

Radiometric Analysis of Scandium

B. C. Purkayastha and K. N. Dutta

In continuation of the study on the estimation of scandium as pyrophosphate by radiometric procedure a lower limit of $\sim 55\gamma$ has been reached using P^{32} as a measuring indicator. As low as 0.3 mg of scandium has also been estimated using Sc^{46} of high specific activity. Trivalent rare earths and yttrium, bivalent ions like Fe (II), Cd (II), Be (II) do not interfere in the estimation, whereas Fe (III), Al (III) interfere to a considerable extent. Pyrophosphate of scandium with two different compositions such as: $ScHP_2O_7$ and $Sc_2(P_2O_7)_3$ have been observed in the course of the study. The precipitate assumes the former composition in presence of excess of pyrophosphate and the latter in presence of excess of scandium.

Scandium has been separated from a complex mineral like beryl mainly through co-precipitation with ceric pyrophosphate using Sc^{46} as an indicator throughout the procedure. The separation procedure is very convenient and is successful even with trace amount of scandium.

Most of the methods described in the literature for the estimation of scandium involve the estimation of macro amount of scandium¹⁻³. γ -order of scandium can, however, be determined spectrophotometrically⁴. The present study is a continuation of the previous work⁵ on the radiometric estimation of scandium as pyrophosphate. Concentration and purification of scandium through ceric pyrophosphate⁶ and subsequent estimation as pyrophosphate has also been attempted.

EXPERIMENTAL

Carrier-free P^{32} was supplied by D.A.E. Trombay. Sc^{46} of high specific activity was procured from Messrs. Philips Duphar, Holland.

Labelled pyrophosphate was prepared by adding carrier-free P^{32} to a solution of disodium hydrogen phosphate, evaporating the solution and heating at 500° for 5-6 hours⁷. A mixture of $Na_4P_2O_7$, (about twice the amount required by the formula $ScHP_2O_7$) and an excess of KI solution was added to a mixture of Tl I and scandium solution and pH was adjusted to 4-5 by ammonium acetate. The precipitate of Tl I (which carried $ScHP_2O_7$) was coagulated by gentle warming. The volume was adjusted to 25 ml and an aliquot was pipetted out for activity measurement. From this the $Na_4P_2O_7$ left in solution was computed.

1. Pokras and Bernays, *Anal. Chem.*, 1951, 23, 757; *J. Am. Soc.*, 1951, 73, 7.
2. I. P. Alimarin and Shen-Han-Si, *Z. Analit. Khim.*, 1960, 15, 1.
3. Y. Takashima, *Nippon Kagaku Zasshi*, 1958, 79, 243.
4. S. S. Berman, *Anal. Chem.* 1963, 35, 1392.
5. B. C. Purkayastha and Pal Vernekar., *J. Ind. Chem. Soc.*, 1957, 31, 487.
6. B. C. Purkayastha and Dutta, K. N., *J. Ind. Chem. Soc.*, 1963, 40, 1025.
7. Audrieth, "Inorganic Synthesis", Vol-III, Mc. Graw-Hill Book Co., p-100 (1950).

In the estimation of scandium with Sc^{46} , about half the quantity of $Na_4P_2O_7$, as required by the formula $Sc_4(P_2O_7)_3$ was added to a scandium solution containing Sc^{46} activity. From the loss in activity, the amount of scandium present in solution was calculated on the assumption that all pyrophosphate was precipitated as $Sc_4(P_2O_7)_3$.

Beryl was procured from Messrs. Starke & Co., New Delhi. It was found to contain SiO_2 61.3%, BeO 12.8%, Fe_2O_3 3.5%, Al_2O_3 20.3%. It was ground to 100 mesh, fused with $NaOH$, cooled and taken with hot water. Alkali was neutralised with HCl and was heated with perchloric acid to fumes to separate silica. H_2S was passed to remove Group II elements, and the excess was then boiled off from solution. Gaseous ammonia was passed and the hydroxide precipitate was dissolved in nitric acid to get the final acid concentration 2-4N. A solution of ceric sulphate [50 mg $Ce(IV)$] was added and cerium was precipitated as iodate with an excess of potassium iodate solution. The precipitate was filtered off. Excess iodate was removed either by boiling with potassium iodide or by precipitating beryllium hydroxide with ammonia which carried scandium. An aliquot of ceric sulphate solution was again added and cerium was precipitated as pyrophosphate. The precipitate was separated and dissolved in acidic hydrogen peroxide. The solution was boiled with 20% nitric acid for several hours to convert pyrophosphate to phosphate. It was made ammoniacal, the precipitate was dissolved in dilute H_2SO_4 , and scandium was estimated in the usual way. Sc^{46} activity was used throughout the procedures to detect any loss of scandium at every stage and as a measuring indicator in the estimation procedure.

TABLE I

Estimation of Scandium or Pyrophosphate by Sc^{46} .
Final volume = 25 ml. Acid concentration = 0.15N H_2SO_4 .

Scandium taken (mg)	$Na_4P_2O_7$ added (mg)	Interfering ions (mg)	Scandium found (mg)	$Na_4P_2O_7$ found (mg)	Error (%)
15.280	35.00	—	14.730	33.78	3.5
7.640	16.46	—	7.74	16.658	1.2
5.280	12.10	—	5.14	11.761	2.8
2.564	7.00	—	2.586	7.056	0.8
1.282	2.244	—	1.247	2.190	2.4
1.112	2.244	—	1.110	2.241	0.2
0.513	1.112	—	0.529	1.157	3.0
*0.278	0.659	—	0.272	0.647	2.0
*0.112	—	—	0.126	—	13.0
7.69	16.46	Ce (III) 100	7.61	16.295	1.0
2.564	7.00	100	2.564	7.00	0.0
1.282	3.50	25	1.253	3.416	2.4
1.112	2.244	Al 25	1.226	2.469	10.0
1.112	2.244	25	1.277	2.581	15.0
1.112	2.244	Fe (III) 10	1.9	—	71.2
2.244	4.488	Fe (II) 25	2.200	4.443	1.0
1.112	2.244	25	1.149	2.311	3.0
1.112	2.244	Cd 25	1.190	2.284	1.8
1.112	2.244	15	1.080	2.186	2.6
1.112	2.244	Y 10	1.140	2.307	2.8
1.112	2.244	Be 15	1.103	2.226	0.8
1.112	2.244	Na_2HPO_4 15	1.114	2.248	0.2
1.112	4.488	15	1.117	4.503	0.4

*pH was raised to 4-5 with ammonium acetate. Scandium pyrophosphate was carried by Tl I.

TABLE II

Estimation of Scandium as Pyrophosphate using P^{32} .

Scandium taken (mg).	Scandium found (mg)	Error (%)
0.112	0.110	1.8
0.112	0.113	0.9
0.112	0.113	0.9
0.056	0.052	7.0
0.056	0.0536	5.0
0.056	0.0533	5.0
0.0112	0.0075	33.0

pH was adjusted between 4 and 5 and scandium pyrophosphate was carried by TiH .

TABLE III

Analysis of Scandium Pyrophosphate.

Sc	Found (%)		Ratio		
	$P_2O_7^{4-}$	H_2O	Sc	$P_2O_7^{4-}$	H_2O
1. Prepared in excess of scandium.					
(a) at ordinary temperature					
17.03	49.2	39.77	4.02	3	20
(b) at 300°C.					
25.51	71.86	2.63	4.11	3	1.08
2. Prepared in excess of pyrophosphate (at 300°)					
19.05	72.0	8.36	1.02	1	1.12

TABLE IV

Recovery and Estimation of Scandium from Beryl.

Sample of beryl taken (gm).	Scandium mixed with beryl (mg).	Recovery %	Scandium found (mg)
1.3800	Tracer Sc	86	No precipitate with $Na_4P_2O_7$
2.3375	1.000	89	1.050
9.1863	0.609	83	0.640
1.2115	1.000	76	1.023
*1.3265	0.756	81	0.783
*1.5291	0.756	79	0.790

*In these cases beryl was mixed with about 10 mg. of Nb, Ta, Zr and Ti and was fused with alkali.

DISCUSSION

Table I shows that as low as 0.5 mg of scandium can be estimated with a fair degree of accuracy using Sc^{45} as a measuring indicator. It may be stated that rare earths and yttrium do not interfere in such estimation. Bivalent elements like Be^{++} , Fe^{++} , Cd^{++} , etc., also do not interfere. But trivalent elements like Fe^{+++} and Al^{+++} do interfere to a considerable extent probably due to complex ion formation. An interesting application of the method lies in the quantitative estimation of pyrophosphate in presence of phosphate.

Previous to this study, the possibility of estimation of scandium as pyrophosphate using P^{32} as a measuring indicator was established in this laboratory and upto 1 mg scandium was estimated with a fair degree of accuracy. The application of P^{32} in the estimation of still lower amounts of scandium has been illustrated in table II. This has been possible by using a suitable carrier like thallos iodide. Keeping the pH between 4 and 6 and carrying scandium pyrophosphate by thallos iodide, upto 58% of scandium has been estimated. Thallos iodide acts as a faithful carrier of both the forms of scandium pyrophosphate. That the carrier and the guest have a morphological relation is well illustrated by the fact that under identical conditions silver iodide does not carry scandium pyrophosphate to the desired extent.

In the course of this work it has been confirmed that there are two pyrophosphates of scandium, so far as the ratios of $Sc:P_2O_5$ are concerned, namely, $ScHP_2O_7 \cdot 3H_2O$ and $Sc_4(P_2O_7)_3 \cdot xH_2O$ (vide table III). The former is precipitated in presence of excess of pyrophosphate and the latter in excess of scandium. The former was described by G. Beck⁸ and the latter one corresponds to the recent observation by B. Hajeck⁹. On heating to 200°—300° the compounds assume the compositions $ScHP_2O_7 \cdot H_2O$ and $Sc_4(P_2O_7)_3 \cdot H_2O$ respectively.

It had been observed earlier⁶ that the partition factor in the uptake of scandium tracer by zirconium and ceric pyrophosphate as hosts is much higher than unity. Purification and concentration of scandium through coprecipitation with ceric pyrophosphate from a complex mineral like beryl has been found to be a successful method. Use of Sc^{45} in such separation helps in tracing the loss of scandium in each stage and in estimating scandium radiometrically when the recovered amount exceeds 0.5 mg. Spectroscopic determination with some varieties of Indian beryl has shown that scandium content¹⁰ is of the order of 10^{-4} — 10^{-5} per cent. Estimation of such a low amount of scandium is beyond the scope of the present method. The feasibility of this method of separation of scandium has therefore been verified by prior addition of known amounts of scandium to beryl (table IV). By this method trace amounts of scandium can also be recovered and subsequently estimated by method of activation.

NUCLEAR CHEMISTRY DIVISION,
SAHA INSTITUTE OF NUCLEAR PHYSICS,
92, ACHARYA PRAFULLA CHANDRA ROAD,
CALCUTTA 9.

Received, October 15, 1966.

8. G. Beck, *Mikrochem.*, 1948, 34-35, 282.
9. B. Hajeck, *Z. Chem.*, 1963, 3, 194.
10. B. Mukherjee, *Nature*, 1951, 167, 602.