

Solvent extraction and determination of scandium(III) with Cyanex272 as an extractant

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A novel method for the solvent extraction separation of scandium(III) at pH 5.0 using 5×10^{-4} M Cyanex272 has been developed. Scandium(III) has been stripped from the organic phase with 1.0 M HNO₃ and determined spectrophotometrically as its complex with Arsenazo(III) at 675 nm. The method developed has been applied for selective separation of scandium(III) from some closely associated elements, viz., La(III), Y(III), Ce(IV), Zr(IV), Dy(III), Nd(III), Pr(III), Yb(III), etc. in their binary mixtures. The method permits mutual separation of scandium(III)-yttrium(III)-lanthanum(III) and scandium(III)-yttrium(III)-cerium(IV) and for recovery of scandium(III) from USGS standard soil sample GXR-2, Japanese stream sediment sample Jsd-3 and ashes from Hutti gold mines in Karnataka. The method presented is simple, rapid and selective for isolation of scandium(III) from complex mixtures. The method developed is reproducible with a relative standard deviation of 0.4%.

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The purification of scandium has much significance as minerals containing it as a major element are few and rare. HDEHP [bis(2-ethylhexyl)phosphoric acid]¹⁻³ has been the most commonly used extractant for recovery of scandium from scrap, waste and residues. The other extractants reported are PC-88A [2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester]⁴, Cyanex923 [a mixture of straight chain alkylated phosphine oxides]⁵ and PIA-8 [bis(2-ethylhexyl) phosphinic acid]⁶. Extraction mechanism of scandium(III) has been studied from sulphuric acid media with Cyanex272 [bis(2,4,4-trimethylpentyl)phosphinic acid]⁷ and its extractability compared with Cyanex302 [bis(2,4,4-trimethylpentyl)monothiophosphinic acid] and Cyanex301 [bis(2,4,4-trimethylpentyl) dithiophosphinic acid]⁸. Incomplete stripping of scandium^{7,8} although easy in comparison to HDEHP and PC-88A, high reagent concentration⁶, and difficulties in stripping scandium⁵ were the limitations of these methods. No attempts have so far been made

to systematically study the influence of various parameters affecting extraction of scandium(III) with Cyanex272 for optimizing the conditions for its quantitative extraction and recovery from complex matrices. Hence in this note, a method free from the above mentioned drawbacks using Cyanex272 is reported. It also permits mutual separation of scandium-yttrium-lanthanum.

Experimental

A Digispec 110 D spectrophotometer (Feedback, India Ltd) with matched 10 mm glass cuvettes, digital pH meter (Elico Private Ltd, India) with combined glass and calomel electrode (Toshniwal -Mollar, India) and a wrist action flask shaker (General Trading Corporation, India) were used.

The stock solution of scandium(III) was prepared from scandium oxide (A.R. grade) and standardized complexometrically⁹. A working solution containing 30 $\mu\text{g cm}^{-3}$ of scandium(III) was prepared by appropriate dilution. Cyanex272 supplied by Cytec Canada as a gift sample was used without further purification. Arsenazo(III) (Loba Chemie) was used as a 0.1% aqueous solution. All the reagents used were of A.R. grade.

Equal volumes of aqueous phase containing scandium(III) (30 μg) and 5×10^{-4} M Cyanex272 in xylene were equilibrated on a wrist action flask shaker for 10.0 min. After phase separation, scandium was stripped from the organic phase with 10 cm^3 1.0 M nitric acid and determined spectrophotometrically in the aqueous phase with Arsenazo(III) at 675 nm¹⁰. A set of six replicate determinations using 30 μg – 50 μg of scandium(III) gave a standard deviation of 0.4%. Distribution ratio (*D*) was calculated from the percentage of scandium(III) extracted in the organic phase.

Results and discussion

The extraction of scandium(III) was studied from pH 1.0-9.0 with 5×10^{-4} M Cyanex272 in xylene. As Cyanex272 is a liquid cation exchanger with $pK_a = 6.4$, the cation exchange mechanism responsible for the extraction of scandium(III) is influenced by the pH of the aqueous phase. The extraction of scandium(III) increased with the increase in pH of the

aqueous phase up to $pH = 5.0$ and decreased beyond $pH = 6.0$. The maximum extraction of scandium(III) at $pH = 5.0$, may be attributed to the extraction of its cationic species at this pH . Thus an optimum $pH = 5.0$ was selected for further studies as scandium(III) was quantitatively extracted at this pH .

Benzene, toluene, xylene, cyclohexane, chloroform and carbon tetrachloride were used as diluents for Cyanex272 and the corresponding percentage extraction of scandium(III) was 91.2, 86.3, 99.4, 87.9, 87.9, and 90.2 respectively. The distribution ratio of scandium(III) was maximum (165.7) when xylene was used as a diluent. Hence, further studies were carried out with xylene as a diluent.

The concentration of Cyanex272 in xylene was varied from $(0.9-5.0) \times 10^{-4} M$. The extraction of scandium increased with increase in concentration of extractant and was quantitative with $5.0 \times 10^{-4} M$ Cyanex272 in xylene. Hence, for further studies $5.0 \times 10^{-4} M$ Cyanex272 in xylene was used.

The nature of extracted species of scandium(III) with the extractant was ascertained using slope analysis. The distribution ratio (D) at $pH 5.0$ for scandium(III) was evaluated from $0.9 \times 10^{-1} - 5 \times 10^{-4} M$ Cyanex272 in xylene. A plot of $\log [D]$ versus $\log [Cyanex272]$ was a straight line graph with a slope of 2.4. This indicates a mole ratio of scandium(III) to Cyanex272 as 1:2.5. Similar stoichiometric ratio of scandium(III):Cyanex272 has been reported from sulphuric acid media⁷.

Hydrochloric acid (0.5-8.0 M), nitric acid (0.5-8.0 M) and sulphuric acid (0.5-3.0 M) were studied as stripping agents. The stripping of scandium(III) was quantitative (99.4%) with 1.0 M nitric acid and 8.0 M hydrochloric acid. 1.0 M nitric acid was selected as the stripping agent.

Extraction of scandium(III) was studied for 0.33, 1.0, 5.0 and 10.0 min. with $5.0 \times 10^{-4} M$ Cyanex272 in xylene, and the corresponding percentage extraction was 96.1, 97.7, 98.4 and 99.4 respectively. A 10.0 min period of equilibration was considered sufficient for optimum extraction.

Effect of diverse ions on extraction of scandium(III)

Scandium(III) (30 μg) was extracted in the presence of other ions, under its optimum conditions. The tolerance limit was set as the amount of foreign ion causing $\pm 2\%$ error in the recovery (99.4%) of scandium(III). The elements Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} and Ti^{4+} were tolerated in 1:167 ratio, while Co^{2+} , Ni^{2+} , Zn^{2+} , V^{3+} and V^{5+} were tolerated in 1:33 ratio, Cr^{6+} , Mn^{2+} , Y^{3+} and La^{3+} in 1:17 ratio and Mo^{6+} and Ce^{4+} in 1:8 ratio. The ratio for tolerance of Zr^{4+} and Fe^{3+} was 1:3.3 and 1:1.7 respectively while that for Dy^{3+} , Nd^{3+} , Pr^{3+} and Yb^{3+} it was 1:1. Anions Cl^- , NO_3^- and SO_4^{2-} were tolerated in 1:167 ratio.

Separation of scandium(III) from binary and multicomponent mixtures

Scandium(III) was separated from some metal ions in binary mixtures. Scandium(III) was preferentially extracted under its the optimum extraction conditions leaving the other metal ion unextracted in the aqueous phase. Thus, a high separation factor β ($\beta = D_{Sc} : D_M$) for Ca(II) 4851, Mg(II) 3720, Co(II) 4039, Ni(II) 41084, Mn(II) 1878, Dy(III) 27434, La(III) 32968, Nd(III) 2997, Pr(III) 9901, Y(III) 66134, Yb(III) 1998, Ce(IV) 4761, Zr(IV) 2757, V(V) 557 and V(IV) 520 was achieved.

Some multicomponent mixtures containing scandium(III) were prepared (Table 1). In these mixtures, scandium(III) was extracted under its

Table 1— Separation of scandium(III) from multicomponent mixtures

| Metal ion | Amount taken (μg) | Aqueous phase | Extractant | Stripping agent | Chromogenic ligand (λ_{max}) | Recovery (%) ^a |
|-----------|--------------------------|---------------|--|-----------------|--|---------------------------|
| Sc(III) | 30 | $pH = 5.0$ | $5 \times 10^{-4} M$ Cyanex272 in xylene | 1 M HNO_3 | Arsenazo(III) (675nm) | 99.5 |
| Y(III) | 30 | $pH = 7.0$ | $5 \times 10^{-4} M$ Cyanex272 in xylene | 4 M HNO_3 | Arsenazo(III) (650nm) | 99.8 |
| La(III) | 30 | Unextracted | --- | --- | Arsenazo(III) (650nm) | 98.1 |
| Sc(III) | 30 | $pH = 5.0$ | $5 \times 10^{-4} M$ Cyanex272 in xylene | 1 M HNO_3 | Arsenazo(III) (675nm) | 99.0 |
| Y(III) | 30 | $pH = 7.0$ | $5 \times 10^{-4} M$ Cyanex272 in xylene | 4 M HNO_3 | Arsenazo(III) (650nm) | 99.8 |
| Ce(IV) | 100 | Unextracted | --- | --- | Arsenazo(III) (665nm) | 99.7 |

^a Average of triplicate analysis. R.S.D. < 0.4%

optimum extraction condition while yttrium(III) which remained unextracted in the aqueous phase was re-extracted¹¹. La(III) and Ce(IV) were not extracted under the extraction conditions of scandium(III) and yttrium(III).

Applications

Samples of USGS standard soil GXR-2, Japanese stream sediment Jsd-3 and ashes from Hutti goldmines in Karnataka (0.5 g of each) were treated with conc. HF and H₂SO₄ in 5:1 ratio at 150°C on hot plate. The residue was cooled and fused with 2.0 g of KHSO₄ for 45 min. The melt was extracted with HCl and made up to a suitable volume and scandium(III) was extracted as per general procedure. Comparing the results obtained with those by ICP-AES indicated 6.83 µg g⁻¹ scandium(III) as against the reported value of 6.88 µg g⁻¹ in USGS standard soil sample, 10.4 µg g⁻¹ scandium(III) in the Japanese stream sediment sample while the reported value was 10.5 µg g⁻¹ scandium(III). Ashes from Hutti gold mines contained 48.2 µg g⁻¹ scandium and 48.0 µg g⁻¹ scandium(III)

was found by the present method. Recovery of scandium(III) was 99.4 ± 0.4% in all these samples.

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