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

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Scandium was quantitatively extracted with 0.1 mol dm^{-3} Aliquat 336S in xylene at pH=6.0 from 0.01 mol dm^{-3} ascorbic acid. It was stripped with 1 mol dm^{-3} hydrochloric acid and determined as its complex with Arsenazo III. It was separated from binary mixtures by exploiting the difference in the extraction behavior from ascorbic acid. Several separations were accomplished by process of selective stripping with concentrated hydrochloric acid. Many interesting separations of scandium from associated elements like yttrium, thorium, uranium, and molybdenum have been carried out.

Solvent extraction separation methods for scandium with liquid anion exchangers from organic acid media are limited. Scandium was separated from solutions of EDTA,[1] malonic,[2] citric,[3] and succinic acids.[4] 4—5% of Amberlite LA-1,[2] Aliquat 336S[3,4] was used with xylene or benzene as the diluent. 0.05—0.1 mol dm^{-3} of organic acid was employed. At pH 2.5—4.5 extraction was carried out while stripping was done from 0.5—8 mol dm^{-3} of mineral acids. However iron(III), zirconium, vanadium (V), thorium, and molybdenum showed strong interference. Similar studies from sulphate[5,6] and nitrate media were also not effective in separating scandium.

In this paper a new method is proposed for extraction of anionic complex of scandium from ascorbic acid at pH 6.0 with 0.1 mol dm^{-3} Aliquat 336S. The chief advantage of the proposed method is the possibility of separation of scandium from large number of less common elements.

Experimental

Apparatus and Reagents. An ECIL spectrophotometer GS866C with matched 10 cm corex glass cuvettes and an ECIL pH meter with combined glass electrodes as well as wrist action flask shaker were used.

A stock solution of scandium was prepared by dissolving 1.50 g of scandium oxide in 100 cm^3 of boiling nitric acid. It was diluted to one liter with distilled water and was standardized complexometrically with EDTA using xylenol orange as an indicator.[8] It contained 1.045 mg cm^{-3} of scandium. The solution containing 40 μg cm^{-3} of scandium was prepared by dilution.

Aliquat 336S (General Mills Ltd., England), Amberlite LA-1 or LA-2 (Rohm and Hass Co., U.S.A.), trioctylamine (Riedel Haen, Germany), and Primene JMT (Rohm and Hass Co., U.S.A.) were used without further purification in the ascorbate form.[9]

General Procedure. To an aliquat of solution containing 40 μg of scandium, 5 cm^3 of 0.01 mol dm^{-3} ascorbic acid was added. The pH of the solution was adjusted to 6.0 with 0.01 mol dm^{-3} ammonia or ascorbic acid. The solution was diluted to 10 cm^3. It was transferred into a separatory funnel. Then 10 cm^3 of 0.1 mol dm^{-3} Aliquat 336S in xylene was added and the solution was shaken on a wrist action flask shaker for 15 minutes. The two phases were allowed to settle and separate. Scandium from the organic phase was stripped with 10 cm^3 of 1 mol dm^{-3} hydrochloric acid. Then 2.5 cm^3 of 8% ascorbic acid, 0.5 cm^3 of 13.6% sodium acetate trihydrate, and 2 cm^3 of 0.1% Arsenazo III were added in total volume of 25 cm^3 to develop blue color. The absorbance was measured spectrophotometrically at 670 nm against a reagent blank. The concentration of scandium was computed from the calibration curve.[10]

Results and Discussion

Extraction of Scandium as a Function of pH. The pH for the quantitative extraction of scandium was ascertained by extracting scandium at pH 1—8 with 4% solutions of various liquid anion exchangers in xylene (Fig. 1). At pH 6.0 the extraction was 15% with Amberlite LA-1 while it was less than 25% with

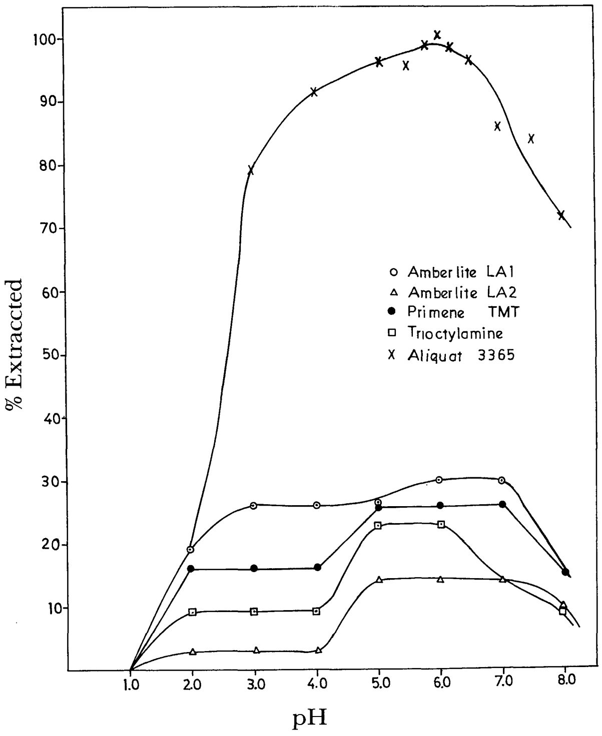

Fig. 1. Extraction of scandium as a function of pH with various liquid anion exchangers.

Primene JMT and Trioctylamine, and with Amberlite LA-1 it was 30%. Since only with Aliquat 336S extraction was quantitative this was used throughout the work.

Effect of Varying Concentration of Aliquat 336S. Scandium was extracted at pH 6.0 with 10 cm^3 of various concentrations and volume of 0.1 mol dm^{-3} Aliquat 336S in xylene. Scandium was quantitatively extracted with 10 cm^3 of 0.1 mol dm^{-3} Aliquat 336S in xylene (Table 1).

Effect of Varying Concentration of Ascorbic Acid. Scandium was extracted at pH 6.0 with 0.1 mol dm^{-3} Aliquat 336S in xylene from varying concentration of ascorbic acid (Table 2). The extraction was quantitative from 0.008 mol dm^{-3} concentration of ascorbic acid. 0.01 mol dm^{-3} ascorbic acid was used in subsequent work.

Effect of Various Diluents. Benzene, toluene, xylene, hexane, cyclohexane, chloroform, and carbon tetrachloride were used as the diluents for Aliquat 336S. The phase volume ratio was maintained as 1 : 1. The aromatic hydrocarbons proved to be efficient while hexane, chloroform, and carbon tetrachloride proved to be poor. Xylene was preferred as the diluent due to nontoxicity and clear phase separation (Table 3).

Period of Shaking. Scandium was extracted for different time of shaking ranging from 2.5, 10, 15, and 20 minutes. The corresponding extraction was 55, 90, 100, and 100% respectively. Hence 15 minutes period of equilibration was employed throughout the work.

Effect of Various Stripping Agents. After extraction, scandium was stripped with various acids and salts (Table 4). 1—8 mol dm^{-3} hydrochloric acid or 0.5—8 mol dm^{-3} sulfuric acid or nitric acid could strip scandium quantitatively. Hydrochloric acid was preferred as it facilitated direct spectrophotometric determination of scandium in the aqueous phase.

Separation from Binary Mixtures. The separation of scandium was attempted from binary mixtures. The alkali, alkaline earths, lead, or iron were not extracted with scandium. This in turn facilitated their separation. Cerium, yttrium, chromium, manganese, cobalt, nickel, copper, zinc, and aluminium formed weak complexes with ascorbic acid, but such complexes could be stripped with water before stripping of scandium with 1 mol dm^{-3} hydrochloric acid. However scandium was coextracted along with titanium, zirconium, hafnium, thorium, vanadium, or molybdenum. Therefore these separations were effected by stripping scandium with 8 mol dm^{-3}

Table 1. Effect of Varying Concentration and Volume of Aliquat 336S

Aliquat 336S 1×10^{-2} mol dm^{-3}	Vol cm^3	% Extracted	D
0.5	10	36	0.5
0.6	10	42	0.76
0.7	10	50	1.0
0.8	10	56	1.2
0.9	10	65	1.8
1.0	10	70	2.3
2.5	10	76	3.1
5.0	10	85	5.6
6.0	10	92	11.5
7.0	10	99.6	249
8.0	10	99.8	499
9.0	10	99.8	499
10.0	10	100	∞
10.0	4	70	2.4
10.0	6	80	4
10.0	8	92	11.5
10.0	15	100	∞

Table 2. Effect of Varying Ascorbic Acid Concentration

Ascorbic acid 1×10^{-3} mol dm^{-3}	% Extracted	D
0.5	25.0	0.33
0.6	32.0	0.47
0.7	40.0	0.66
0.8	48.0	0.90
0.9	55.0	1.1
1.0	62.0	1.3
2.0	70.0	2.30
3.0	73.0	2.70
4.0	80.0	4.00
5.0	89.0	8.00
6.0	92.0	11.50
7.0	98.0	49.00
8.0	99.8	499
9.0	99.8	499
10.0	100.0	∞

Table 3. Effect of Various Diluents

Diluent	Dielectric constant (ε)	Extraction %	Distribution ratio (D)
Benzene	2.28	99.7	332.4
Toluene	2.38	99.0	99
Xylene	2.30	100.0	∞
Hexane	1.89	80.0	40
Cyclohexane	2.05	98.0	49
Chloroform	4.8	92.0	11.5
Carbontetrachloride	2.24	92.0	11.5

Table 4. Effect of Different Stripping Agents

Stripping agent	% Recovery					
mol dm^{-3}	0.5	1	2	4	6	8
HCl	85	100	100	100	100	100
H_2SO_4	99	100	100	100	100	100
HNO_3	100	100	100	100	100	100
HBr	—	95.0	96.0	96.0	97.0	98.0
$NaNO_3$	80.2	82.0	—	—	—	—
NH_4Br	85.0	83.0	—	—	—	—

Table 5. Effect of Diverse Ions
(Sc=20 µg, pH=6.0, 0.1 mol dm^{-3} Aliquat 336S in Xylene)

Element	Added as	Foreign ion added	Recovery	Ratio
		mg	%	
Li^+	$LiSO_4\cdot H_2O$	6	100	1:300
Na^+	$NaCl$	6	100	1:300
K^+	KCl	6	100	1:300
Rb^+	$RbCl$	5	99.6	1:250
Mg^{2+}	$MgSO_4\cdot 7H_2O$	4	100	1:200
Ca^{2+}	$Ca(NO_3)_2$	5	100	1:300
Sr^{2+}	$Sr(NO_3)_2\cdot 2H_2O$	4	100	1:200
Ba^{2+}	$Ba(NO_3)_2\cdot 4H_2O$	5	100	1:250
Fe^{2+}	$FeSO_4\cdot 7H_2O$	1.5	99	1:75
Pb^{2+}	$Pb(NO_3)_2$	1.5	99.2	1:75
Al^{3+}	$Al(NO_3)_3\cdot 9H_2O$	4	99.6	1:200
Co^{2+}	$Co(NO_3)_2\cdot 6H_2O$	1	99	1:250
Ni^{2+}	$Ni(NO_3)_2\cdot 6H_2O$	1	99	1:50
Cu^{2+}	$CuSO_4\cdot 5H_2O$	1.8	99.2	1:90
Mn^{2+}	$MnSO_4\cdot 7H_2O$	1.5	100	1:75
Ce^{3+}	$Ce(SO_4)_3\cdot 8H_2O$	1	99.2	1:50
Y^{3+}	$Y(NO_3)_2\cdot 2H_2O$	1	100	1:50
Cr^{2+}	$Cr(NO_3)_3\cdot 9H_2O$	0.5	99	1:25
Tl^+	Tl_2SO_4	2.5	100	1:125
V^{4+}	$VOSO_4\cdot 5H_2O$	0.100	100	1:5
Zr^{4+}	$Zr(NO_3)_4\cdot 5H_2O$	0.500	99	1:25
Hf^{4+}	$Hf(NO_3)_2$	0.250	99	1:125
UO_2^{2+}	$UO_2(NO_3)_2\cdot 6H_2O$	0.100	99	1:5
$Mo_7O_{24}^{6-}$	$(NO_4)_6Mo_7O_{24}\cdot 4H_2O$	0.500	100	1:25
Th^{4+}	$Th(NO_3)_2\cdot 4H_2O$	0.025	100	1:1.25

Table 6. Separation of Scandium from Multicomponent Mixtures

Metal	Amount taken	Amount found	Recovery	Stripping agent	Chromogenic agent	λ_{max} for spectro photometer
	µg	µg	%	mol dm^{-3}		
1) Mn(II)	800	799.8	99.2	H_2O	Formaldoxime	450
Sc(III)	40	40	100	8 HCl	Arsenazo III	670
V(V)	40	40	100	0.1 HCl	Xylenolorange	520
2) Fe(II)	800	799	99.8	Unextracted	Thiocyanate	480
Sc(III)	40	39.5	99.7	10 HCl	Arsenazo III	670
Hf(IV)	100	99	99	1 HCl	Arsenazo III	625
3) Ce(III)	500	498	99.6	H_2O	Xylenolorange	575
Sc(III)	40	40	100	5 HNO_3	Arsenazo III	670
Th(IV)	25	25	100	2 HCl	Arsenazo III	650
4) Ce(III)	500	498	99.6	H_2O	Xylenolorange	575
Sc(III)	40	40	100	5 HCl	Arsenazo III	670
U(VI)	100	99	99	0.5 NaOH	Arsenazo III	665
5) Al(III)	500	498	99.6	H_2O	Alizarin RedS	520
Sc(III)	40	40	100	4 HCl	Arsenazo III	670
Mo(VI)	100	99	99	4 HNO_3	Phenylfluorone	525
U(VI)	100	99.6	99.6	0.5 NaOH	Arsenazo III	665
6) Ce(III)	500	498	99.6	H_2O	Xylenolorange	575
Sc(III)	40	40	100	5 HNO_3	Arsenazo III	670
U(VI)	100	99	99	0.5 NaOH	Arsenazo III	665
Th(IV)	25	25	100	2 HCl	Arsenazo III	650

hydrochloric acid followed by, stripping of these elements with 1 mol dm^{-3} hydrochloric acid. During stripping these elements formed anionic chlorocomplexes with hydrochloric acid and were in turn reextracted in Aliquat 336S and were back washed with 1 mol dm^{-3} hydrochloric acid.

Separation of Scandium from Multicomponent Mixtures. When a mixture of manganese, scandium, and vanadium was extracted, manganese was first stripped with water, then scandium with 8 mol dm^{-3} hydrochloric acid and finally vanadium with 0.1 mol dm^{-3} hydrochloric acid.

Iron(II), scandium(III), and hafnium(IV) were separated after extraction by first stripping scandium with 10 mol dm^{-3} hydrochloric acid, then hafnium with 1 mol dm^{-3} hydrochloric acid and finally unextracted iron was determined directly in the aqueous phase.

Cerium(III), scandium(III), and thorium(IV) were separated after extraction by stripping of scandium with 5 mol dm^{-3} nitric acid, thorium with 2 mol dm^{-3} hydrochloric acid and cerium was stripped with water.

After extraction, cerium(III), scandium(III), and uranium(VI) were separated by washing cerium with water, then stripping scandium with 8 mol dm^{-3} hydrochloric acid and finally uranium with 0.5 mol dm^{-3} sodium hydroxide.

Aluminium(III), scandium(III), molybdenum(VI), and uranium were separated after extraction, by stripping aluminium with water, scandium with 4 mol dm^{-3} hydrochloric acid, molybdenum with 4 mol dm^{-3} nitric acid and uranium with 0.5 mol dm^{-3} sodium hydroxide.

Cerium(III), scandium(III), uranium(VI), and thorium(IV) were separated by stripping cerium with water, scandium with 5 mol dm^{-3} nitric acid, uranium with 0.5 mol dm^{-3} sodium hydroxide and thorium with 2 mol dm^{-3} hydrochloric acid (Tables 5 and 6).

The proposed method is simple, rapid, selective, and applicable at tracer concentration. Scandium was separated from uranium, thorium, hafnium, molybdenum, and vanadium which are generally associated with it in fission products.

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