary. 0.5 μc $^{152+154}$Eu tracer and 8 mg Y were found to be quantitatively extracted with undiluted TBP from 7 N aluminium nitrate solutions containing 0, 0.2, 1.0 and 2.0 N nitric acid respectively.

TBP extracts were scrubbed* with two 10 ml portions of 10 N ammonium nitrate solution; a shaking time of 0.5 min was employed for each scrub**. Rare earths and yttrium were stripped from the scrubbed TBP by shaking it with five 20 ml portions of deionised water; a shaking time of 1 min was employed for each extraction.

The combined aqueous extracts were carefully evaporated to dryness in the presence of 10 mg of graphite powder. The resultant residue was analysed spectrographically by the procedure described by CARTER AND DEAN[7].

After elution with 300 ml of 0.25 N nitric acid at a flow rate of 2 ml/min, the column was again ready for use.

<div align="center">RESULTS</div>

Recovery of rare earths

The recovery of known amounts of Eu, Gd, Dy, Sm and Er added to 1 g $ThF_4 \cdot 3 H_2O$ samples is shown in Table I.

<div align="center">TABLE I</div>

<div align="center">RECOVERY OF RARE EARTHS</div>

Sample no.	Rare earth added	Rare earth recovered (μg)				
		Eu	Gd	Dy	Sm	Er
1	5 μg each of	4.8	4.9	4.8	4.8	4.8
2	Eu, Gd, Dy, Sm and Er	4.9	4.9	4.9	4.9	4.9
3		5.2	5.1	5.1	5.1	5.2
4	20 μg each of	19.5	19.5	19.5	19.6	19.6
5	Eu, Gd, Dy, Sm and Er	20.1	20.0	20.0	19.9	19.9
6		19.5	19.4	19.5	19.3	19.4

A reagent blank carried through all the steps of the separation procedure showed no detectable Eu, Gd, Dy, Sm and Er, and Y. Thorium was not detected in the rare earth residues.

The recommended procedure should be equally effective for separating trace amounts of other rare earths from thorium tetrafluoride.

Behaviour of diverse elements during the separation procedure

In addition to rare earths, thorium tetrafluoride may contain alkali metals, calcium, magnesium and iron impurities[16]. Although these elements would accompany the rare earths in the anion-exchange step[9-11], they are not extracted into TBP from 7 N aluminium nitrate solution[12].

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* Rare earth detection limits would be lowered if the aluminium entrained in the TBP was not removed.
** When 20 ml of undiluted TBP loaded with 0.5 μc [152+154]Eu tracer and 8 mg Y were scrubbed with 2 × 10 ml of 10 N ammonium nitrate solution under conditions similar to those employed above, < 1% of each element was removed from the TBP.

SUMMARY

A combined anion exchange–solvent extraction procedure has been developed to facilitate the spectrographic determination of trace quantities of Eu, Gd, Dy, Sm and Er in thorium tetrafluoride.

RÉSUMÉ

Une méthode combinée, échangeur d'anions et extraction par solvant, est proposée pour faciliter le dosage spectrographique de traces d'Eu, Gd, Dy, Sm et Er dans le tétrafluorure de thorium.

ZUSAMMENFASSUNG

Für die spektrographische Bestimmung von Spuren von Eu, Gd, Dy, Sm und Er in Thorium-tetrafluorid wird eine Abtrennungsmethode beschrieben, die auf einer Kombination von Anionen-austausch und Lösungsmittelextraktion beruht.

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CHEMICAL METHODS FOR THE DETERMINATION OF THE "OXIDIZING (OR REDUCING) POWER" OF CERTAIN MATERIALS CONTAINING A MULTIVALENT ELEMENT IN SEVERAL OXIDATION STATES*

R. J. NADALIN AND W. B. BROZDA

Westinghouse Central Laboratories, Pittsburgh 35, Pennsylvania (U.S.A.)

A knowledge of the valence states of the various atoms in thermoelectric materials is necessary to the solid state chemist or physicist because these are related to the number of charge carriers. From X-ray diffraction, magnetic susceptibility, Hall Effect, thermoelectric power and conductivity observations, a measure of the number of charge carriers can be deduced. However, such physical data would be of greater value if correlated with reliable charge carrier contents obtained by an independent method, such as direct chemical determination of the amounts of a multivalent element in its various valence states.

The results of such determinations have been expressed as "oxidizing (or reducing) power" by many[1-4]. "Amount of oxidation" or "average oxidation number" were used by WARD and coworkers[5,6], "active oxygen content" by VICKERY[7], "oxidation capacity" by JONKER[8], "excess oxygen" by INGAMELLS[9], "total oxidation content of the material" by WOLD AND ARNOTT[10], and "surplus oxygen" by SACHSE[11]. In this report the generally accepted practice of reporting the "oxidizing (or reducing) power" as the weight percent of a material in some pertinent valence state (*e.g.* % Mn-(III)) will be followed, although in some cases several reactive valence states may be present.

Materials for which valence determinations are of interest are: (*1*) non-stoichiometric oxides, such as $M_{(1-x)}O$, in which x is small and is expressed as the amount of M present in the unusual valence state, (*2*) controlled valence compounds, $A_xM_{(1-x)}O_y$, in which the amount of the unusual valence state of M is equivalent to that of an alkaline earth metal (A) added as a "doping agent", (*3*) compounds, BMO_y, in which the valence state of M is all in an unusual valence state, and (*4*) compounds combining (*2*) and (*3*), $A_xB_{(1-x)}MO_y$, in which the valence states of M are regulated by the proportions of two metals of different valences (A and B). Since our work was with Types *2*, *3*, and *4* materials, methods for the determination of reasonably large "oxidizing (and reducing) powers" were required. This report is limited to the various chemical methods used or considered feasible for this purpose. These described methods are thus not suited, unless so stated, to finding the small deviations from stoichiometry in Type *1* materials, or for determining other low "oxidizing (or reducing) powers".

Since many of the oxidized or reduced ionic species of interest are unstable in solution unless strongly complexed, the useful procedures are generally limited to weight gain (or loss) of the dry sample or to volumetric methods involving solution of the sample in an excess of the reacting reagent, followed by the titration of the excess or of ions formed in the reaction. Titration methods for practically all of the oxidized or reduced species encountered are described in compilations such as KOLTHOFF AND BELCHER[12]. However, difficulties are encountered in the sample preparation and dissolution of the often refractory samples without significant loss of the "oxidizing (or reducing) power". As these methods are non-specific, all other oxidizing or reducing substances must be absent in the material analyzed. A careful blank on reagents must always be determined.

A more complicated problem is met in certain materials, exemplified by the manganese-containing perovskites, in which oxidized manganese occurs in both the manganese(III) and -(IV) states. Assuming that manganese(II) (the normal reduced state) and manganese(IV) cannot co-exist in a material, the manganese(III) and -(IV) contents may be calculated from the "oxidizing power" (in terms of the lower oxidized state) and the total manganese content by solution of two simultaneous equations. The determination by similar methods of various reduced titanium oxidation states occurring together in a material has been reported by GOTO AND TAKEYAMA[13].

A still more complex system in which two multivalent elements, iron and manganese, occur as di- and trivalent ions has been considered by WICKHAM[14]. Although the total number of equivalents in the trivalent state, the ratio of di- to trivalent ions, and the total iron and manganese contents can be found, it is not possible to obtain the concentrations of each ionic species present. VESELAGO[15] has reported chemical methods claimed to be selective for determining iron(II) and titanium(III) contents in admixture. The application of "oxidizing (or reducing) power" methods to materials which contain, in addition to the cationic multivalent element, an anionic multivalent element, such as sulfur, selenium or tellurium, has not been reported.

With the exception of the anion-forming elements only a few general analytical methods for the determination of one valence state of a multivalent element in the presence of its other valence states are known. SCOTT[16] describes quantitative procedures only for iron(II) contents of minerals, for PbO_2 in the presence of Pb_3O_4, for "available oxygen" in oxygenated compounds, such as MnO_2, BaO_2, etc., and for "available chlorine" in bleaches.

HILLEBRAND, LUNDELL, BRIGHT AND HOFFMANN[17] give an excellent discussion of the methods used for iron(II) determination. MRGUDICH AND CLARK[3] critically considered various methods for the determination of the "oxidizing power" (PbO_2 content) of red lead. Various volumetric procedures are given by ROSIN[18] for the determination of the small impurity concentration of one oxidation state in compounds of some multivalent elements, such as copper, iron, mercury, uranium and vanadium. JOHNSTON[2] has outlined many of the methods currently used by solid state chemists for the determination of the "oxidizing (and reducing) power" of solid state materials. We found generally that these chemical methods are based on five or six general methods which are listed and briefly described in the following section.

Methods for "oxidizing power" determination

(1) Dissolution of the sample by heating it in dilute sulfuric acid containing a

known amount of iron(II), and titration of the excess iron(II) by a standard oxidant solution. This standard "available oxygen" procedure[19] was used by JOHNSTON[20] on complex cobalt, copper and nickel materials. It is restricted to materials easily soluble in acids.

(*1A*) As in (*1*), but using vanadyl sulfate as the reducing agent, and then titrating the vanadate ions formed by a standard iron(II) sulfate solution. This procedure, used by WICKHAM[14], is preferable to the Ox Method *1* as in solution both the vanadyl and vanadate ions are quite air-stable.

Other variations include use of hydrogen peroxide or oxalic acid by MRGUDICH[3], arsenite ions by FOSTER[1], and manganous ions by INGAMELLS[9] as the standard reducing agent.

(*2*) Dissolution of the sample by heating in dilute hydrochloric acid containing potassium iodide, and titration of resulting iodine by a standard sodium thiosulfate solution. This standard method[21] for the determination of peroxides is also used by ROSIN[22] for the determination of oxidized ions, such as copper(II). It has more recently been used by WARD *et al.*[23,24] for "oxidizing power" determinations on a number of materials. It is restricted to acid-soluble materials.

As a variation, SACHSE[11] has reported using a sealed tube method with the same reagents to determine the "surplus oxygen" in certain non-stoichiometric oxides.

(*3*) Reaction and dissolution of sample by heating in concentrated hydrochloric acid in a distilling flask, distillation of the chlorine formed into a potassium iodide solution, and titration of the resulting iodine by a standard sodium thiosulfate solution. This standard method[19] for "available oxygen" determinations has been used extensively on solid state materials[6,25-28]. If precautions are taken to avoid iodine losses, it is an excellent method for difficultly soluble materials.

(*4*) Sealed tube reaction and dissolution of the sample at 250 to 300° by a dilute (60–80%) sulfuric acid solution containing vanadyl sulfate, and titration of the vanadate ions formed by a standard iron(II) sulfate solution. GORDON[29] has adapted the Carius-type analytical techniques for the safe dissolution of very difficultly soluble inorganic materials under moderate pressure (4–5 atm). In various modifications, it has been used for the determination of the "oxidizing power" of various materials by COSSEE[30] and JONKER AND VAN SANTEN[31]. Although time-consuming, it is applicable to samples that cannot be handled by the simpler methods. Unfortunately, samples larger than 0.2 g cannot be handled because of the difficulty in dissolving the sample.

(*5*) ENGELL[32,33] working on the non-stoichiometry of certain oxides, claims enhanced sensitivity with an electrochemical procedure in which the mixed valence material is made one of the electrodes of a cell. During application of an external potential, the electrode (sample) is partially dissolved in an acid solution giving rise to a current which is measured and related to the "oxidizing power". The sample necessarily has to be in a massive form to be used as an electrode.

(*6*) Polarographic determination of the oxidized form of a multivalent element in a solution made in such a way that the amounts of oxidized and reduced ions are not altered. The highest valence form of the multivalent element will be polarographically reduced at a lower negative voltage to give a measure of the "oxidizing power". Necessarily the solution must be free of other polarographically reducible ions at this or lower negative voltages. KUBOTA[34] has used this method for the determination of the uranium(VI) content of uranium dioxide.

Methods for "reducing power" determination

(*1*) Weight gain of the dry material when heated in air or oxygen. This is a common method for reducing power, and is widely used for a quick check on the composition of a material. However, in many cases, the weight changes are not large, causing a limitation in the obtainable accuracy. The composition of the material after weight gain must be known and definite. It has not been used here as a formal analytical procedure.

(*2*) Dissolution of sample in acid under an inert atmosphere and direct titration of the soluble reduced species by a solution of a standard oxidizing agent or addition of excess of oxidizing agent and back-titration. This is a standard method[35] for the determination of the ferrous content of minerals. Its limitations are its inapplicability to ;difficultly soluble materials and the necessity of working under an inert atmosphere.

(*2A*) Dissolution as in *2* except that the solution includes excess ferric ammonium sulfate to react with reduced species to form an equivalent amount of more stable iron(II), which is titrated by a standard oxidizing agent. This method is superior to Red Method *2*, as loss of "reducing power" during dissolution is minimized; but it is limited to readily acid-soluble samples. ROSIN[22] used this method for the assay of copper(I) salts.

Other variations of this method include use of potassium dichromate by THEODORE[36] and manganese(III) ions by INGAMELLS[9] as the standard oxidizing agent. HEY[37] has determined the iron(II) content of minerals by a iodine monochloride procedure using potassium iodate solution as the titrant.

(*3*) Reaction and dissolution of the sample by heating in a mixture of dilute sulfuric and hydrofluoric acids containing ammonium fluoride and a known amount of ammonium vanadate, followed by titration of the excess vanadate ions by a standard ferrous sulfate solution. This procedure[38] is a modification of the hydrofluoric acid dissolution method for ferrous-containing minerals discussed by HILLEBRAND *et al.*[17]. It was used for "reducing power" determination by KESTIGIAN AND WARD[39]. We have found it especially useful for titanium-containing materials.

As a variation, KESTIGIAN, DICKINSON AND WARD[40] have also titrated the reduced titanium content in the form of the fluoride complex directly with a potassium permanganate solution after complexing the excess fluoride with boric acid.

(*4*) Sealed tube reaction and dissolution of the sample by heating in a mixture of 60–80% sulfuric acid containing iron(III) sulfate, and titration of the resulting iron(II) by a standard potassium dichromate solution. This is the Mitscherlich method discussed by HILLEBRAND[17] for iron(II) determination, but modified by the addition of the iron(III) to stabilize the reducing power in the form of air-stable iron(II). Sealed tube procedures have sample size limitations and are tedious, but can be used on almost any type of material. We have used it for the "reducing power" determination of very insoluble niobium-containing materials. SMILTENS[41] has recently used this method to determine the "reducing power" of iron–cobalt oxides.

(*5*) Reaction of the sample with a non-oxidizing flux in a controlled atmosphere, and dissolution of the cooled fusion mass in a solution containing a standard oxidizing agent. MAZELSKY[42] used potassium bisulfate for a flux for the reaction of niobium- and tantalum-containing materials, and KESTIGIAN AND WARD[43] have used potassium bifluoride to react titanium-containing materials. GROVES[44] used a sodium fluoride and boric acid flux mixture to dissolve ferrous materials. Our attempts to use fusion methods have resulted in oxidation of the material to be analyzed.

(6) SEIL[45] has reacted difficultly soluble materials in a closed vessel with a mixture of sulfuric and phosphoric acids and distilled, aided by a stream of carbon dioxide, the equivalent amount of sulfur dioxide formed into a known excess of standard potassium dichromate. The unused dichromate is then titrated.

(7) ENGELL[32,33] has reported electrochemical procedures (see Ox Method 5).

(8) Controlled potential coulometry has been used by STROMATT[46] to obtain concentrations of Np(VI), Np(V) and Np(IV) in solutions of neptunium salts that have been partially reduced. This is a special method of limited applicability.

<div align="center">EXPERIMENTAL AND RESULTS</div>

General information

Of the several methods listed previously, directions are given for the five "oxidizing power" and three "reducing power" methods used here. Samples are subject to partial decomposition by air and moisture, and must be protected during storage. Samples must be ground immediately before weighing for analysis. Grinding has been done in air, but a more elaborate grinding procedure may be needed for sensitive materials. Sample size is limited by the solubility of the sample, but generally samples containing 0.10 to 0.20 g of the species to be determined are used. The procedures as given may be varied by substitution of suitable reagents, indicators, titrants, or other methods of end-point detection. For smaller amounts, weaker titrants can be used, but with more difficult end-point detection and greater blank uncertainty. In all cases a careful blank determination is necessary to correct for the effects of any oxidizing or reducing impurities. The "oxidizing (or reducing) powers" are calculated by:

$$\% \text{ M}^x = \frac{V_{tit} \cdot N_{tit} \cdot EW_M \cdot 100}{\text{wt. sample} \cdot 1000} \tag{1}$$

or, in the case of back-titration methods:

$$\% \text{ M}^x = \frac{(V_B - V_{tit}) \cdot N_{tit} \cdot EW_M \cdot 100}{\text{wt. sample} \cdot 1000} \tag{2}$$

where $\% \text{ M}^x$ = "oxidizing (or reducing) power" stated as a percentage of the variable valence metal in a pertinent oxidation state (x).

EW_M = equivalent weight of metal being determined for desired oxidation change.

V_B = ml of titrant equivalent to the standard amount of oxidizing (or reducing) agent added to the sample.

Special apparatus and reagents

For Ox Method *3* – Modified all-glass arsenic-distilling apparatus described by HILLEBRAND et al.[47] including a Liebig-type receiving vessel connected to the condenser, and a by-pass tube so that acid may be added while passing nitrogen gas through the apparatus.

For Ox Method *4* and Red Method *4* – Vycor tubes, 11″ long, 8 mm O.D., constricted at open end (wall thickness 1.5 mm and approximate sealed volume of 20 ml), special funnel to fit neck, and Carius Furnace to heat 6 tubes at a time.

Ammonium vanadate solution (0.2 N)

Dissolve 24 g in 36 N sulfuric acid. Dilute, filter residue and make up to 1 l.

Vanadyl sulfate solution (0.2 N)

Reduce the vanadium content of the 0.2 N ammonium vanadate solution to the blue tetravalent state by boiling with aqueous sulfur dioxide. Expel excess and dilute to original volume.

PROCEDURES

Oxidizing power Method 1

Transfer a weighed sample to a 250-ml Erlenmeyer flask containing 10 ml of 10% sulfuric acid and a weighed amount of ferrous ammonium sulfate in solution sufficient to give an excess of 0.1 g. A second weighed portion of the weighed ferrous salt serves as a blank. Heat slowly to dissolve the sample, dilute, add 10 ml of 85% phosphoric acid, and titrate the iron(II) contents of sample and blank solutions with standard 0.1 N potassium dichromate solution using 1% diphenylamine indicator in 36 N sulfuric acid. Calculate the "oxidizing power" using eqn. (2).

Oxidizing power Method 1A

As in 1 except that the weighed sample is dissolved in 50 ml of vanadyl sulfate solution and 10 ml of 18 N sulfuric acid, and the vanadate ions formed (equivalent to the "oxidizing power") are titrated by a standard 0.1 N ferrous ammonium sulfate solution using phosphoric acid and diphenylamine indicator.

Oxidizing power Method 2

Transfer a weighed sample into a dry beaker, and add 100 ml of dilute (2.4 N) hydrochloric acid containing 6 g of potassium iodide. Titrate the iodine formed by a standard 0.1 N sodium thiosulfate solution as the sample is dissolved by gentle heating and grinding with the stirring rod. Starch (a 1% solution) added at the beginning is used as the indicator.

Oxidizing power Method 3

Transfer a weighed sample into a dry distilling flask, and fill the receiving vessel with 100 ml of distilled water containing 6 g of potassium iodide. Purge the closed apparatus with a slow stream of nitrogen gas, and add 20 ml of 12 N hydrochloric acid through the thistle tube. Heat the reaction flask so that the sample goes into solution and most of the resulting chlorine gas has passed into and is absorbed by the potassium iodide solution until the liquid has almost evaporated. Continue a stream of nitrogen to carry over the last traces of chlorine, and finally titrate the iodine content of the diluted absorbate with standard 0.1 N sodium thiosulfate solution using starch indicator.

Oxidizing power Method 4

Transfer up to 0.2 g of a finely ground sample into a dry Vycor sealing tube by means of a special funnel. Add 6 ml of vanadyl sulfate solution and 6 ml of 36 N sulfuric acid in such a way that all of the sample is immersed. Prepare a second tube omitting the sample for a blank determination. Slowly evacuate the sealing tube (to about 10 mm Hg) to remove dissolved gases and seal the Vycor tube with an oxy-hydrogen torch while the vacuum is on. Place the sealed tube in the cold Carius fur-

nace and heat overnight or longer at a maximum temperature of 200–250°. After removal of the cold tubes from the furnace, examine the reacted mixture in the tube with a low power microscope to ascertain that all of the original material has reacted. Although the reaction products also have a limited solubility in the sulfuric acid, usually there is a marked change in color and form of the insoluble material as well as color changes in the liquid in the tube. If the sample remains partially unreacted, the tube is reheated for periods up to 350° until the sample is completely reacted. Open the cooled tube by cutting a ring around the upper end, and transfer the contents to a beaker using a Teflon policeman. Add 10 ml of 85% phosphoric acid and titrate the vanadate ions formed in the sample and blank solutions by a standard 0.1 N ferrous ammonium sulfate solution using diphenylamine indicator.

Reducing power Method 2A

Prepare 75 ml of an oxygen-free solution containing 50 ml of 0.1 N ferric ammonium sulfate, 10 ml of 12 N hydrochloric acid, and 10 ml of 85% phosphoric acid in a 250-ml Erlenmeyer flask by outgassing it with a lump of solid carbon dioxide. Transfer a weighed sample into this previously prepared solution, and immediately titrate the resulting iron(II) with standard 0.1 N potassium dichromate solution using diphenylamine indicator.

Reducing power Method 3

Transfer a weighed sample into a dry platinum dish, and add exactly 10 ml of 0.2 N ammonium vanadate solution, 20 ml of 48% hydrofluoric acid, 5 ml of 18 N sulfuric acid, and about 5 g of solid ammonium fluoride. Slowly heat until the sample has reacted and the volume has been reduced to approximately half. Additional dissolution reagents may be added to achieve complete reaction, which usually takes about 1 h. Transfer and dilute the reacted sample mixture into a 400-ml beaker where any unreacted sample will be clearly visible. If completely reacted, add additional sulfuric acid and 10 ml of 85% phosphoric acid, and titrate the excess vanadate ions by a standard 0.1 N ferrous ammonium sulfate solution using diphenylamine indicator. Obtain a reagent blank to fix the volume of titrant equivalent to 10 ml of the ammonium vanadate solution, and calculate the "reducing power" by eqn. (2).

Reducing power Method 4

Proceed according to Ox Method 4 to react up to 0.2 g of the finely ground sample and a reagent blank in a sealed Vycor tube, but using 12 ml of a 67% sulfuric acid solution containing 0.8 g of solid ferric sulfate nonahydrate. After reaction and opening, add additional sulfuric acid and 10 ml of 85% phosphoric acid to the resulting solutions, and titrate the iron(II) contents of the sample and blank solutions by a standard 0.1 N potassium dichromate solution using diphenylamine indicator.

Analysis of standard samples

Standard samples of the experimental materials of interest were difficult to prepare and keep. Consequently, manganese dioxide (Baker and Adamson, minimum assay 99.0%), in which the total manganese content (63.19%) is almost completely in the tetravalent state, was chosen as the standard "oxidizing power" substance. When properly dried and stored, this stable, acid-soluble substance is ideal for testing

"oxidizing power" methods to be used on acid-soluble materials — as were most of the materials analyzed. Three standard samples of varying solubilities were used to test the various "reducing power" methods. These substances, cuprous chloride (64.28% Cu(I)) prepared according to WALTON[48], titanium sesquioxide (66.62% Ti(III)), and niobium dioxide (74.38% Nb(IV)) prepared by reducing niobium pentoxide in hydrogen, were carefully dried and had purities of at least 99.5%.

It was assumed that these materials were pure, uniform, and had the stated compositions, and they were repetitively analyzed 5 or more times using 0.1–0.2 g samples to obtain estimates of the accuracy and precision of the seven methods. The other described method, Ox Method 4, was not evaluated because it was only used once. These data are given in Table I.

TABLE I

ANALYSIS OF STANDARD SAMPLES BY VARIOUS METHODS

Method	Standard used	M^x theory (%)	Average M^x found (%)	σ of single det. (%)
Ox 1	MnO_2	63.19	63.19	0.18
Ox 1A	MnO_2	63.19	63.21	0.18
Ox 2	MnO_2	63.19	63.19	0.18
Ox 3	MnO_2	63.19	62.97	0.28
Red 2A	CuCl	64.28	64.03	0.15
Red 3	Ti_2O_3	66.62	66.53	0.37
Red 4	NbO_2	74.38	73.30	1.29

Determination of contents of multiple oxidized species of an element

To estimate the precision obtainable in this case, three samples of $Ca_xLa_{(1-x)}MnO_3$, prepared to contain respectively 25, 50 and 75% of the total manganese in the tetravalent state and none in the bivalent state, were repetitively analyzed for their "oxidizing power" contents by the Ox 1A Method and for total manganese contents by the bismuthate method. These results are listed in Table II.

TABLE II

ANALYSIS OF $Ca_xLa_{(1-x)}MnO_3$ FOR Mn(III) AND Mn(IV)

	$x = 0.75$	$x = 0.50$	$x = 0.25$
Average total Mn found (%)	32.24 ± 0.10	28.45 ± 0.08	25.09 ± 0.04
Theory (%)	32.76	28.55	25.30
Average "oxidizing power" found (% Mn(III))	55.12	41.37	30.63
Theory (% Mn(III))	56.42	42.69	31.36
Calculated (% Mn(III))	9.36	15.53	19.76
σ of single det. (% Mn(III))	0.38	0.28	0.32
σ (relative %) of average Mn(III) found	4.1	1.8	1.6
Theory [$(1 - x)$ total Mn found (%)]	8.06	14.23	18.82
Calculated (% Mn(IV))	22.88	12.92	5.44
σ of single det. (% Mn(IV))	0.32	0.22	0.31
σ (relative %) of average Mn(IV) found	1.4	1.7	5.7
Theory [(x) total Mn found (%)]	24.18	14.23	6.27

Analysis of laboratory samples

A variety of materials were analyzed for "oxidizing power" and "reducing power" contents using these outlined procedures. These materials and the methods used are listed in Table III. In some cases total multivalent contents were also determined on separate samples.

<div align="center">TABLE III</div>

<div align="center">LIST OF SAMPLES ANALYZED</div>

For "oxidizing power"		For "reducing power"	
Material	Method	Material	Method
$Ni_xCo_{(1-x)}O$, $x = 0.25-0.75$	Ox 1	Reduced $SrTiO_3$	Red 3
$La_xCa_{(1-x)}MnO_3$, $x = 0-1.0$	Ox 1, $1A$	Reduced $BaTiO_3$	Red 3
$La_{0.95}Sr_{0.c5}CrO_3$	Ox 4	$Na_xCa_{(1-x)}NbO_3$, $x = 0-0.90$	Red 4
$BaNiO_{2.5}$, $SrNiO_{2.5}$	Ox 3	La_xTiO_3, $x = 0.75-1.0$	Red 3
$LaNiO_3$	Ox 2	$Ba_xLa_{(1-x)}TiO_3$, $x = 0.23-0.98$	Red 3
$BaFeO_x$, $SrFeO_3$, $x = 2.5-3.0$	Ox 3		
$BaCoO_{2.5}$, $SrCoO_3$	Ox 2		
$La_xSr_{(1-x)}CoO_3$, $x = 0.85-1.0$	Ox 3		

<div align="center">DISCUSSION</div>

Acceptable results were obtained by the eight outlined methods on the standard and experimental samples, and no attempt was made to evaluate the other potentially useful procedures. These methods are quite general and the choice of method for a particular sample depends on its composition and solubility. Obviously the simplest method that accomplishes the determination with acceptable accuracy is preferable. The more readily soluble a material is, the more easily and accurately can the analysis be made. For materials easily soluble in acids, Ox Methods *1* and *1A*, and Red Method *2A* may be used; for less soluble materials, Ox Methods *2* and *3*, and Red Method *3*; and for quite insoluble materials, the sealed tube methods (Ox Method *4* and Red Method *4*), although tedious, are particularly suited.

When choosing the proper standard oxidizing or reducing agent to be added, the stability of both oxidized and reduced forms and the ease of subsequent determination must be considered. The redox potentials are also important, but the ionic species being determined are usually strong oxidizing or reducing agents. In addition, many of the redox potentials of the pertinent species are difficult to obtain, so that predictions of probable reactions are often difficult. In some cases, it may be possible to choose oxidizing or reducing agents, as did VESELAGO[15], that react selectively with one of several oxidized or reduced species present. We found, however, that in the presence of their oxidized forms, known amounts of iron(II) and titanium(III) could not be determined by his selective oxidation methods.

The stability of the reagents, which is experimentally reflected in the magnitude of the blank, is very important. We found that iron(II), vanadyl and iodide ions are satisfactory reducing agents for the determining of "oxidizing power". The air-stable vanadyl–vanadate system is probably the best one for general use. With the iodine–iodide system, iodine is sometimes lost if formed too rapidly, causing low results. For the determination of "reducing power", the iodine–iodide system is not conveniently

used, but both iron(III) and vanadate ions can be used as the standard oxidizing agent. We have found that the vanadate is the preferred method for open vessel reactions, but in closed tubes only iron(III) gives a suitably low blank.

Blank values for all of the "oxidizing (and reducing) power" methods are suitably low, except for protracted dissolution periods. A definite blank is obtained in Ox Method *1*, due to partial air oxidation of the iron(II). For the sealed tube method (Red Method *4*) attempts to use oxidizing agents other than ferric sulfate (such as potassium dichromate, ceric sulfate, or manganese dioxide) gave unsuitably high blanks. As the solvent in the sealed tube experiments, only sulfuric acid solutions (60 or more weight percent) were found feasible. Other acids had either too high vapor pressures or gave too high blank values.

Results obtained by these "oxidizing (and reducing) power" methods (given in Table I) on the "standard" samples indicate that the accuracy and precision of the simpler methods is better than those of the more complicated ones. Nevertheless, the results obtained by the most difficult method (Red Method *4*), although somewhat lower than theory and less precise, show that this method gives reasonable estimates of the "reducing power" of very difficultly soluble materials. Since the experimental samples are probably less homogeneous, somewhat less accuracy and precision are to be expected when analyzing samples.

It is felt that part of the estimated standard deviation (see Table II) found for the determination of the manganese(III) and -(IV) contents of these materials containing several oxidized forms of manganese, reflects inhomogeneity of the samples. This is also shown by the generally poorer than usual agreement in the duplicates for the total manganese results. Because simultaneous equations are involved in the calculations, the accuracy for the determination of small amounts ($<5\%$) of one species is poor.

Most of the "oxidizing (and reducing) power" results (not given) for the materials in Table III are lower than the expected contents of the oxidized or reduced multivalent element. The total multivalent contents, when determined, however, were generally found to be quite close to the theoretical compositional contents. Previous X-ray diffraction and spectrographic examinations had proved that these samples were pure, single-phase materials. Minor impurities, which seldom affect the oxidizing or reducing properties, were those derived from the containers in which the materials had been prepared, heated or ground. Possible reasons for these observed negative deviations are the possible loss of oxidized or reduced ion content during handling or storage before analysis; or, more probably, because of preparation problems in making truly stoichiometric materials of the stated composition. Small deviations in the oxygen content of a material would be reflected in much larger, usually negative, deviations in the observed "oxidizing (or reducing) power".

The range of these methods is rather large; but, unfortunately, some of the materials to be analyzed have "oxidizing (or reducing) powers" equivalent to very small concentrations of a "doping" agent. As large samples cannot be handled, blank values become increasingly greater as the "oxidizing (or reducing) power" content decreases, and the accuracy of the determination is very poor. For these low ($<2\%$) content samples, better volumetric or other determination methods for the oxidized or reduced ions should be applied to the solution obtained by the usual methods of dissolution and stabilization of the "oxidizing (or reducing) power".

Some of the standard materials were prepared by Dr. W. D. JOHNSTON and Dr. R. MAZELSKY. The statistical calculations were performed by Dr. D. H. SHAFFER, and Dr. F. P. BYRNE helped to prepare this manuscript.

SUMMARY

General chemical methods for determining the "oxidizing (or reducing) power" of certain materials containing a multivalent element in several oxidation states have been considered. These determinations are important as representing the charge carrier concentration.

The general methods available are listed and the criteria for selecting the best method for a particular material are considered. Experimental procedures and estimates of the accuracy and precision of eight methods for the determination of the "oxidizing power" and the "reducing power" are given. The application of these methods to thermoelectric materials is also described.

RÉSUMÉ

Quelques méthodes chimiques sont décrites pour déterminer le pouvoir oxydant (ou réducteur) de certaines substances renfermant un élément multivalent.

ZUSAMMENFASSUNG

Beschreibung und kritische Betrachtung bekannter Methoden zur Bestimmung der Oxydations-bzw. Reduktionswirkung von Verbindungen, die ein mehrwertiges Element enthalten.

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Short Communications

Determination of titanium and zirconium and their separation from each other with chelidonic acid

Chelidamic acid (I) was previously proposed as a specific reagent for the spectrophotometric determination of iron[1]. In order to assess the difference in reactivity when the centre of coordination was changed from nitrogen to oxygen, chelidonic acid (II), which resembles chelidamic acid closely, was prepared and its analytical characteristics studied. SIDGWICK[2] considers that both oxygen and nitrogen are equally effective as centres of coordination in the formation of chelates, but that titanium(IV), zirconium(IV), niobium(V) and tantalum(V) favour oxygen more.
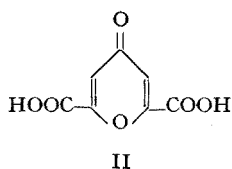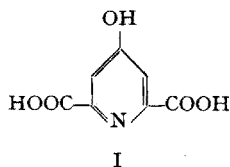
Unlike chelidamic acid, chelidonic acid was found to react with titanium, zirconium, thorium and rare earths, and to be suitable for the separation and gravimetric determination of titanium and zirconium. Zirconium forms a complex of composition $ZrO(C_7H_2O_6) \cdot 2H_2O$, but the titanium complex is of indefinite composition.

The zirconium and titanium complexes are quantitatively precipitated from solutions of pH 1.0–6.5 and 1.5–4.0 respectively; hydrogen peroxide, which forms a stable

peroxy compound with titanium, ensures their separation from each other.

Many organic reagents have been described for the gravimetric determination of zirconium but few, e.g. mandelic acid and its derivatives[3-5] and N-benzoyl-N-phenyl-hydroxylamine[6], form precipitates which can be weighed directly after drying at a suitable temperature.

Apparatus and reagents

Apparatus. A Chevenard thermobalance, type 3, No. 107 of A.D.A.M.E.L. (Paris) and a Cambridge pH indicator.

Chelidonic acid was prepared by the method of BLATT[7]. A 1% solution of the reagent was prepared by dissolving 1 g of the reagent in water containing 1 ml of dilute ammonia solution and diluting to 100 ml.

All other chemicals were of analytical reagent grade.

Zirconium oxychloride

A solution of zirconium oxychloride in dilute hydrochloric acid was prepared; the zirconium content was determined as oxide in an aliquot.

Titanium solution

3.68 g of potassium titanyl oxalate were heated in a Kjeldahl flask with 8 g of ammonium sulphate and 100 ml of concentrated sulphuric acid gradually to boiling. The mixture was allowed to cool, poured into 350 ml of water and diluted to 500 ml. The titanium content of an aliquot was determined as TiO_2.

Procedures

For the determination of zirconium, dilute the solution containing about 4–30 mg of ZrO_2 to 150 ml and adjust to pH 1.0–6.5 by addition of dilute hydrochloric acid or ammonia solution. Warm the solution and add excess of reagent solution (10 ml for each 5 mg of metal present). Heat to boiling, allow the precipitate to settle, filter on a weighed glass or Gooch crucible and wash well with hot water. Dry at 100–110° and weigh as $ZrO(C_7H_2O_6) \cdot H_2O$, or ignite and weigh as the oxide.

For the determination of titanium, proceed similarly but adjust the solution to pH 1.5–4.0 and ignite the precipitate.

Results and discussion

When the zirconium complex was precipitated as described above and dried in air, determination of its zirconium content by ignition to the oxide after decomposition of the precipitate and precipitation as hydroxide, indicated that the composition of the precipitate was $ZrO(C_7H_2O_6) \cdot 2H_2O$ (% Zr calculated 28.04; % Zr found 28.06, 28.03). The titanium complex proved to be of indefinite composition.

Thermolysis curves indicated that the air-dried zirconium complex starts to lose one molecule of water at about 70°; the second molecule of water is lost at about 120° and conversion to zirconium oxide is complete at 530°. The temperature limits for the monohydrate are thus rather narrow, but accurate results can readily be obtained by weighing the monohydrate provided that the drying time is not longer than 2 h. On the other hand, the thermolysis curve for the titanium complex indicated that the complex loses water gradually with rise in temperature.

A study of the optimum pH for precipitation over the range 0.5–7 showed that precipitation of zirconium is complete at pH 1.0–6.5 while that of titanium is complete at pH 1.5–4.0 .

Effect of diverse ions. No interference in the determinations of zirconium and titanium was caused by even 10-fold excesses of the following ions: Cu^{2+}, Cd^{2+}, Hg^{2+}, As^{3+}, Sb^{3+}, Sn^{4+}, Bi^{3+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Mg^{2+}, UO_2^{2+}, VO_3^-, MoO_4^{2-} and WO_4^{2-}. Zirconium could also be determined in presence of Pb^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}. Thorium, cerium and rare earths were precipitated under the pH conditions used and interfered seriously. Oxalic, citric and tartaric acids and EDTA held zirconium and titanium in solution, owing to the formation of stable complexes.

Separation and determination of zirconium and titanium

For the separation of zirconium from titanium and their subsequent determination, sufficient hydrogen peroxide (20 vol.) was added to the mixed solution of the two elements. The zirconium was then precipitated by the addition of an excess of the reagent solution to a warm solution of the mixture maintained at a pH of about 1.0. The precipitate was filtered, washed and ignited to the oxide. The filtrate and washings were then made alkaline and evaporated to a small volume to remove hydrogen peroxide completely. The concentrate was diluted to about 150 ml and the pH of the solution was adjusted to 1.5–4.0. The titanium was then precipitated as described above and determined after ignition to the oxide. The results are given in Table I.

TABLE I

SEPARATION OF Zr FROM Ti

ZrO_2 taken (mg)	TiO_2 taken (mg)	ZrO_2 found (mg)	TiO_2 found (mg)
3.6	10.2	3.6	10.2
10.8	10.2	10.8	10.2
21.6	10.2	21.5	10.1
28.8	5.1	28.7	5.1
7.2	15.3	7.2	15.3
3.6	15.3	3.5	15.4
7.2	20.4	7.2	20.4

University College of Science,
Jadavpur University, Calcutta-32 (India)

A. K. MAJUMDAR
S. P. BAG

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Titrimetric microdetermination of copper and zinc with EDTA

Murexide is said to be an unsuitable indicator for the titration of zinc with EDTA. WELCHER[1] states that the zinc–murexide complex is of little use analytically; WEST AND SYKES[2] imply that murexide cannot be used as an indicator for the titration of zinc ions in ammoniacal solution because the zinc–murexide complex is destroyed by ammonia. The latter fact was confirmed but it was found that zinc and copper could be simultaneously and quantitatively titrated in ammoniacal solution using murexide if the zinc content did not exceed that of the copper. This is utilised in a method for the microdetermination of zinc and copper. The zinc is determined separately in presence of xylenol orange indicator[3] after the copper has been complexed with thiosulphate.

Procedure

Preparation of solution. Weigh 10–15 mg of the zinc–copper alloy accurately on a micro balance, transfer to a beaker and dissolve in minimum amount of 1 : 1 nitric acid (A.R.). Warm the solution to dissolve the alloy and slowly evaporate to a low volume. When a moist solid remains, cool, add 2.2 ml of 1 N sulphuric acid and warm to dissolve the residue. Cool and dilute to volume in a 15-ml graduated flask.

Zinc determination. Transfer an aliquot of the prepared solution (approximately equivalent to 2 mg) to a 50-ml conical flask and add, in the order given, 3 ml of water, 0.3 g of hexamine and several crystals of sodium thiosulphate until the initial green colour produced disappears and the solution remains colourless; then add two crystals in excess followed by 3–4 drops of aqueous 0.1% xylenol orange indicator and titrate the red zinc–xylenol orange complex to a clear yellow with 0.004 M EDTA solution. Prepare the EDTA solution by dilution of a stock 0.02 M solution of EDTA (disodium salt). Store these solutions in polythene bottles and standardise against pure zinc.

Copper and zinc determination. Transfer an aliquot of the prepared solution, approximately equivalent to 2 mg, to a 50-ml conical flask, carefully add 1 N ammonia solution until a royal blue colour is obtained and then add three drops in excess; if the copper concentration is so small that the blue colour is not visible, add a minute piece of litmus paper and ammonia until it turns blue, then three drops in excess (avoid a large excess). Adjust the volume to approximately 10 ml, add 20–30 mg of murexide indicator (0.2 g ground with 100 g anhydrous sodium sulphate), 2 ml of ethyl alcohol (A.R.), and titrate immediately with 0.004 M EDTA solution. The colour change at the end-point for copper alloys which are low in zinc is from greenish yellow to lilac; for brasses a pink intermediate colour appears and the end-point is taken as the point when the most intense magenta colour is obtained.

Calculation of results

$$\% \text{ Zn} = \frac{\text{Zn titre} \times \text{molarity} \times 0.06538 \times 10^5}{\text{Weight of sample used in titration in mg}}$$

$$\% \text{ Cu} = \frac{(\text{Cu} + \text{Zn titre} - \text{Zn titre}) \times \text{molarity} \times 0.06354 \times 10^5}{\text{Weight of sample used in titration in mg}}$$

Results

The metal contents of different volumes of solutions of known concentration were determined for copper and zinc. Table I shows the results obtained when the solutions contained copper and zinc in the percentages normally found in 'cap copper', the analysis of which was of particular interest.

TABLE I

DETERMINATION OF ZINC AND COPPER

Copper found (μg)	Copper present (μg)	Zinc found (μg)	Zinc present (μg)
—[a]	1000	49.7, 51.0	50.2
—[a]	2000	99.9, 102.0	100.4
—[a]	5000	251.1, 253.7	251.0
943, 953	953	—[a]	50
1911, 1899	1906	—[a]	100

[a] Not determined

TABLE II

INFLUENCE OF THE ZINC-COPPER RATIO ON THE DETERMINATION OF ZINC

Ratio Zn : Cu	Cu present (μg)	Zn present (μg)	Zn found (μg)
1 : 10	500	51	50.8, 49.5
1 : 2	100	51	51.3, 50.0
1 : 1	100	102.1	102.4, 99.7, 101.0
2 : 1	50	102.1	end-point unsatisfactory

Since the yellow zinc–murexide complex is destroyed by the addition of ammonia[2], zinc alone cannot be titrated in ammoniacal solution using this indicator, but zinc and copper ions when present in the same solution can be titrated up to a ratio of 1 : 1. If the amount of zinc appreciably exceeds that of copper then the end-point is not satisfactory (Table II).

In the titration of 5% to 10% zinc/copper alloys the colour change at the end-point was very sharp from greenish yellow to lilac. As the relative zinc concentration increased to 40–50%, the colour change was less sharp and became similar to that in the titration of calcium with EDTA using murexide as indicator. Satisfactory results were obtained by titrating to the most intense magenta colour. The addition of large amounts of indicator mixture made observation of the end-point difficult. Satisfactory results were obtained (Table III).

The following ions interfere in the titration of zinc using xylenol orange as indicator[2]: Al, Fe(III), Fe(II), Bi, Th, Sc, Pb, La, Cd, Zn, Hg(II). Iron(III) 'blocks' the indicator, but interference by traces of iron(III) can be eliminated by reduction with

TABLE III

RESULTS OF ANALYSIS OF CAP COPPER AND BRASS SAMPLES

Zinc %	Copper %	Total %	Weight of sample used for the individual determination in mg
Cap copper			
3.03	96.54	99.57	2.110
3.27	96.74	100.01	2.527
3.18	96.48	99.66	2.760
3.34	96.90	100.24	2.148
3.42	96.47	99.89	2.113
3.58	96.50	100.08	2.096
3.75	96.40	99.15	2.340
3.15	96.60	99.75	1.965
3.29	96.56	99.85	2.003
3.34	96.88	100.22	2.003
3.27	96.81	100.08	3.004
3.33	96.37	99.70	2.003
Brass			
37.63	61.58	99.21	2.238
33.73	65.20	98.93	2.167
40.94	57.40	98.34	1.010
29.6	70.7	100.3	3.423

ascorbic acid[4]. In this case a few mg of ascorbic acid was added to the aliquot before the addition of hexamine.

National Coal Board, Scientific Department,   A. A. ASHTON*
North Western Divisional Laboratory,
Manchester (Great Britain)

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* Present address: Science Department, St. Helens Technical College, Lancashire (Great Britain).

Some theoretical considerations in analytical chemistry
Part VIII. Rigorous calculation of the hydrogen ion concentration of acids and bases[1].

CLAEYS[2] has recently drawn attention to the need for a general formula or equation (*a*) for the calculation of the hydrogen ion concentration of a moderately strong acid, and (*b*) embracing solvent interaction. Requirement (*a*) at concentrations remote from solvent interaction is met by the classical equation[3], and requirement (*b*) is accessible by standard methods. Solvent interaction was not explicitly treated[3], because the need is not analytically frequent. The equation of CLAEYS[2] is a dimensionally homogeneous quadratic, whereas correction for solvent ionisation should yield a cubic, and full correction for interaction between two simultaneous equilibria of this type should yield a quartic. The equation at first sight appears potentially quartic, but closer inspection will show that it is in fact an unresolvable equation of infinite order.

The two equilibria are:

$$HA \rightleftharpoons H^+ + A^- \quad : \quad H^+ + OH^- \rightleftharpoons H_2O \tag{1a)(1b}$$
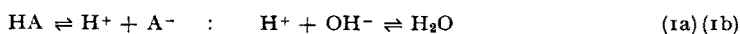
$$K_a = \frac{[H^+][A^-]}{[HA]} \quad : \quad K_w = [H^+][OH^-] \tag{2a)(2b}$$

The ion balance equation (3) is:

Total hydrogen ion concentration $[H^+]$ = hydrogen ion produced by acid (h_a) + hydrogen ion produced by solvent (h_w) (3)

From (1b) each hydrogen ion produced by the solvent is accompanied by one hydroxyl ion. The solvent is the sole source of hydroxyl ion, so from (2b)

$$h_w = [OH^-] = \frac{K_w}{[H^+]} \tag{4}$$

From (1a) each hydrogen ion produced by the acid is accompanied by an A^- ion, and from (3) and (4):

$$[A^-] = h_a = [H^+] - h_w = [H^+] - \frac{K_w}{[H^+]} \tag{5}$$

The concentration of unionised acid HA is the total initial acid concentration c_a (= $[HA] + [A^-]$) less the amount that has ionised,

$$[HA] = c_a - [A^-] = c_a - [H^+] + \frac{K_w}{[H^+]} \tag{6}$$

Substitution of these values in (2a) and (3) gives

$$[H^+] = \frac{c_a - [H^+] + \dfrac{K_w}{[H^+]}}{[H^+] - \dfrac{K_w}{[H^+]}} K_a + \frac{K_w}{[H^+]} \tag{7}$$

This is a quartic which simplifies to

$$[H^+]^4 + K_a[H^+]^3 - (c_a K_a + 2K_w)\,[H^+]^2 - K_a K_w[H^+] + K_w^2 = 0 \qquad (8)$$

Applying the condition that solvent interaction is negligible, *i.e.*, that $[H^+] > 10^{-5}\ M$, (8) resolves into the classical equation (9)

$$[H^+]^2 + K_a[H^+] - c_a K_a = 0 \qquad (9)$$

To yield meaningful solutions in the region where its application is necessary, (8) must be supplied with accurate values of K_w. Equation (8) is dimensionally homogeneous and is linear in both c_a and K_a. Ready solution is therefore accessible by the inversion device[4], and the more useful solution for c_a in the dimensionally minimal form suitable for rapid manual or computer operation is given by (10)

$$c_a = \frac{[H^+]^2}{K_a} + [H^+] - \frac{2K_w}{K_a} - \frac{K_w}{[H^+]} + \frac{K_w^2}{K_a[H^+]^2} \qquad (10)$$

A few supplied values of $[H^+]$ followed by interpolation, or defined-precision computer automatic-approximation[5], will give the required solution. The arrangement for solution in terms of K_a for fixed values of c_a is:

$$K_a = \frac{[H^+]^4 - 2K_w[H^+]^2 + K_w^2}{c_a[H^+]^2 - [H^+]^3 + K_w[H^+]} \qquad (11)$$

For a weak base of ionisation constant K_b and total concentration c_b, argument on similar lines gives an equation analogous to (8) in terms of $[OH^-]$. Conversion to $[H^+]$ by (2b) gives the equation for the hydrogen ion concentration of any base as

$$[H^+]^4 - K_b[H^+]^3 - (c_b K_b + 2K_w)[H^+]^2 + K_b K_w[H^+] + K_w^2 = 0 \qquad (12)$$

which can be rearranged as linear equations in c_b or K_b as before.

Under the exceptional circumstances requiring the use of eqns. (8) or (12), activity coefficients in pure solution are virtually unity, but in the presence of significant amounts of other electrolytes, activities must be substituted for concentrations.

Washington Singer Laboratories,   E. BISHOP
The University, Exeter, Devon (Great Britain)

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