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THE SEPARATION AND DETERMINATION OF SCANDIUM

Spectrophotometric Method Using Alizarin Red S

A. R. Eberle and M. W. Lerner

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C. J. Rodden, Area Manager

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ABSTRACT

A colorimetric method for the determination of scandium has been developed. The scandium alizarin sulfonate lake is used as the color complex in an ammonium acetate buffer medium. The color reaction conforms to Beer's Law in the concentration range of 10 to 120 γ of scandium oxide per 100 ml. Scandium is isolated stepwise from all interferences by (1) a cupferron-chloroform extraction; (2) an iodate precipitation in nitric acid; (3) a tributyl phosphate extraction in a hydrochloric acid system; (4) an ammonium tartrate precipitation; (5) a tributyl phosphate extraction in a hydrochloric acid system. Extraction data for scandium in hydrochloric acid-tributyl phosphate systems is presented. Results are reported on the recovery of scandium in the presence of the major metal ions and of the analyses of some waste residues, process liquors and minerals.

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INTRODUCTION

A reliable method for the determination of scandium in uranium feed materials, waste products, ores and minerals was required in connection with the recovery of scandium from these materials.

Existing qualitative tests for scandium were reviewed for possible quantitative development. The known color and fluorescence reactions of scandium have limited applicability and are not specific. Numerous color reactions of scandium have been reported[1-5, 8, 12, 13]. Some of these reactions are applicable only for spot-test and microscopic techniques and are unsuitable for colorimetric determinations because of the formation of insoluble products and numerous interferences.

Miller[10] separated scandium from iron, titanium, zirconium, and vanadium by a chloroform extraction of the cupferrates in mineral acid solution. Lundell and Hoffman[9] have shown that the other elements which are completely removed by this extraction are hafnium, gallium, tin, molybdenum, antimony and bismuth.

Fischer and Bock[6] separated scandium as the insoluble ammonium scandium tartrate in a hot ammoniacal medium. They found, however, that it was difficult to effect a quantitative separation from thorium, iron, zirconium, and manganese.

Fischer and co-workers[7] found that small quantities of scandium were carried when yttrium was precipitated as ammonium yttrium tartrate from a hot ammoniacal medium. They then separated scandium from yttrium by extraction with ether from a hydrochloric acid solution containing a high concentration of ammonium thiocyanate.

Peppard and co-workers[11] showed that scandium could be separated completely from the rare earths, without loss of scandium, by extraction from a hydrochloric acid system with tributyl phosphate.

Singly, none of these methods will isolate scandium in a sufficiently pure state to permit a color development with existing organic reagents without interference from other metal ions. However, by combining these separation schemes, a procedure has been devised by the authors whereby scandium is isolated sufficiently pure to permit a spectrophotometric determination by color development with alizarin red S.

The method developed involves a cupferron-chloroform extraction to remove many metals, including zirconium, from a sulfuric or hydrochloric acid solution of the sample. After conversion to a nitric acid system, thorium is removed by coprecipitation with mercury as the insoluble iodate. A tributyl phosphate extraction of the scandium then follows to remove the bulk of all of the remaining elements with the exception of uranium. The scandium is separated from the uranium by means of a series of tartrate precipitations with yttrium as the carrier. Separation of the scandium from the yttrium is then accomplished by extraction from a hydrochloric acid system with tributyl phosphate. The scandium is removed from the tributyl phosphate and the color developed with alizarin red S in a buffered medium. For materials which contain no zirconium and thorium, the method is considerably simplified by omission of the steps used for their removal.

The distribution of scandium between tributyl phosphate and hydrochloric acid was investigated for low and high concentrations of the acid, extending the existing data[11] . The recovery of scandium in an extraction, washing, and stripping procedure was studied. The efficiency of yttrium as a carrier for scandium was studied for low concentrations of scandium in pure solution and in the presence of many common ions.

APPARATUS AND REAGENTS

Spectrophotometer. Absorbancy measurements were made with a Beckman spectrophotometer, Model DU, using 5.00-cm. matched Corex cells.

Filtration Apparatus. An 85-ml. sintered-glass Buchner funnel of medium porosity and a Fisher filtrator were used for all filtrations.

Standard Scandium Solution. Dissolve 50 mg. of scandium oxide in 25 ml. of concentrated hydrochloric acid and dilute to 500 ml. Dilute 10 ml. of the stock solution to a volume of 100 ml. to obtain a standard solution of 10 γ scandium oxide per milliliter.

Yttrium Chloride Solution. Dissolve 1.0 g. of yttrium oxide in 10 ml. of concentrated hydrochloric acid and dilute to 200 ml. with water.

Alizarin Red S Solution. Prepare a 0.1% solution by dissolving 0.250 g. of alizarin red S in 250 ml. of water.

Ammonium Tartrate Solution. Prepare a 40% solution by dissolving 100 g. of reagent-grade ammonium tartrate in 200 ml. of 10% ammonium hydroxide and dilute up to 250 ml. For washing purposes dilute one part of this solution with four parts of water.

Ammonium Acetate Buffer. Dissolve 100 g. of reagent-grade ammonium acetate in 300 ml. of water. Adjust the solution to a pH of 3.5 with concentrated hydrochloric acid and dilute to 500 ml.

Mercurous Nitrate Solution. Dissolve 5 g. of reagent-grade mercurous nitrate monohydrate in 200 ml. of 20% nitric acid.

Potassium Iodate Solution. Saturate 500 ml. of 10% nitric acid with reagent-grade potassium iodate.

Hydrogen Peroxide. 30% analytical reagent.

Cupferron. Prepare a 6% aqueous solution from reagent-grade material.

Tributyl Phosphate.

Diethyl Ether. Analytical reagent.

EXPERIMENTAL

Extraction of Scandium from Hydrochloric Acid with Tributyl Phosphate. Peppard and co-workers[11] have reported distribution data for scandium and the rare earths in tributyl phosphate-hydrochloric acid systems. Their data is reproduced in Table I.

TABLE I. EXTRACTION OF SCANDIUM, YTTRIUM AND PROMETHIUM INTO TRIBUTYL PHOSPHATE FROM HYDROCHLORIC ACID[a]

(From Data of Peppard, Faris, Gray, and Mason[11])

	K for HCl of Indicated Conc.		
Element	3.0 M	6.4 M	8.0 M
Sc	0.04	32	50.
Y	< 0.001	0.001	0.005
Pm	< 0.001	< 0.001	0.01

a. Tributyl phosphate (TBP) was washed with 2N NaOH followed by water and then pre-equilibrated with HCl of the proper concentration. Tracers used were 85-d Sc^{46}, 61-d Y^{91} and 3.7-y Pm^{147}.

It was desired to know how completely scandium could be extracted with tributyl phosphate at higher hydrochloric acid concentrations. It was also necessary to have extraction data at low hydrochloric acid concentrations in connection with the subsequent removal of scandium from the organic phase. Extraction data was obtained over a wide range of hydrochloric acid concentrations with the beta-emitting tracer Sc^{46}. The results are given in Table II.

TABLE II. EXTRACTION OF SCANDIUM INTO TRIBUTYL PHOSPHATE FROM HYDROCHLORIC ACID[a]

K for HCl of Indicated Conc.							
2.3M	3.5M	4.7M	5.8M	7.0M	8.2M	9.4M	10.5M
0.02	0.07	0.26	1.4	7.6	36	110	>1000

a. Tributyl phosphate (TBP) was used as received. No pre-equilibrations were made with HCl. Tracer used was Sc^{46}.

Effectiveness of Yttrium as a Carrier for Traces of Scandium.

A known quantity of Sc^{46} tracer was added to 100 ml. of a 10% hydrochloric acid solution of 25 mg. of yttrium oxide. To the solution was added 25 ml. of 40% ammonium tartrate. The solution was made alkaline with ammonium hydroxide and heated just to the boiling point. After being stirred for a few minutes to flocculate the ammonium yttrium tartrate, the mixture was filtered. The activity determinations made on the precipitate and filtrate showed that the yttrium carried the scandium completely.

To study the effect of diverse ions on the recovery of scandium, a known quantity of Sc^{46} tracer was added to 100 ml. of a 10% hydrochloric acid solution in which was dissolved 0.5 g. of a sample and 25 mg. of yttrium oxide.

A typical analysis of the type of sample used is given in Table III.

TABLE III. TYPICAL ANALYSIS OF SAMPLE USED FOR SCANDIUM RECOVERY TESTS

Constituent	Percent	Constituent	Percent
NiO	4.6	CaO	21.5
CoO	3.7	MgO	9.0
U_3O_8	0.3	MoO_3	0.4
Al_2O_3	9.1	Mn_2O_3	0.2
Fe_2O_3	3.6	V_2O_5	0.4
		CuO	2.3

The yttrium was precipitated as ammonium yttrium tartrate and filtered. From the activity determinations it was found that 96% of the Sc^{46} was present in the yttrium precipitate.

PROCEDURE

Preparation of the Standard Curve. Pipette a suitable aliquot of the standard scandium chloride solution into a 100-ml. beaker to give from 0 to 120γ of scandium oxide and add 5.0 ml. of the yttrium chloride solution. Dilute the solution to 30 ml. with water and add 25 ml. of the 40% ammonium tartrate solution and 10 ml. of concentrated ammonium hydroxide. Heat the solution just to the boiling point. Stir until the tartrate precipitate becomes flocculent and filter the precipitate on an 85-ml. sintered-glass Buchner funnel. Dissolve the tartrate from the funnel with 25 ml. of concentrated hydrochloric acid and collect the solution in the beaker used in the precipitation step. Wash the funnel with 25 ml. of concentrated hydrochloric acid and hold the washing in reserve.

Transfer the acid solution to a 125-ml. separatory funnel and equilibrate with 25 ml. of tributyl phosphate for about 30 seconds. Discard the aqueous phase. Backwash the organic phase containing the scandium with the reserved washing and then with two additional 25-ml. portions of concentrated hydrochloric acid. Discard the washings. Wash the scandium from the organic phase by shaking with 50 ml. of water, and transfer the water phase containing the scandium to a 125-ml. separatory funnel. Free the solution of residual tributyl phosphate by washing with 25 ml. of diethyl ether and transfer to a 150-ml. beaker.

Add 8.0 ml. of concentrated ammonium hydroxide and stir the solution until the ether, which is dissolved in the solution, stops evolving. Add 2.0 ml. of the alizarin red S solution and titrate carefully with concentrated ammonium hydroxide until the red end-point is reached. If the end-point is passed, add a few drops of hydrochloric acid and repeat the titration. To the solution add 5.0 ml. of the 20% ammonium acetate buffer, cool to room temperature and dilute to 100 ml. with water.

Measure the absorbancy of the solution with a Beckman Model DU spectrophotometer at 520 mμ., slit width 0.04 mm., with 5.00-cm. Corex cells. As a reference solution use a standard containing no scandium which has been carried through the above procedure.

Procedure in Absence of Zirconium and Thorium. Prepare a solution of the sample in concentrated hydrochloric acid. Transfer an aliquot containing from 10 to 120γ of scandium oxide to a 125-ml. separatory funnel and adjust the volume to not less than 25 ml. with concentrated hydrochloric acid. Add 0.5 ml. of 30% hydrogen peroxide and 25 ml. of tributyl phosphate. Extract the scandium and discard the aqueous phase. Backwash the organic phase with three 25-ml. portions of concentrated hydrochloric acid. Discard all the washings. Add 70 ml. of water to the separatory funnel, and wash out the scandium by shaking the contents for 30 seconds. Transfer the aqueous phase to another 125-ml. separatory funnel. Add 25 ml. of diethyl ether and extract the residual tributyl phosphate. Draw the aqueous solution into a 150-ml. beaker and add 5.0 ml. of the yttrium chloride solution.

Add 25 ml. of the 40% ammonium tartrate solution. Slowly add concentrated ammonium hydroxide, in small portions and with constant stirring, until the solution is alkaline and then add a few milliliters in excess. When most of the ether has been expelled, heat the solution on a hot plate to a near boil. Discontinue heating and stir the mixture for a few minutes. Filter the insoluble tartrates on a sintered-glass Buchner funnel and wash the precipitate with 25 ml. of the ammonium tartrate wash solution. Dissolve the tartrates with 50 ml. of 20% hydrochloric acid and collect the solution in the 150-ml. beaker used for the tartrate precipitation. Add 25 ml. of the 40% ammonium tartrate and precipitate and filter the tartrates as before. Dissolve the tartrates with 50 ml. of 20% hydrochloric acid and repeat the precipitation and filtration. Finally, dissolve the tartrates with 25 ml. of concentrated hydrochloric acid and transfer the solution to a 125-ml. separatory funnel. Wash the Buchner funnel with 25 ml. of concentrated hydrochloric acid and hold the washing in reserve.

Separate the scandium from the yttrium by equilibrating the solution of dissolved tartrates with 25 ml. of tributyl phosphate for about 30 seconds. Discard the aqueous phase. Backwash the organic phase containing the scandium with the washing held in reserve and then with two 25-ml. portions of concentrated hydrochloric acid. Discard the washings. Remove the scandium from the organic phase by washing with 50 ml. of water. Transfer the water phase to a 125-ml. separatory

funnel and remove the residual tributyl phosphate by washing with 25 ml. of diethyl ether. Deliver the solution into a 150-ml. beaker. Develop the color for scandium with alizarin red S in the same manner as described under the preparation of the standard curve. Determine the absorbancy of the solution against a reference solution which is prepared as previously described.

Procedure in the Presence of Zirconium and Thorium. Prepare a solution of the sample in either sulfuric or hydrochloric acid, free of nitrate and fluoride ions. Transfer an aliquot containing from 10 to 120γ of scandium oxide to a 250- ml. separatory funnel. Dilute the aliquot to a volume of 100 ml. with water and sulfuric or hydrochloric acid so that a concentration of 10% acid is obtained. Add 10 ml. of the 6% cupferron solution to precipitate the cupferrates and extract with three 25-ml. portions of chloroform. Add an additional 5 ml. of the 6% cupferron solution and extract with four 25-ml. portions of chloroform to remove the cupferrates and excess cupferron. (Additional cupferron extractions should be made if the initial amount of impurities is very high and a heavy precipitate is obtained after the second addition of cupferron.)

Transfer the solution into a 400-ml. beaker and dilute to about 300 ml. with water. Boil out any chloroform droplets and then make the solution slightly alkaline with ammonium hydroxide. If no precipitate is observed, make the solution acid with nitric acid, add about 200 mg. of aluminum nitrate and precipitate the aluminum with

ammonium hydroxide. Macerate 2 or 3 Whatman filter accelerators (1" x 3/4") in 10 ml. of water and add this pulp to the mixture. Filter the hydroxides on an 85-ml. sintered-glass Buchner funnel. Dissolve the hydroxides with 100 ml. of warm 20% nitric acid. If a hydrochloric acid solution was used in the cupferron extraction, the hydroxides must be reprecipitated to free the solution of chloride. If sulfuric acid was used, the hydroxides need not be reprecipitated.

Add 2.0 ml. of the mercurous nitrate solution to the nitric acid solution of the hydroxides. Add 75 ml. of the saturated potassium iodate solution and stir frequently for 15 minutes. Filter the insoluble iodates on a sintered-glass Buchner funnel. Wash the beaker and the iodates with 25 ml. of the saturated potassium iodate solution. (The Buchner funnel containing the iodates can be cleaned in a hood with concentrated hydrochloric acid.)

Dilute the filtrate and washing containing the scandium to about 300 ml. with water. Make the solution alkaline with ammonium hydroxide and heat to about 80°C. Add 2 or 3 macerated Whatman filter accelerators and filter. Dissolve the hydroxides with 25 ml. of concentrated hydrochloric acid and collect the solution in a 100-ml. beaker. Wash the Buchner funnel with 25 ml. of concentrated hydrochloric acid and reserve the washing.

Transfer the acid solution of the hydroxides to a 125-ml. separatory funnel. Add 0.5 ml. of 30% hydrogen peroxide and 25 ml. of tributyl phosphate and extract the scandium. Discard the aqueous phase. Wash

the tributyl phosphate with the washing which was held in reserve and to which is added 0.5 ml. of hydrogen peroxide. Wash the tributyl phosphate phase with two additional 25-ml. portions of concentrated hydrochloric acid. Add 70 ml. of water to the separatory funnel and wash out the scandium by shaking for 30 seconds. Transfer the aqueous phase to another 125-ml. separatory funnel. Add 25 ml. of diethyl ether and extract the residual tributyl phosphate. Draw the solution into a 150-ml. beaker and add 5.0 ml. of the yttrium chloride solution. Perform the ammonium tartrate precipitations and the yttrium separation as described for the procedure in the absence of zirconium and thorium.

TABLE IV. RECOVERY OF SCANDIUM IN THE PRESENCE OF FOREIGN IONS

Synthetic Solutions

No. 1		No. 2		No. 3		No. 4		No. 5		No. 6	
Element	Quantity, mg.	Element	Quantity, mg.	Element	Quantity, mg.	Element	Quantity, mg.	Element	Quantity, mg.	Element	Quantity, mg.
Al	10	Al	10	Al	10	Al	10	Be	10	Ce	10
Be	10	Ba	10	Fe	10	Ca	10	Bi	10	Th	10
Bi	10	Ca	10	Mg	10	Ce	10	Cd	10	Ti	10
Cd	10	Co	10	Ni	10	Cu	10	La	10		
Co	10	Cu	10	Ti	10	Ga	10	Pb	10		
Cr	10	Fe	10	U	10	La	10	Sn	10		
Mn	10	Mg	10	Zn	10	Mo	10	Th	10		
Sb	10	Ni	10	Zr	10	Sn	10	Zn	10		
Th	1	Sr	10								
Ti	1	Th	2								
V	10	U	10								
Zr	1										
Added Sc_2O_3	20γ		25γ		25γ		20γ		25γ		25γ
Found Sc_2O_3	22γ		25γ		26γ		20γ		24γ		24γ

RESULTS

Recovery of Scandium in the Presence of Foreign Ions. Six synthetic solutions were prepared to contain known quantities of scandium together with other metal ions. The solutions were analyzed by the appropriate procedure with the results given in Table IV.

Analysis of Samples. Two minerals and two process residues were analyzed for scandium. The results obtained are compared with the spectrographic results in Table V.

TABLE V. ANALYSIS OF MINERALS AND RESIDUES

Material	Scandium Found, %	
	Spectrographic	Colorimetric
Beryl	0.01-0.1	0.11
Rutile	0.1-1.0	1.1
Carbonate Residue	0.004-0.007	0.006
Limestone Residue	0.004-0.007	0.006

In Table VI the results of the analyses of a scandium-bearing sample together with the distribution of scandium found in the various fractions resulting from acid leaching this sample is presented to show the material balance obtained.

TABLE VI. ANALYSIS OF INITIAL AND PROCESS SAMPLES

Material	Quantity	Sc_2O_3 Found	Total Sc_2O_3, mg.
Initial Sample	2500 g.	0.0095%	237.5
Wash Liquor	14.5 l.	n.d.	--
Acid Leach Liquor	2.37 l.	0.070 g/l	165.9
Leach Wash Liquor	2.20 l.	0.014 g/l	30.8
Leach Residue	546 g.	0.006 %	32.8
Total, mg.			229.5
Recovery,%			96.6

Similarly, Table VII gives the distribution of scandium found in various fractions resulting from processing the above acid-leach liquor for its uranium, copper, cobalt and nickel content.

TABLE VII. ANALYSIS OF ACID LEACH LIQUOR AND PROCESS SAMPLES

Material	Quantity	Sc_2O_3 Found	Total Sc_2O_3, mg.
Acid Leach Liquor	1.0 l.	0.070 g/l	70.0
Copper Sulfide Cake	14.3 g.	0.030 %	4.3
Uranium Product	3.5 g.	1.36 %	47.6
Cobalt-Nickel Cake	134.0 g.	0.011 %	14.7
Final Filtrate	1.93 l.	0.0004 g/l	0.8
Total, mg.			67.4
Recovery,%			96.3

DISCUSSION

The cupferron-chloroform extraction removes many metals which interfere with the color development with alizarin red S. The chief need for this extraction, however, is the removal of zirconium (and probably hafnium). Zirconium, if not removed before the extraction of the scandium from hydrochloric acid with tributyl phosphate, prevents the complete washing out of the scandium from the organic phase with water. Qualitative tests with tracer Sc^{46} showed that small quantities of zirconium prevented the complete removal of scandium from the organic phase even after repeated backwashings with equal volumes of water. No other metal ion tested exhibited this effect.

The iodate precipitation is required for the removal of thorium. Thorium is not removed in the cupferron-chloroform extraction, cannot be separated from scandium by the tributyl phosphate extraction from concentrated hydrochloric acid, and cannot be removed completely by repeated ammonium yttrium tartrate precipitations. Mercurous nitrate is added before the thorium is precipitated as the iodate since microgram quantities of thorium are not removed quantitatively if the mercury carrier is absent.

After the removal of the zirconium and thorium, a preliminary tributyl phosphate extraction is made to separate scandium from the bulk of the remaining elements, which are essentially aluminum, beryllium, uranium, chromium and the rare earths. Hydrogen peroxide retains cerium in the

trivalent state and prevents its extraction. The peroxide also prevents the extraction of titanium if this element is present. Uranium and iron extract completely. On washing out the scandium with water, however, some of the uranium is retained in the organic phase. If the preliminary tributyl phosphate extraction is not carried out, the rare earths will interfere in the tartrate precipitations.

The multiple tartrate precipitations are made to free the scandium of any remaining traces of impurities. If thorium, zirconium, titanium and rare earths other than yttrium, e.g. cerium, are present, the ammonium yttrium tartrate is slimy in nature and does not completely carry the scandium. Aluminum, iron and uranium in quantities up to 10 mg. do not effect the tartrate precipitation.

The final tributyl phosphate extraction is made to separate scandium from yttrium. Traces of yttrium may still be present after the hydrochloric acid washings of the organic extract. For this reason, the reference solution for the spectrophotometric determination is prepared by precipitating yttrium as the tartrate and extracting a hydrochloric acid solution of the tartrate with tributyl phosphate.

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