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MASTER

SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF RARE EARTHS

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Summary - At the present time arsenazo appears to be widely used for the spectrophotometric determination of rare earths. Unfortunately, the method is not selective. The separation of rare earths and yttrium from interfering elements has been studied, and the following method has been proposed. Rare earths are precipitated as fluorides using calcium fluoride as the carrier. Thorium and zirconium are removed by extraction with thenoyltrifluoroacetone (TTA) in xylene at pH 1.3. Small amounts of residual aluminum, iron, etc. are removed by extraction with 8-quinolinol-chloroform at pH 4.5. Rare earths are separated from calcium by TTA extraction at the same pH, and they are then back-extracted into 1 M nitric acid. After evaporation of the solution, the rare earths are determined spectrophotometrically with arsenazo.

INTRODUCTION

Although arsenazo is not particularly selective, it appears to be widely used for the spectrophotometric determination of the rare earths and yttrium at the present time. New reagents such as bromopyrogall red,¹ salicylfluorone,² and arsenazo III³ do not seem to be definitely more selective than arsenazo. Yttrium may

be determined spectrophotometrically with pyrocatechol violet after a preliminary separation from iron, uranium, zirconium, thorium, and molybdenum with tri-n-octylphosphine oxide.⁴ However, the behavior of rare earths and scandium remains to be established. Thus a generally applicable method is needed for the separation of rare earths.

Arsenazo has been used for the determination of rare earths in uranium,^{5,6} cast steels,⁷ ores and rocks,⁸ and soils.⁹ A method was proposed for the successive determination of rare earths and thorium with arsenazo.¹⁰

For the purpose of extending the applicability of the spectrophotometric determination of rare earths with arsenazo, the separation of these elements from interfering elements have been studied.

APPARATUS

Absorbance measurements were made with a Beckman Model DU spectrophotometer, using 1-cm. cells. A Beckman Model G pH meter was used for pH measurements. For centrifugal separations, an International clinical centrifuge with 50-ml. Lusteroid tubes was used. A shaking machine, Burrell shaker, with a time switch was used for extractions.

REAGENTS

Calcium nitrate, 10 mg. Ca/ml.: 5.89 g. of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 100 ml. of water.

Thenoyltrifluoroacetone (TTA), 0.5 M: 45 g. in 400 ml. of xylene.

8-quinolinol: 5.0 g. of 8-quinolinol was dissolved in 10 ml. of glacial acetic acid and the solution was diluted to 100 ml. with water.

Ammonium acetate, 3.5 M: 135 g. in 500 ml. of water.

Acetic acid-sodium acetate: 0.1 M acetic acid and 0.1 M sodium acetate (13.6 g. of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ in 1 l. of water) were mixed so that the pH of the mixture became 4.6 ± 0.1 . Instead of sodium acetate, ammonium acetate may be used.

Arsenazo: 0.10 g. in 100 ml. of water.

Triethanolamine buffer: 400 ml. of 15% (w/v) triethanolamine solution, 330 ml. of 1 M nitric acid, and 70 ml. of water were mixed. The pH was adjusted to 7.2 ± 0.1 with dilute nitric acid or ammonium hydroxide.

Standard cerium solution, 1.00 mg. Ce/ml.: 10 ml. of water, 10 ml. of 70% perchloric acid, and 1 ml. of 30% hydrogen peroxide were added to 0.1228 g. of CeO_2 that was previously ignited. On heating, the oxide dissolved and the resulting solution was evaporated to dryness. Ten ml. of 1 M nitric acid and 1 ml. of 30% hydrogen peroxide were added, and the solution was boiled for 5 minutes. After cooling, the solution was diluted to exactly 100 ml. with water.

Standard solutions of gadolinium (1 mg. Gd/ml.) and yttrium (1 mg. Y/ml.): The oxides were ignited and weighed. They were dissolved in a slight excess of nitric acid, and the solutions were diluted to appropriate volumes with water.

EXPERIMENTAL WORK

Fluoride precipitation. Transfer the sample solution (0.5 M in nitric acid and containing 20 to 100 $\mu\text{g.}$ of rare-earth metals or 10 to 60 $\mu\text{g.}$ of yttrium in a volume of approximately 50 ml.) to a polyethylene beaker and add 1.0 ml. of calcium nitrate solution and 10 ml. of 48% hydrofluoric acid. Set the solution aside overnight.

Transfer the fluorides to a 50-ml. Lusteroid centrifuge tube and separate at the full speed of the centrifuge for about 5 minutes. Carefully pour off the supernatant liquid. Wash the precipitate 3 times with 10-ml. portions of 1:5 hydrofluoric acid. Transfer the precipitate to a platinum dish with a minimum amount of 2 M nitric acid. Add 2 ml. of 70% perchloric acid and evaporate the solution to near dryness. (Note: If iron is present, it is important that the solution not be evaporated to complete dryness.).

TTA extraction at pH 1.3. Dissolve the residue in 7.0 ml. of 0.1 M nitric acid and transfer the solution to a 60-ml. separatory funnel. Wash the dish with 7 ml. of water. (If necessary, confirm that the pH of the solution is 1.3 ± 0.1). Shake the solution for 5 minutes with 10 ml. of TTA solution. When the layers have separated, drain off the aqueous phase into a second separatory funnel. Discard the organic phase. Add 10 ml. of TTA solution to the second separatory funnel. Shake the system for 5 minutes and discard the organic phase. Wash the aqueous phase by shaking it for 10 seconds with 10 ml. of xylene and discard the organic phase.

8-Quinolinol extraction. To the aqueous phase add 1.0 ml. of 8-quinolinol solution, 1.0 ml. of ammonium acetate solution, and 1.0 ml. of 0.7 M ammonium hydroxide. If the pH of the solution is not in the range 4.5 to 4.8, adjust with dilute nitric acid or ammonium hydroxide. Add 20 ml. of chloroform and shake the system for 1 minute. When the layers have separated, drain off and discard the organic phase. Add 0.3 ml. of 8-quinolinol solution and 20 ml. of chloroform and equilibrate the phases for 1 minute. Discard the organic phase. Wash the aqueous phase by shaking it for 10 seconds with 20 ml. of chloroform and discard the organic phase.

TTA extraction at pH 4.5. Shake the aqueous phase for 5 minutes with 15 ml. of TTA solution. When the layers have separated, drain off the aqueous phase into a second separatory funnel. Add 15 ml. of TTA solution to the second separatory funnel. Shake the system for 5 minutes and discard the aqueous phase. Combine the second extract with the first and wash the extracts by equilibrating them for 10 seconds with 10 ml. of acetic acid-sodium acetate solution. Discard the aqueous phase.

Shake the organic phase for 5 minutes with 25 ml. of 1 M nitric acid. Transfer the aqueous phase to another separatory funnel. Discard the organic phase. Shake the aqueous phase for 10 seconds with 10 ml. of xylene. Transfer the aqueous phase to a 50-ml. beaker and evaporate to dryness. To the residue add 1 ml. of 70% perchloric acid and 1 ml. of concentrated nitric acid. Evaporate the solution to dryness. Wash the sides of the beaker with a minimum amount of water and evaporate the solution to dryness.

Spectrophotometric determination of rare earths. Dissolve the residue in 1.0 ml. of 0.1 M nitric acid. Add 4 ml. of water, mix, and add 2.0 ml. of arsenazo solution. Add 5.0 ml. of triethanolamine buffer solution and 1.0 ml. of 0.1 M ammonium hydroxide. Confirm that the pH of the solution is 7.2 ± 0.1 . Transfer the solution to a 25-ml. volumetric flask and dilute to the mark with water. Measure the absorbance of the solution in a 1-cm. cell at 580 m μ , using water (or reagent blank) as the reference.

Construct a calibration curve by taking, for example, 0, 25, 50, and 75 μ g. of rare-earth metals or 0, 20, 40, and 60 μ g. of yttrium and carrying them through the entire procedure using water (or reagent blank) as the reference.

RESULTS AND DISCUSSION

Interference study. Kuznetsov¹¹ has reported that arsenazo forms colored solutions or precipitates with the following ions in neutral media: rare earths, scandium, yttrium, uranium(VI), copper, aluminum, vanadium(IV), thorium, zirconium, gallium, indium, palladium, iron(III), titanium, and chromium(III). Beryllium¹² also gives a color. Because no quantitative data on interferences in the determination of the rare earths have been published, the absorbances of the solutions (pH 7.2, 25 ml.) containing metal ions and arsenazo were measured at 580 m μ . The results are shown in Table I. Gadolinium was chosen to represent rare earths. Previous work¹⁰ has shown that the absorbance of 20 μ g. Th is nearly the same as that of 16 μ g. Gd.

TABLE I. COLOR REACTIONS OF METALS WITH ARSENAZO

Metal, mg.		Absorbance	Gd Equal to Absorbance, $\mu\text{g.}$
Al(III)	0.030	0.526	76
Ca(II)	0.10	0.012	2
Cd(II)	0.10	0.015	2
Co(II)	0.10	0.087	13
Cr(III)	0.10	0.032 ^a	46
Cu(II)	0.10	0.174	25
Fe(III)	0.10	0.369	53
Mg(II)	0.10	0.041	6
Mn(II)	0.10	0.095	14
Mo(VI)	0.20 ^b	0.000	0
Ni(II)	0.10	0.075	10
Pb(II)	0.10 ^b	0.007	1
Sc(III)	0.050	0.678	98
U(VI)	0.050	0.171	25
Zn(II)	0.050	0.050	7
Zr(IV)	0.10	0.563	81

^a Absorbance increases with time. Measurement was made 25 minutes after addition of reagents.

^b This amount of Mo or Pb does not interfere with the determination of 53 $\mu\text{g.}$ Gd.

Fluoride precipitation. Sandell¹³ has suggested the use of calcium salts or strontium salts as a carrier in the precipitation of small amounts of rare earths as fluorides or oxalates. Bornong

and Moriarty⁷ used thorium as a carrier for the precipitation of rare-earth fluorides and oxalates. Because thorium is a more serious interference in the arsenazo method than is calcium, the latter was chosen as a carrier in the present work. The optimal conditions for the fluoride precipitation, as described in the procedure, gave 92 to 94% recovery of the gadolinium. Calcium was removed by TTA extraction at pH 4.5 prior to the gadolinium determination.

All the recoveries in Tables II to V were calculated by referring to the calibration curve obtained without the separation of gadolinium, cerium, or yttrium. The recoveries from fluoride precipitation and TTA extraction are close to those from TTA extraction at pH 4.5 (Table III) indicating almost complete precipitation of gadolinium as fluoride.

Under the optimum conditions for the precipitation of gadolinium fluoride, 5 and 21 mg. of iron(III) gave absorbances corresponding to 15 μ g. and 14 μ g. Gd, respectively. Ten mg. of aluminum gave an absorbance of about 1.8; more than 0.1 mg. of aluminum was therefore found in the fluoride precipitate.

8-Quinolinol-chloroform extraction. Since complete removal of iron and aluminum from rare earths was not effected either by fluoride precipitation or by TTA extractions, 8-quinolinol-chloroform extraction was examined. The following method was found to be applicable to at least 1 mg. each iron and aluminum.

To a 10-ml. aqueous solution, 1.0 ml. of 5% 8-quinolinol in dilute acetic acid, 1.0 ml. of 3.5 M ammonium acetate, and

3 ml. of water were added. The pH of the solution was 4.8. Twenty ml. of chloroform was added and the system was shaken for 1 minute. After removal of the organic phase, 0.3 ml. of 5% 8-quinolinol solution and 20 ml. of chloroform were added and the system was shaken for 1 minute. The organic phase was removed and the aqueous phase was shaken for 1 minute with 20 ml. of chloroform. The aqueous phase was evaporated to dryness. Three ml. of concentrated nitric acid and 1 ml. of concentrated hydrochloric acid were added and the solution was again evaporated to dryness. Gadolinium was then determined by the arsenazo method.

By this method, 53 μ g. of gadolinium was separated from the solutions containing 1 mg. each aluminum and iron(III). The recovery of gadolinium was 98 to 99%.

At pH 4.5 the following ions will be extracted into 8-quinolinol-chloroform: aluminum, copper, iron(III), gallium, indium, molybdenum(VI), niobium, nickel, tin(IV), titanium, thallium(III), and vanadium.^{13,14,15} Cobalt, manganese, and lead will not be extracted.

TTA extraction at pH 1.3. Feldman and Ellenburg¹⁶ separated a small amount (not specified) of thorium from rare earths by extraction with TTA in xylene at pH 1.0 and at 60°C. The following experiments were conducted in order to know if complete removal of thorium would be achieved at room temperature ($\sim 25^\circ\text{C}.$).

Aqueous phase: about 15 ml., pH 1.3 (0.05 M in nitric acid).

Three extractions (5 minutes each) with 10-ml. portions of 0.5 M TTA in xylene.

The aqueous phase was washed with 10 ml. of xylene and evaporated to dryness. After destruction of organic matter with nitric and perchloric acids, gadolinium was determined with arsenazo.

As shown in Table II, gadolinium can be separated from 10 mg. of thorium. For less than 1 mg. of thorium, two extractions are sufficient. The TTA extraction at pH 1.3 also removes copper, scandium, and zirconium. Extractions of iron(III) and uranium(VI) are very incomplete.

TABLE II. DETERMINATION OF GADOLINIUM AFTER TTA EXTRACTION AT pH 1.3

Addition	Gd Taken, μg	Gd Found, ^a μg	Average Recovery, %
-	-	0.7, 0.7	-
-	53.0	49.5, 50.0	94.0
1.0 mg. Cu	-	0.0 ^b , 0.0 ^b	-
1.0 mg. Cu	53.0	50.0 ^b , 50.0 ^b	94.3
0.10 mg. Fe(III)	-	17.0, 10.5	-
0.0125 mg. Fe(III)	-	1.0, 1.0	-
0.0125 mg. Fe(III)	53.0	48.5, 48.5	91.5
0.10 mg. Sc	-	0.7, 1.0	-
0.10 mg. Sc	53.0	48.0, 48.5	91.1
10 mg. Th	-	1.5, 1.5	-
10 mg. Th	53.0	50.0, 50.5	94.9

TABLE II (Concluded)

Addition	Gd Taken, μg	Gd Found, ^a μg	Average Recovery, %
20 mg. Th	-	4.5, 5.5	-
20 mg. Th	53.0	49.0, 50.0	93.4
5 mg. Th, 0.014 mmole Na_2SO_4	-	0.0, 0.0	-
5 mg. Th, 0.014 mmole Na_2SO_4	53.0	50.0, 50.0	94.3
0.10 mg. U(VI)	-	22.5, 24.0	-
0.10 mg. U(VI)	53.0	48.0, 49.0	91.5
1.0 mg. Zr	-	0.0, 0.0	-
1.0 mg. Zr	53.0	49.5, 49.0	93.0

^a Values obtained with 53 μg . Gd were corrected for respective blanks.

^b Two TTA extractions.

TTA extraction at pH 4.5. After removal of thorium, Feldman and Ellenburg¹⁶ extracted rare earths with TTA in xylene at pH 4.5 and at 60°C. and determined them spectrographically. Menis et al.¹⁷ extracted lanthanum into TTA in 4-methyl-2-pentanone and determined it by a flame photometer. In the present work, the extraction of gadolinium at room temperature was studied under the following conditions:

Aqueous phase: about 10 ml., pH 4.5 (0.1 M in acetate).

Two extractions (5 minutes each) with 10-ml. portions of 0.5 M TTA in xylene. The combined organic phase was washed with 10 ml. of pH 4.5 solution (0.1 M in acetate).

Back-extraction (5 minutes) of gadolinium with 15 ml. of 1 M nitric acid. The back-extract was washed with 10 ml. of xylene.

The aqueous phase was evaporated to dryness. After destruction of organic matter, gadolinium was determined with arsenazo.

The results are shown in Table III.

TABLE III. DETERMINATION OF GADOLINIUM AFTER TTA EXTRACTION AT pH 4.5.

Addition	Gd Taken, μg	Gd Found, ^a μg	Average Recovery, %
-	15.9	14.5, 14.5	91.2
-	53.0	50.0, 50.0	94.1
-	79.5	75.0, 75.0	94.3
1.0 mmole Na_2SO_4	53.0	49.0, 50.0	93.4
10 mg. Mg	53.0	48.5, 49.5	92.4
10 mg. Ca	53.0	51.0, 50.5	95.8
20 mg. Ca	53.0	50.5, 51.0	95.8
1.0 mg. Cd	53.0	50.0, 50.0	94.3

^a Corrected for blanks which were in the range 1.0-2.5 μg . Gd.

Back-extraction of gadolinium with 2 M nitric acid gave the same recovery, i.e., 94.9% with 53 μg . Gd. Double back-extractions with 15 ml. and 10 ml. of 1 M nitric acid did not improve the recovery, i.e., 95.3% with 53 μg . Gd.

Positive interferences were observed with 1.0 mg. Ag, 1.0 mg. Mo(VI), 1.0 mg. Pb, and 0.1 mg. Zn. It may be concluded

that the TTA extraction at pH 4.5 is suitable only for the separation of rare earths from magnesium, calcium, and probably strontium and barium.

By carrying out three TTA extractions at pH 1.3 and two TTA extractions at pH 4.5, 53 μ g. of gadolinium was separated from 10 mg. each thorium and calcium. The recovery of gadolinium was 91%.

Procedure in the absence of thorium. When thorium and zirconium are absent in the sample, the TTA extraction at pH 1.3 can be omitted. If the sample contains microgram amounts of thorium, the method described previously by Onishi *et al.*¹⁰ can be applied. The procedure that consists of fluoride precipitation, 8-quinolinol-chloroform extraction at pH 4.5-4.8, and TTA-xylene extraction at the same pH provides for the presence of many elements (Table IV). The separation of milligram amounts of lead and uranium from rare earths is not satisfactory. Lead was precipitated almost completely as fluoride, and further purification steps did not remove lead. Methods for the separation of rare earths from uranium^{5,6} have previously been published.

TABLE IV. SEPARATION OF GADOLINIUM FROM OTHER ELEMENTS

(TTA extraction at pH 1.3 omitted)

Addition	Gd Taken, μg	Gd Found, ^a μg	Average Recovery, %
-	-	1.5, 1.7	-
-	53.0	50.5, 50.5	95.3
20 mg. Al	-	0.7, 0.4	-
20 mg. Al	53.0	49.5, 50.0	94.0
1.0 mg. Co(II)	-	0.7, 0.4	-
1.0 mg. Co(II)	53.0	50.5, 50.0	94.9
1.0 mg. Cr(III)	-	0.0, 0.0	-
1.0 mg. Cr(III)	53.0	50.0, 50.0	94.3
51 mg. Cu (as CuSO_4)	-	1.0, 0.7	-
51 mg. Cu (as CuSO_4)	53.0	50.0, 50.5	94.9
42 mg. Fe(III)	-	0.6, 1.3	-
42 mg. Fe(III)	53.0	50.0, 49.0	93.4
84 mg. Fe(III)	-	0.4, 1.3	-
84 mg. Fe(III)	53.0	50.0, 49.5	94.0
10 mg. Mn(II)	-	7.0, 7.5	-
10 mg. Mn(II)	53.0	49.5, 48.2	92.2
1.0 mg. Mn(II)	-	2.0, 2.5	-
1.0 mg. Mn(II)	53.0	51.0, 51.0	96.2
20 mg. Mo (as ammonium molybdate)	-	1.6, 1.4	-
20 mg. Mo (as ammonium molybdate)	53.0	50.5, 50.0	94.9
20 mg. Nb	-	0.0, 0.0	-
20 mg. Nb	53.0	50.0, 49.0	93.4

TABLE IV (Concluded)

Addition	Gd Taken, μg	Gd Found, ^a μg	Average Recovery, %
15 mg. Ni	-	0.6, 0.3	-
15 mg. Ni	53.0	50.0, 50.5	94.9
10 mg. P (as KH_2PO_4)	-	0.0, 0.0	-
10 mg. P (as KH_2PO_4)	53.0	50.5, 51.0	95.8
5.0 mg. Pb	-	110, 110	-
0.10 mg. Pb	-	2.4, 2.1	-
0.10 mg. Pb	53.0	50.0, 49.0	93.4
20 mg. Ti	-	0.2, 0.6	-
20 mg. Ti	53.0	51.0, 49.5	94.9
10 mg. U(VI)	-	31.5, 31.5	-
0.20 mg. U(VI)	-	2.5, 2.0	-
0.20 mg. U(VI)	53.0	51.0, 51.0	96.2
5.0 mg. V(V)	-	0.9, 0.0	-
5.0 mg. V(V)	53.0	50.5, 50.0	94.9
10 mg. W(VI)	-	1.9, 1.4	-
10 mg. W(VI)	53.0	50.0, 49.5	94.0
2.0 mg. Zn	-	2.2, 1.9	-
2.0 mg. Zn	53.0	50.5, 50.5	95.3

Values obtained with 53 μg . Gd were corrected for respective blanks.

General procedure. Results obtained in applying the proposed procedure are collected in Table V.

TABLE V. SEPARATION OF RARE EARTHS FROM OTHER ELEMENTS - GENERAL PROCEDURE

Addition	Rare Earth	μg Taken	μg Found ^a	Average Recovery, %
-	-	-	0.0-0.6 ^b	-
-	Gd	21.2	20.0, 19.0	92.0
-	Gd	53.0	48.0, 48.0	90.6
-	Gd	79.5	71.0, 71.5	89.7
-	Ce	58.0	51.5, 52.0	89.7
-	Y	39.0	35.2, 35.2	90.2
10 mg. Th	-	-	1.1 ^c , 1.1 ^c	-
10 mg. Th	Gd	53.0	40.0 ^c , 39.5 ^c	75.1
10 mg. Th	-	-	1.9 ^d , 1.7 ^d	-
10 mg. Th	Gd	53.0	46.0 ^d , 46.0 ^d	86.8
1.0 mg. Sc	-	-	2.4, 2.4	-
1.0 mg. Sc	Gd	53.0	46.5, 47.0	88.3
0.10 mg. Zr	-	-	0.0, 0.3	-
0.10 mg. Zr	Gd	53.0	47.0, 47.0	88.6
1.0 mg. Th	-	-	0.6, 0.4	-
1.0 mg. Th	Gd	53.0	48.0, 48.5	91.1
42 mg. Fe(III), 1.0 mg. Th	-	-	0.9, 0.9	-
42 mg. Fe(III), 1.0 mg. Th	Gd	53.0	47.0, 47.5	89.2

^a Values obtained with rare earths were corrected for respective blanks.

^b Av. of 10 experiments = 0.2 μg .

^c Fluoride precipitation without Ca; three TTA extractions at pH 1.3.

^d Three TTA extractions at pH 1.3.

In the presence of 1 mg. Zr, emulsion was formed during the TTA extraction at pH 1.3. It was found that the evaporation of perchloric acid solution of calcium and zirconium to dryness caused this emulsion formation. From Table V it is seen that 10 mg. Th is not so effective as 10 mg. Ca as a carrier for gadolinium.

The average recovery of the last 4 experiments in Table V is 89.3% (coefficient of variation = 1.4%). This value is very close to the average of 90.4% for the first 5 experiments in the same table (coefficient of variation = 0.9%), and the construction of the calibration curve through the entire procedure is justified. It may be mentioned that the method of Bornong and Moriarty⁷ for the determination of rare earths in cast steels gave an average recovery of 89%, with a coefficient of variation of 7%.

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