

Separation of Scandium(III) as Citrate Complex by Extraction with Aliquat 336S

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Scandium(III) has been quantitatively extracted with 0.1 *M* Aliquat 336S in xylene between pH 4 and 8 from 0.001 *M* citric acid medium and stripped with 0.5 *M* hydrochloric acid. It is determined spectrophotometrically at 525 nm with alizarin red S. The separation of scandium in binary, ternary and quaternary combination with a large number of metal ions, some of them associated with it in ores, fission products etc. is also described.

Liquid anion exchangers like Amberlite LA-1¹, methyltriethylammonium chloride² and triethylamine³ have been recently used for the extraction of scandium from sulphate medium¹, as EDTA², malonate¹ and succinate³ complexes. However, no systematic efforts have been made to extract scandium from citric acid solutions. As a matter of fact this medium offers better possibilities of separations. Therefore this note presents results of studies on extractive separation of scandium with Aliquat 336S from citrate media.

The apparatus used was similar to one described earlier⁴.

The stock solution of scandium was prepared by dissolving scandium oxide (1.77 g) in nitric acid (100 ml). The solution was boiled till it was clear, diluted to one litre with distilled water and standardised complexometrically with EDTA using xylenol orange as an indicator⁵. This solution contained 1.056 mg/ml of scandium. The diluted solution containing 25.6 $\mu\text{g/ml}$ of scandium was prepared by forty-fold dilution.

Solutions of Aliquat 336S (2.5 *M*) (General Mills Ltd. England), Amberlite LA-1 (1.5 *M*) or LA-2 (2.0 *M*) (Rhone and Hass Co., USA), and triethylamine (2.75 *M*) (Riedel Haen. Germany) were prepared from samples as received in suitable solvents. The liquid anion exchangers were converted into citrate forms by equilibrating equimolar solutions (equal volumes) of anion exchanger and citric acid (Sambhai Merck) for 10 min. A 0.1% aqueous solution of Alizarin redS (E Merck) was used. The buffer solution of pH 3.5 was prepared by dissolving potassium hydrogen phthalate (10.423 g) in distilled water (250 ml) containing 0.1 *M* hydrochloric acid (7.5 ml) and diluting the total volume to one litre.

General procedure

An aliquot of solution containing 52.5 μg of scandium was mixed with 0.001 *M* citric acid solution (5 ml). The pH of the resulting solution was adjusted to 5.5 with dil. sodium hydroxide or citric acid. The solution was made up to 10 ml, 0.1 *M* Aliquat 336S solution (10 ml) in xylene added to it and the mixture shaken on wrist action flask shaker for 10 min. Two phases were allowed to separate. In order to strip scandium, organic phase was equilibrated with 0.5 *M* hydrochloric acid. The acid solution containing the metal ion was evaporated almost to dryness, mixed with buffer solution (5 ml) of pH 3.5 and 0.1% aq. alizarin redS (2 ml). The total volume of the solution was made up to 25 ml with distilled water and the absorbance of the violet red coloured complex measured spectrophotometrically at 525 nm against the reagent blank. The amount of scandium was computed from the calibration curve⁶.

The extraction of scandium was carried out in the pH range of 1.0-9.0. Scandium could be quantitatively extracted in the pH range 3.5-8.0 with Aliquat 336S or in the pH range 3.0-3.5 with Amberlite LA-1. However, Amberlite LA-2 and triethylamine showed incomplete extraction (max. 41%). Therefore Aliquat 336S was selected as an extractant.

Diluents such as benzene, toluene, xylene, hexane, cyclohexane, carbon tetrachloride chloroform etc., were tested. The extraction was quantitative in the presence of all diluents except chloroform (65.3%). Emulsion formation with hexane and cyclohexane below 1:1 ratio could be mitigated by keeping volume ratio 1:1. Xylene was found to be the most useful diluent and hence it was used as a diluent.

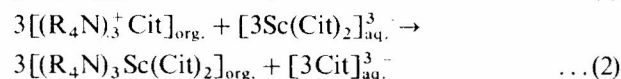
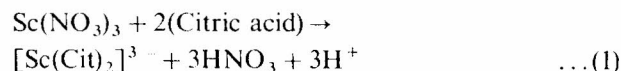
The results of varying Aliquat 336S concentrations showed quantitative extraction with 10×10^{-2} *M* solution of Aliquat 336S in xylene. The extraction was also quantitative with 7.5×10^{-2} *M* solution of Aliquat 336S but the magnitudes of corresponding distribution ratios were 2.03, 7.1, 15.9 and 61.3 with Aliquat 336S concentrations of 2.5×10^{-2} *M*, 3.75×10^{-2} *M*, 5×10^{-2} *M* and 7.5×10^{-2} *M*.

Scandium was extracted at pH 5.5 with varying concentrations of the citric acid (1.0×10^{-4} to 10×10^{-4} *M*) with 0.1 *M* Aliquat 336S in xylene. The extraction of scandium was quantitative at pH 5.5 at citric acid concentration greater than 7×10^{-4} *M*. The optimum concentration of citric acid used was 1×10^{-3} *M*.

Scandium was stripped with varying concentrations of hydrochloric, hydrobromic, nitric and sulphuric

acids. The stripping was complete with 0.1 to 8 *M* hydrochloric, 0.5-8 *M* hydrobromic, 1-8 *M* nitric acid or 0.5-8.0 *M* sulphuric acids, but it was poor with alkalis and salts. The lower concentration of sulphuric acid was not preferred for stripping on account of the formation of anionic sulphato complexes¹ which in turn were extracted. At any concentration of hydrochloric acid, no anionic chloro complexes were formed. Therefore it was found useful not only as the stripping agent⁷, but also for the purpose of separations. Thus 0.5 *M* hydrochloric acid was used as the stripping agent.

The extraction mechanism may be represented by Eqs (1) and (2):



This was confirmed by plotting $\log D$ versus $\log [\text{Aliquat 336S}]$ at a fixed [citric acid] and $\log D$ versus $\log [\text{citric acid}]$ at a fixed [Aliquat 336S]. The slopes of these linear plots were 2.98 and 1.8 respectively, confirming the probable composition of extracted species as $[(\text{R}_4\text{N})_3\text{Sc}(\text{Cit})_2]_{\text{org.}}$. Due to the absence of chromogenic group in the extracted species, conventional mol ratio method or continuous variation of mol fraction method could not be adopted to ascertain the composition of the extracted species.

Separation of scandium from binary mixtures: It is interesting at this stage to compare the distribution ratios of various metal ions with the distribution ratio of scandium under identical extraction conditions. Alkali and alkaline earths had small distribution ratios while distribution ratio of scandium was high (> 999.0), consequently the separation factor was very large, predicting best separations. Bismuth, germanium, titanium and thorium had very high distribution ratios compared to that of scandium hence separation factor was almost unity, indicating thereby no possibility of separation. However such separations were accomplished by resorting to chloride and sulphate media. Antimony, iron (III), zirconium, uranium and tungsten had lower distribution ratios, consequently separation factor was large hence best separations could be achieved.

Scandium was separated from alkali and alkaline earth, thallium(I), silver(I), iron(II) as these elements did not form any citrato complexes and were not extracted. An examination of distribution ratios (D)† of metal ions shows that manganese (0.5), cobalt (2.2), nickel (1.05), copper (3.5), zinc (0.65), cadmium (0.90),

lead (0.85), cerium(III) (0.95), yttrium (0.09) and lanthanum (0.075) formed weak citrato complexes, which dissociated in the presence of water and hence were scrubbed with water before stripping out scandium with 0.5 *M* hydrochloric acid. Scandium was separated from bismuth (999), antimony (99.0), germanium (999.0), iron(III) (149.9), gallium (787), uranium (VI) (165.7) and tungsten (141.5) by stripping first scandium with 5 *M* hydrochloric acid. These elements were reextracted into the organic phase as their chloro complexes⁷. They were latter stripped with dil. sulphuric acid or suitable alkalis.

Scandium was separated from zirconium (49.0) in sulphate medium, wherein scandium was first stripped with 0.5 *M* sulphuric acid while extracted sulphato complex of zirconium was stripped with 2 *M* hydrochloric acid. The separation of scandium from indium (0.515) and thorium (149.0) was carried out in nitrate media⁸, wherein after extraction, scandium was stripped with 5 *M* nitric acid followed by stripping of indium and thorium with 1.0 *M* sulphuric acid.

Separation of tertiary mixtures: In general the metal ions in ternary mixtures were co-extracted and the individual metals separated by stripping as follows (see also Table 1).

(i) In the ternary system yttrium + scandium + zirconium, yttrium was stripped with water, scandium with 0.5 *M* sulphuric acid and zirconium with 2 *M* hydrochloric acid (Table 1).

(ii) For lanthanum + scandium + thorium, lanthanum was stripped with water, scandium with 5 *M* nitric acid and thorium with 2 *M* hydrochloric acid.

Table 1—Separation of Scandium from Multicomponent Mixtures

Mixture	Taken (μg)	Found (μg)	Stripping agent (<i>M</i>)
Ternary mixtures			
Y +	379.0	379.0	H ₂ O
Sc +	52.5	52.5	0.25 H ₂ SO ₄
Zr(IV)	103.4	103.3	2HCl
La(III) +	507.8	507.7	H ₂ O
Sc +	52.5	52.5	5HNO ₃
Th(IV)	110.5	110.5	2HCl
Mn(II) +	674.5	673.9	H ₂ O
Mo(VI) +	100.0	100.0	0.25NH ₃
Sc	52.5	52.5	0.5H ₂ SO ₄
Ce(III) +	725.8	724.7	H ₂ O
Sc +	52.5	52.4	5HCl
U(VI)	152.3	152.2	0.5NaOH
Quaternary mixture			
Mn(II) +	675.5	675.0	H ₂ O
W(VI) +	225.4	225.0	0.1 NaOH
Sc +	52.5	52.5	5HCl
Fe(III)	220.7	220.6	2HNO ₃

†In the subsequent discussion D values for metal ions are given in parentheses against each metal ion.

(iii) In case of manganese + molybdenum + scandium, the ions were separated after extraction, by stripping manganese with water, molybdenum with 0.1 *M* sodium hydroxide and scandium with 0.5 *M* sulphuric acid.

(iv) In case of cerium + scandium + uranium, cerium(III) was washed with water, scandium with 5 *M* hydrochloric acid and uranium with 0.5 *M* sodium hydroxide.

(v) For the separation of manganese + tungsten, scandium and iron, manganese was stripped with water, tungsten with 0.1 *M* sodium hydroxide and scandium with 5 *M* hydrochloric acid and iron with 2 *M* nitric acid.

Analysis of scandium in a mineral: About 1.2g of ore was opened as per earlier procedure⁹. To an aliquot of solution (5 ml), 0.01 *M* citric acid (5 ml) was added and the pH adjusted to 5.5. It was extracted with Aliquat 336S in xylene. Those of the elements which were not extracted remained behind in the aqueous phase. Manganese, tungsten and iron were coextracted with scandium. They were separated as given in (v) above.

The results showed that the amount of scandium was 173 ppm against standard value of 174 ppm.

The separation of scandium from zirconium, thorium, cerium and yttrium is important as these elements are associated in minerals. The separation of scandium from uranium, silver, antimony, bismuth is equally important in fission products. The optimum range of extraction is 25-1300 μg of scandium. The proposed method is rapid, simple and selective.

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