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**REPORT NO. 1956**

**AN IMPROVED ION-EXCHANGE SEPARATION  
OF RARE-EARTH ELEMENTS FOR  
SPECTROGRAPHIC ANALYSIS**

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**Date** 10th March, 1978

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# NATIONAL INSTITUTE FOR METALLURGY

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Programme No. 262  
Project No. 01477  
Project Report No. 1

ISBN 0 86999 423 9

### **SYNOPSIS**

Rare-earth elements are separated from scandium and base metals by adsorption onto anion resin BIORAD AG1-X8 in the nitrate form from a mixture of 5 per cent 7 M nitric acid and 95 per cent methanol. The yttrium subgroup is eluted with a mixture of 45 per cent 7 M nitric acid and 55 per cent methanol, followed by elution of the cerium subgroup with 8 M nitric acid. This separation facilitates the determination of the traces of the heavier yttrium subgroup of rare-earth elements.

### **SAMEVATTING**

Seldsameaarde-elemente word in die nitraatvorm van skandium en onedele metale geskei deur adsorpsie op die anioonhars BIORAD AG1-X8 uit 'n mengsel van 5 persent 7 M-salpetersuur en 95 persent metanol. Die yttriumsubgroep word uitgewas met 'n mengsel van 45 persent 7 M-salpetersuur en 55 persent metanol gevolg deur die uitwassing van die ceriumsubgroep met 8 M salpetersuur. Hierdie skeiding vergemaklik die bepaling van die spore van die swaarder seldsameaarde-elemente van die yttriumsubgroep.

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## 1. INTRODUCTION

The method now in use at the National Institute for Metallurgy (NIM) for the separation and determination of rare-earth elements in various minerals and geological samples involves a cation-exchange separation of the rare-earth elements and scandium from other elements such as calcium, iron, and aluminium. This is followed by an anion-exchange separation of the rare-earth elements from scandium, which is used as an internal standard in the subsequent spectrographic determinations<sup>1</sup>. The rare-earth elements are determined either in a solution, in which case they are excited by a plasma-jet solution method, or they are precipitated in a matrix of aluminium oxide, when a d.c. arc is used to excite the spectra. There is a limit to which high concentrations of the abundant rare-earth elements (cerium subgroup) can be present in a sample during the detection and determination of traces of the heavier rare-earth elements (yttrium subgroup). The abundant rare-earth elements cause matrix effects in the determination of trace rare-earth elements. Dilution does not eliminate these effects because it results in a loss of sensitivity where it is most needed. Moreover, the effects of large and variable amounts of abundant rare-earth elements, in association with a fixed amount of aluminium oxide and the internal standard, are not compensated for in terms of the internal standard used, with a consequent loss in accuracy.

It was therefore decided in the present investigation that an attempt should be made to separate the cerium and yttrium subgroups of the rare-earth elements, although an absolutely clean separation would not be necessary. Although no significant adsorption of rare-earth elements on strongly basic anion-exchange resins has been observed at any acid concentration<sup>2-5</sup>, several investigators have reported on the anion-exchange behaviour of rare-earth elements from a medium of nitric acid and methanol<sup>3,6,7</sup>. Korkisch and Tera<sup>8</sup> found that rare-earth elements and thorium were adsorbed strongly from nitric acid-methanol and thus separated from many other elements. Faris and Warton<sup>9</sup> studied the adsorption of the rare-earth elements yttrium and scandium. Roelandts and Duyckaerts<sup>10</sup> investigated the adsorption of rare-earth elements and other elements from nitric acid-methanol media of varying composition, and suggested a scheme for the separation of rare-earth elements from other elements and separation into the cerium and yttrium subgroups. The distribution ratios for the adsorption of rare-earth elements and other elements from nitric acid-methanol media adsorbed onto a strongly basic anion-exchange resin in the nitrate form show that scandium and other base metals are not adsorbed from solutions with a high methanol content. However, the rare-earth elements are adsorbed, their distribution ratios increasing from ytterbium, the least strongly held, to lanthanum, the most strongly held. The scandium and base metals pass into the eluate with the major part of any calcium present (calcium being the most strongly adsorbed of the base metals) and other anions such as phosphates. The rare-earth elements also separate into two groups: the cerium subgroup of elements (lanthanum to neodymium), which have high distribution ratios, and the yttrium subgroup (samarium to lutetium), which have lower distribution ratios varying very little from one to another. Edge<sup>11</sup> separated rare-earth elements from thorium by elution from an anion-exchange resin with 8 M nitric acid. The thorium is adsorbed with the rare-earth elements and will not be eluted when the rare-earth elements are eluted with nitric acid-methanol eluants or with nitric acid eluants.

In view of this information, a method was developed at NIM for the separation of rare-earth elements from other elements and phosphoric acid (a possible source of rare-earth elements in South Africa), and separation into the cerium and yttrium subgroups.

## 2. EXPERIMENTAL METHOD

An 8 per cent cross-linked AG1 strongly basic anion-exchange resin of the quaternary amine type in chloride form was suspended in water, and colloidal particles were removed by several decantations. It was then transferred to a large preparation column and converted to the nitrate form by sequential treatment with 1 M to 7 M nitric acid until no chloride was detectable in the effluent. The resin was rinsed with methanol, removed from the column, and left to dry overnight while exposed to the air. The resin was finally dried in an air-oven at 70°C for three hours and stored in a screwcap bottle. The columns used were of borosilicate glass and were 32 cm in length and 1 cm in diameter, with a broadened section of 5 cm in length and 2 cm in diameter on top. The resin was supported by a sintered-glass disc.

In the investigations described here, the elution curves for ytterbium, the least strongly adsorbed rare-earth element, were used in the determination of the length of the column, the mesh size of the resin, and the volume of eluant required for the separation of scandium and base metals from the adsorbed rare-earth elements.

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2.1. Elution of Base Metals and Scandium

Resin columns were prepared with AG1-X8 resin in the nitrate form and were equilibrated with a mixture of 5 per cent 7 M nitric acid and 95 per cent methanol. Solutions containing 1 mg of scandium and 0,5 mg of ytterbium were evaporated to dryness, redissolved in 50 ml of a mixture of 5 per cent 7 M nitric acid and 95 per cent methanol, and passed through the column. The elution was continued with a further 200 ml of eluant, 5 ml fractions being collected with an automatic fraction collector from the start of the elution. Scandium and ytterbium were determined in the fractions by atomic-absorption spectrophotometry. The volumes of eluate for the elution of scandium and the breakthrough of ytterbium for different column lengths, mesh size of resin, and elution rate are given in Table 1, and the elution curves are shown in Figures 1 and 2.

TABLE 1

*Separation of scandium and ytterbium*

Internal diameter of column 1 cm

Resin BIORAD AG1-X8 (nitrate form)

Eluant 5% 7M nitric acid and 95% CH<sub>3</sub>OH

Test no.	Column length cm	Mesh size	Elution rate ml/min	Volume of eluate for Sc elution ml	Volume of eluate for Yb breakthrough ml
1	14	100 to 200	2,0	96	25
2	32	100 to 200	1,5	140	75
3	20	200 to 400	0,8	110	110
4	32	200 to 400	0,7	135	230

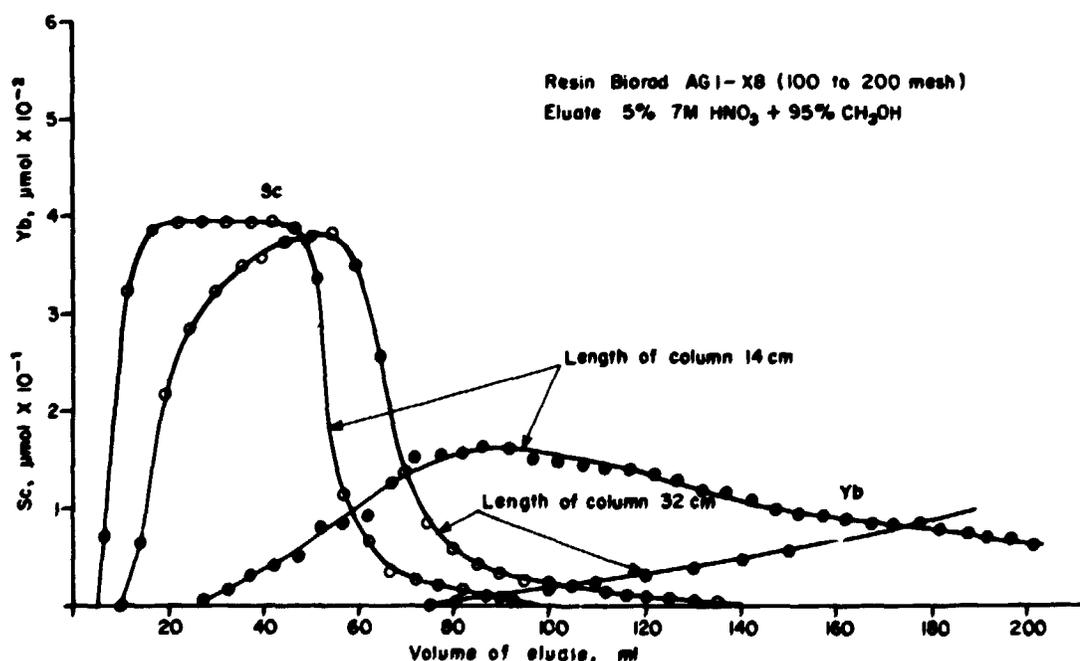


FIGURE 1. Elution curves for scandium and ytterbium (mesh size of resin 100 to 200)

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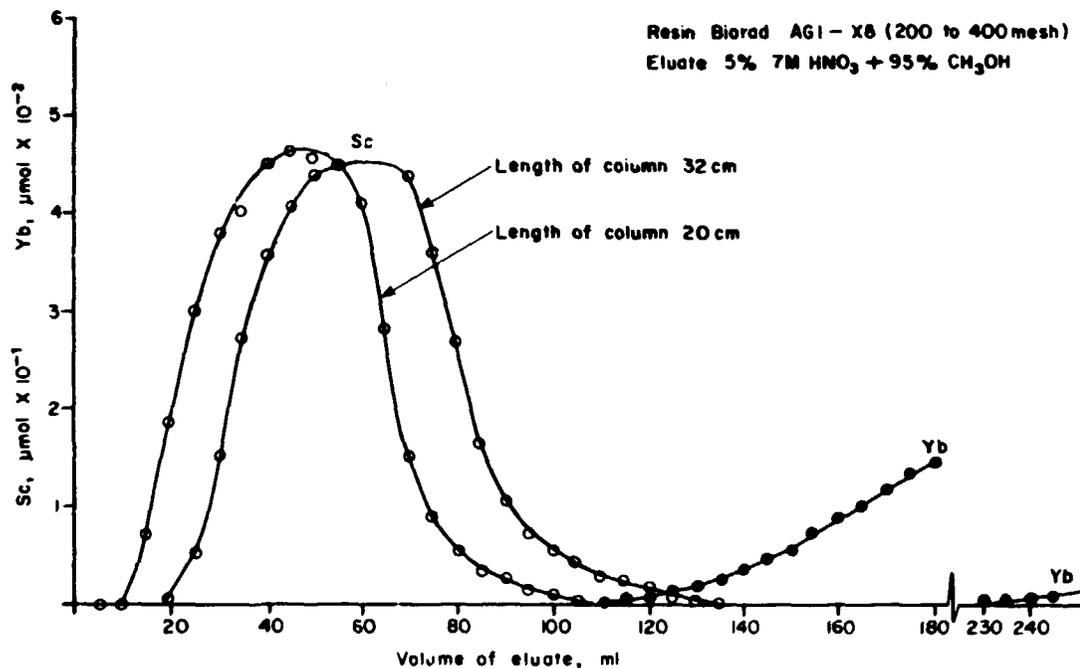


FIGURE 2. Elution curves for scandium and ytterbium (mesh size of resin 200 to 400)

From Table 1 it is evident that the conditions that give a clean separation of scandium and ytterbium are those used in Test no. 4, in which there was a slow rate of elution.

Roelands<sup>10</sup> stated that the major part of the calcium present in the sample solution would be eluted with the scandium and base metals. The elution curve for 300 mg of calcium, equivalent to a 1 g sample with a calcium content of 30 per cent, compared with that for 1 mg of scandium using a 32 cm long column of BIORAD AG1-X8 (200 to 400 mesh) anion resin and a flow-rate of 0.7 ml/min, is shown in Figure 3. The fraction collected was 10 ml, and calcium was determined by atomic-absorption spectrophotometry. Calcium was not completely eluted before ytterbium started eluting at 230 ml, but the calcium that will be eluted with the yttrium subgroup represents less than 10 per cent of the calcium present in the sample and will be separated when the rare-earth elements of the yttrium subgroup are precipitated with alumina for spectrographic determination by the d.c. arc technique.

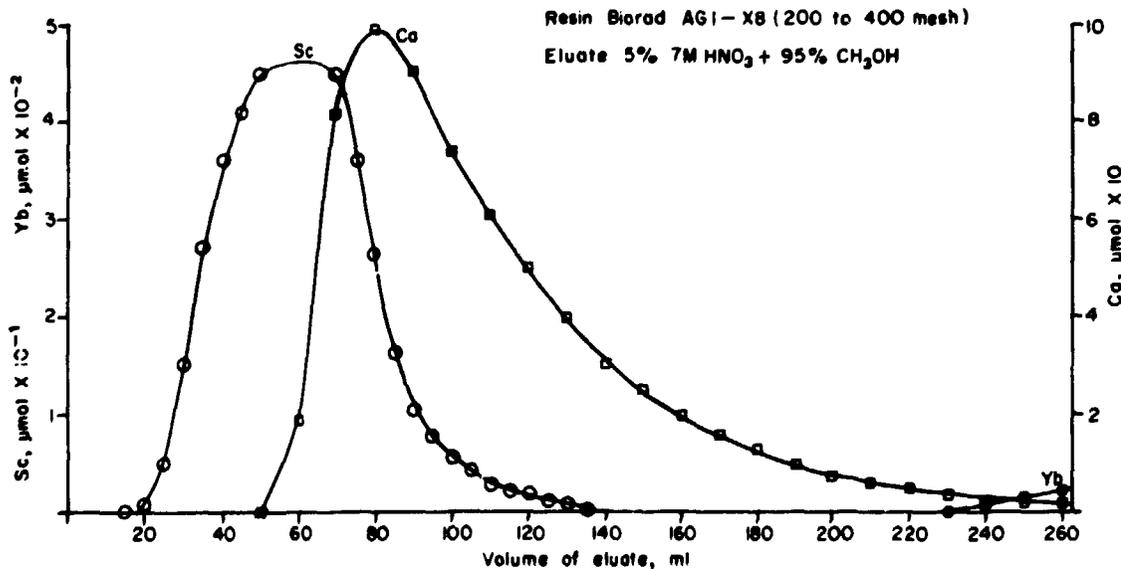


FIGURE 3. Elution curves for scandium, calcium, and ytterbium

## 2.2. Elution of Rare-earth Elements

### 2.2.1. The Yttrium Subgroup

Samarium, the most strongly adsorbed element of the yttrium subgroup elements, was used in the determination of the volume of eluant to be used for the elution of the yttrium subgroup, the eluant being a mixture of 45 per cent 7 M nitric acid and 55 per cent methanol as recommended by Roelandts<sup>10</sup>. The yttrium subgroup consists of lutetium to samarium and is thus the last group to be eluted. A solution containing 2 mg of samarium was evaporated to dryness, and the samarium was redissolved in 50 ml of a mixture of 5 per cent 7 M nitric acid and 95 per cent methanol. This solution was passed through a column of AG1-X8 (200 to 400 mesh) 32 cm in length, and the column was washed with 150 ml of the adsorbing solution. Samarium was then eluted with 250 ml of a mixture of 45 per cent 7 M nitric acid and 55 per cent methanol, and 12 ml fractions were collected with an automatic fraction collector. Samarium was determined in the fractions with xylenol orange<sup>12</sup>. The elution curve is shown in Figure 4.

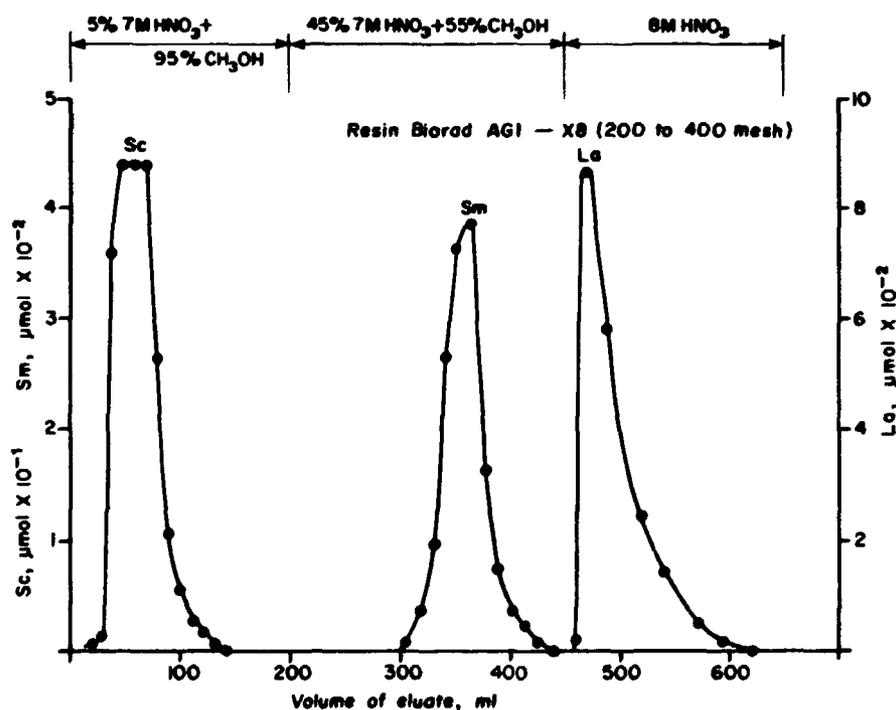


FIGURE 4. Elution curves for scandium, samarium, and lanthanum

Samarium was eluted with 240 ml of the same mixture (45 per cent 7 M nitric acid and 55 per cent methanol). The other elements of the yttrium subgroup, europium to lutetium, would be eluted completely before the complete elution of samarium. The element yttrium accompanies this group<sup>9</sup>. A curve for the elution of 10 mg of neodymium (the rare-earth element adjacent to samarium and the most easily eluted of the cerium subgroup) carried out under the same conditions as for samarium showed that neodymium did not start eluting with 400 ml of a mixture of 45 per cent 7 M nitric acid and 55 per cent methanol. This shows that the yttrium subgroup was completely separated from the cerium subgroup.

### 2.2.2. The Cerium Subgroup

For elution of the cerium subgroup, use was made of lanthanum, the most strongly adsorbed element of the cerium subgroup elements neodymium to lanthanum, and thus the last to be eluted. A solution containing 1 mg of lanthanum was adsorbed onto the resin from 50 ml of a mixture of 5 per cent 7 M nitric acid and 95 per cent methanol, and the resin was washed with a further 150 ml of adsorbing eluant. The removal of the yttrium subgroup was simulated as follows: the resin was washed with 250 ml of a mixture of 45 per cent 7 M nitric acid and 55 per cent methanol, and the lanthanum

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was eluted with 400 ml of 8 M nitric acid, 16 ml fractions of the eluate being collected with an automatic fraction collector. Lanthanum was determined in the fractions with xylenol orange<sup>12</sup>. The elution curve is shown in Figure 4.

Lanthanum was completely eluted with 170 ml of 8 M nitric acid solution. The elements of the cerium subgroup, neodymium to lanthanum, would be eluted completely before the complete elution of lanthanum.

### 2.3. Removal of Thorium

Thorium is readily adsorbed with the rare-earth elements onto anion-exchange resins from mixtures of nitric acid and methanol<sup>3</sup>. As a check on whether the thorium was being eluted with the rare-earth elements, 10 mg of thorium was adsorbed from a mixture of 5 per cent 7 M nitric acid and 95 per cent methanol, and the resin was then washed with 150 ml of adsorbing eluant, followed by 250 ml of a mixture of 45 per cent 7 M nitric acid and 55 per cent methanol and by 170 ml of 8 M nitric acid. In each eluate, thorium was determined spectrophotometrically with thoria<sup>12</sup>. No thorium was found to be present in any of the eluates. The thorium can be eluted from the resin by washing with 300 ml of water<sup>10</sup> so that the resin is not poisoned nor its capacity reduced with continuous use.

### 2.4. Effect of Phosphoric Acid

Because the methanol content for adsorption must be 95 per cent, the maximum concentration of phosphoric acid permissible in the adsorption solution is 0,3 M. Synthetic solutions of the rare-earth elements in the presence of 0,3 M phosphoric acid were taken through the procedure outlined in Section 2.5, and the total rare-earth elements in the cerium and yttrium subgroups were determined with xylenol orange<sup>12</sup>. As shown in Table 2, the presence of 0,3 M phosphoric acid does not affect the separation and recovery of the rare-earth elements.

### 2.5. Recovery of Rare-earth Elements from a Synthetic Solution

Synthetic solutions of the following compositions were prepared: lanthanum 1,5 mg, neodymium 1 mg, samarium 0,15 mg, yttrium 0,15 mg, and ytterbium 0,05 mg, with and without the following base metals: carborundum 50 mg, ferric oxide 100 mg, lime 100 mg, magnesia 50 mg, scandium 0,1 mg, and thorium 0,1 mg. The solutions were evaporated to dryness, and, after the solids had been redissolved in 50 ml of a mixture of 5 per cent 7 M nitric acid and 95 per cent methanol, the solutions

TABLE 2

*Recovery\* of rare-earth elements*

Amount of yttrium subgroup	0,35 mg
Amount of cerium subgroup	2,5 mg
Eluant for yttrium subgroup	250 ml of 45 % 7 M HNO <sub>3</sub> + 55 % CH <sub>3</sub> OH
Eluant for cerium subgroup	200 ml of 8 M HNO <sub>3</sub>

Subgroup	Elements	Separated from	Recovery
Yttrium	Sm, Y, Yb	-	99 (3)
		0,3 M H <sub>3</sub> PO <sub>4</sub>	98 (2)
		Fe, Al, Ca, Mg, Th, Sc	97 (3)
Cerium	La, Nd	-	96 (3)
		0,3 M H <sub>3</sub> PO <sub>4</sub>	92 (2)
		Fe, Al, Ca, Mg, Th, Sc	99 (3)

( ) Number of determinations

\*In this report, *recovery* means amount determined as a percentage of the amount present

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were passed through 32 cm columns of BIORAD AG1-X8 (200 to 400 mesh) resin in the nitrate form. The resins were washed with a further 150 ml of adsorbing solution for the removal of scandium and the base metals, and this was followed by elution of the yttrium subgroup elements with 250 ml of a mixture of 45 per cent 7 M nitric acid and 55 per cent methanol. The cerium subgroup elements were eluted with 180 ml of 8 M nitric acid. The total rare-earth elements in each subgroup were determined in the appropriate eluate with xylenol orange<sup>12</sup>. As shown in Table 2, the recoveries ranged from 96 to 99 per cent.

2.6. Analysis of Reference Sample NIM 18/69

A carbonate sample, NIM 18/69, was analysed by the procedure outlined in the Appendix. The results are shown in Table 3. For purposes of comparison, the results obtained at NIM by instrumental neutron-activation analysis<sup>14</sup> and emission spectrography<sup>15</sup> and at the Council for Scientific and Industrial Research by spark-source mass spectrometry<sup>15</sup> are quoted.

TABLE 3

*Precision and accuracy of determination in carbonatite sample NIM 18/69*

Rare earth	Preferred value <sup>15</sup> and R.S.D., %	Range after rejecting outliers <sup>15</sup>	Mean <sup>15</sup> values* and R.S.D.	SSMS <sup>15</sup>	SPEC <sup>15</sup>	INAA <sup>14</sup>	Proposed method
Ce <sub>2</sub> O <sub>3</sub>	0,45 (10)	0,40 to 0,51 %					0,39 %
Nd <sub>2</sub> O <sub>3</sub>	0,13 (30)	0,096 to 0,18 %					0,21 %
Eu <sub>2</sub> O <sub>3</sub>	49 (10)	44 to 56 p.p.m.					60 p.p.m.
Y <sub>2</sub> O <sub>3</sub>	234 (24)	161 to 315 p.p.m.					340 p.p.m.
La <sub>2</sub> O <sub>3</sub>			0,26 % (25)	0,25 %	0,29 %	0,34 %	0,27 %
Pr <sub>2</sub> O <sub>3</sub>			528 p.p.m. (50)	468 p.p.m.	749 p.p.m.	659 p.p.m.	470 p.p.m.
Sm <sub>2</sub> O <sub>3</sub>				238 p.p.m.	280 p.p.m.	295 p.p.m.	280 p.p.m.
Gd <sub>2</sub> O <sub>3</sub>				140 p.p.m.	117 p.p.m.	ND	120 p.p.m.
Tb <sub>2</sub> O <sub>3</sub>			14† p.p.m.	14 p.p.m.	<2 p.p.m.	ND	13 p.p.m.
Dy <sub>2</sub> O <sub>3</sub>			59 p.p.m. (58)	66 p.p.m.	42 p.p.m.	103 p.p.m.	50 p.p.m.
Ho <sub>2</sub> O <sub>3</sub>			6† p.p.m.	9 p.p.m.	<1	189 p.p.m.	6 p.p.m.
Er <sub>2</sub> O <sub>3</sub>			10† p.p.m.	19 p.p.m.	<1	ND	15 p.p.m.
Tm <sub>2</sub> O <sub>3</sub>			3† p.p.m.	2 p.p.m.	<2	ND	1,4 p.p.m.
Yb <sub>2</sub> O <sub>3</sub>				10 p.p.m.	<2	ND	10 p.p.m.
Lu <sub>2</sub> O <sub>3</sub>			1† p.p.m.	1 p.p.m.	<1	ND	<1

Notes:

- R.S.D. Relative standard deviation
- SSMS Spark-source mass spectrometry
- SPEC Emission spectrography
- INAA Instrumental neutron-activation analysis
- ND Not determined
- \* Insufficient values for preferred mean
- † Mean values based on limited data

The differences between the preferred or mean values for the cerium and yttrium subgroups and those obtained in this investigation are within the differences to be expected at the 95 per cent confidence limits when account is taken of the relative standard deviations for the preferred or mean values and the combined separation-spectrographic procedure (approximately 10 per cent). The results obtained for the yttrium subgroup after the more abundant cerium subgroup has been separated, resulting in the removal of the spectral interference of these abundant elements, would have a higher degree of accuracy. Comparison with the available mean values shows that the emission-spectrographic results are now closer both to the mean values and to those obtained from spark-source mass spectrometry.

The results for the three instrumental techniques for the determination of the individual rare-earth elements given in Table 3 indicate, in general, a reasonably close measure of agreement.

### 3. DISCUSSION

The one-column anion-exchange separation of the rare-earth elements from scandium and base metals, followed by the separation of the rare-earth elements into subgroups of cerium and yttrium, can be used in place of the two-column cation separation of total rare-earth elements from base metals followed by anion separation of the rare-earth elements from scandium<sup>1</sup>. The former method is described in the Appendix.

The more abundant cerium subgroup elements can be determined direct on the sample solution, after dissolution or after ion-exchange separation in the appropriate eluate, by emission spectrography using the induction-coupled plasma torch. The traces of the yttrium subgroup elements can be precipitated in the eluate after ion-exchange separation by 8-hydroxyquinoline (with alumina as a carrier) and can then be ignited to the oxides for determination by a d.c. arc technique<sup>1</sup>.

The only base metal that may be present after the separation in small amounts (less than 10 per cent of that present in the sample) is calcium. Its presence does not affect spectrographic determination of the rare-earth elements by induction-coupled plasma torch, nor spectrophotometric determination with xylenol orange. In the precipitation with 8-hydroxyquinoline, calcium is not precipitated and will therefore be separated from the rare-earth elements that are to be determined by the d.c. arc technique. As the internal standard (scandium) used in the spectrographic procedure is incorporated into the alumina carrier, the variations in the normally small mass of the yttrium subgroup will not seriously affect the concentration of scandium in the total mass of alumina and rare-earths, and the accuracy of measurement will be better.

The cerium subgroup, by virtue of the higher concentration of these elements, would normally be determined by a solution emission-spectrographic procedure, the internal standard being added to the eluate to provide a given constant concentration. Should it be necessary for one element of the subgroup to be determined by the d.c. arc procedure, it would be more appropriate to precipitate the rare-earth elements with pure alumina, to homogenize the precipitate after ignition, and then to dilute a portion with an equal portion of alumina and internal standard. This would eliminate variation in internal standard with varying masses of rare-earths, and would reduce variations in the concentration of the matrix. Some loss of sensitivity would have to be tolerated for an improvement in accuracy.

If total rare-earth elements are required, these elements, after adsorption from a mixture of 5 per cent 7 M nitric acid and 95 per cent methanol and separation from scandium and base metals, can be eluted as a group with 8 M nitric acid, the less strongly adsorbed yttrium subgroup being completely eluted before the complete elution of the cerium subgroup. The total rare-earth elements can then be determined spectrophotometrically with xylenol orange<sup>12</sup>.

The procedure is not suitable for individual rare-earth elements in phosphoric acid, since the methanol content of the eluant for adsorption must be 95 per cent and the maximum phosphoric acid concentration in the adsorbing solution can therefore be only 0,3 M. Individual rare-earth elements can be separated as a group<sup>16</sup> from phosphoric acid solutions up to 6 M by adsorption onto BIORAD AG50 W-X8 (200 to 400 mesh). The two subgroups can then be separated by the anion-exchange separation proposed in this investigation.

### 4. CONCLUSION

A procedure has been developed for the one-column anion-exchange separation of rare-earth elements from scandium and base metals, and for the separation of the rare-earth elements into the cerium and yttrium subgroups so that the limits of their determination can be reduced. The individual rare-earth elements can be determined spectrographically by use of the induction-coupled plasma torch for concentrations that are sufficiently high, or of a d.c. arc technique for traces of the heavier yttrium subgroup. The comparative analysis of these elements is good. The total rare-earth elements in the subgroups can be determined spectrophotometrically with xylenol orange.

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## APPENDIX

THE SEPARATION AND DETERMINATION OF RARE-EARTH ELEMENTS IN SILICATE ORES  
(LABORATORY METHOD No. 57/14)

## E.1. Rare earths

## E.2. Silicon, rare earths in

## 1. OUTLINE

After the sample has been fused with potassium bifluoride, the insoluble rare-earth elements and calcium fluorides are filtered off and dissolved. These elements are then separated on an anion-exchange resin from scandium, calcium, and the base metals associated with silicate ores. The rare-earth elements are separated into the cerium and yttrium subgroups, and the cerium subgroup elements are determined by emission spectrography using the induction-coupled plasma torch. The yttrium subgroup elements are precipitated with 8-hydroxyquinoline, alumina being used as the carrier. After ignition to the oxides, these rare-earths are determined spectrographically by a carrier-distillation technique.

## 2. APPLICATION

The separation procedure is applicable to a wide range of silicate ores containing rare-earth elements from trace amounts to major concentrations in a 1 g sample.

## 3. REAGENTS

## (1) Nitric Acid, 7 M

Dilute 488 ml of Merck A.R.-grade nitric acid to 1000 ml with water.

## (2) Nitric Acid, 8 M

Dilute 557 ml of Merck A.R.-grade nitric acid to 1000 ml with water.

## (3) Methanol

## (4) Mixture of 7 M Nitric Acid (45 per cent) and Methanol (55 per cent)

Mix 450 ml of 7 M nitric acid with 550 ml of methanol.

## (5) Mixture of 7 M Nitric Acid (5 per cent) and Methanol (95 per cent)

Mix 25 ml of 7 M of nitric acid with 475 ml of methanol.

## (6) Hydrofluoric Acid, 1 per cent (v/v)

Transfer 400 ml of water to a plastic bottle, add 4 ml of hydrofluoric acid, and mix.

## (7) Anion Resin

BIORAD AG1-X8 (200 to 400 mesh) chloride form.

## 4. PREPARATION OF RESIN

- a. Transfer approximately 100 g of BIORAD AG1-X8 (200 to 400 mesh) to an 800 ml beaker. Add 700 ml of water and stir. Allow to settle, and then decant the colloidal particles. Twice repeat the addition of water and decantation.
- b. Transfer the resin to a large column and convert to the nitrate form by sequential washing with 1 M to 7 M nitric acid in 100 ml portions. Continue washing with 7 M nitric acid until no further chloride is detectable in the eluate.
- c. Rinse the resin with methanol, remove from the column, and dry overnight exposed to the air.
- d. Dry the resin in an air-oven at 70°C for 3 hours and store in a screwtop bottle.

## 5. PROCEDURE

The procedure is described in three sections: fusion of the sample, separation of the rare-earth elements, and determination of the rare-earths.

## 5.1. Fusion of the Sample

- a. Transfer 1 g of finely ground sample into a platinum crucible. Place the crucible in a muffle furnace and heat it to 900°C for 10 minutes. Cool.
- b. Carefully fuse the residue in the crucible with 10 g of potassium bifluoride. Place the crucible over a low flame, and gradually increase the heat of the flame. Fuse over a full flame until the melt is a clear red-hot molten mass. As the melt cools, swirl it so that it forms a thin coating on the sides of the crucible.

## IMPROVED ION-EXCHANGE SEPARATION

- c. Transfer the cold crucible to a 250 ml plastic beaker and add 180 ml of hot water. Add 20 ml of hydrofluoric acid. Using a pipette, add 0,5 ml of hydrochloric acid, and mix with a plastic rod. Digest on a steam-bath with occasional stirring until the soluble salts have been completely dissolved and the rare-earth fluorides have been precipitated. Remove the crucible and rinse. Digest on the steam-bath for 2 hours and cool. Add 0,5 g of cellulose powder, stir, and filter through a Whatman no. 42 filter paper, using a plastic funnel and beaker. Wash eight times with a cold washing solution of 1 per cent hydrofluoric acid, and finally rinse with water.
- d. Transfer the filter paper and precipitate to a 400 ml squat beaker. Add 20 ml of nitric acid and 5 ml of perchloric acid, cover with a watch-glass, and transfer the beaker to a hot-plate. Bring to fumes of perchloric acid. Cool, rinse the cover and the sides of the beaker, and transfer the contents to a 150 ml beaker. Evaporate to a moist state (Note 1).
- e. Remove the watch-glass and evaporate just to dryness.
- f. Add 2,5 ml of 7 M nitric acid and swirl the beaker to dissolve the salts. Add 47,5 ml of methanol and mix thoroughly.

### 5.2. Separation of the Rare-earth Elements

#### 5.2.1. Removal of Scandium and Base Metals

- a. Prepare an anion-exchange column by placing a water slurry of AG1-X8 (200 to 400 mesh) in the nitrate form in a borosilicate glass column 1 cm in diameter and with a resin bed of 32 cm. Rinse the column with 50 ml of the mixture of 5 per cent 7 M nitric acid and 95 per cent methanol, and drain to the top of the resin.
- b. With the aid of a glass rod, run the sample solution down the sides of the column, taking care not to disturb the surface of the resin. Allow the solution to drain to the top of the resin (Note 2).
- c. Elute the scandium and base metals by washing with a further 130 ml of the same nitric acid-methanol mixture, allowing the solution to drain to the top of the resin.

#### 5.2.2. Separation of the Yttrium Subgroup

Elute the yttrium subgroup rare-earth elements with 250 ml of the mixture of 45 per cent 7 M nitric acid and 55 per cent methanol, carefully adding the eluting solution with the aid of a glass rod. Collect the eluate in a 400 ml beaker, and allow the solution to drain to the top of the resin. Proceed as in Section 5.3.

#### 5.2.3. Separation of the Cerium Subgroup

Elute the cerium subgroup rare-earth elements with 200 ml of 8 M nitric acid, carefully adding the eluting solution with the aid of a glass rod. Collect the eluate in a 400 ml beaker, and allow the solution to drain to the top of the resin. Proceed as in Section 5.3 (Note 3).

### 5.3. Determination of the Rare-earth Elements

The analysis for the rare-earth elements should now proceed as follows.

#### 5.3.1. High Concentrations, Cerium Subgroup

For high concentrations of rare-earth elements in the cerium subgroup (all usually high in South African samples) and the yttrium subgroup, the rare-earth elements can be determined by emission spectrography using a d.c. plasma arc or an induction-coupled plasma torch.

#### 5.3.2. Low Concentrations, Yttrium Subgroup

For low concentrations of rare-earth elements in the yttrium subgroup, the rare-earth elements can be precipitated with alumina containing scandium as internal standard and can be determined by a d.c. arc technique<sup>1</sup>.

#### 5.3.3. Low Concentrations, Cerium Subgroup

For low concentrations of one or more rare-earth elements in the cerium subgroup, the rare-earth elements can be precipitated with alumina (no scandium), separated, and ignited, and then a portion of ignited oxide can be mixed with an equal portion of alumina containing scandium as internal standard and the rare earths can be determined by a d.c. arc technique<sup>1</sup>.

## IMPROVED ION-EXCHANGE SEPARATION

### 6. NOTES

- (1) If the perchloric acid turns dark brown, cool it slightly, add more nitric acid, and evaporate to fumes again.
- (2) Disturbance of the resin during the addition of solutions or washing may result in channelling, which would lower the efficiency of the resin.
- (3) To clean the AG1-X8 (200 to 400 mesh) anion resin, wash it with 300 ml of water and allow it to drain.

### 7. REFERENCE

1. JONES, E.A., *et al.* The separation and determination of trace and minor amounts of individual rare earths in silicates. Johannesburg, National Institute for Metallurgy, *Report no. 1428*. 22nd May, 1972.