

# Articles

## The Gravimetric Determination of Scandium by di-(2-ethylhexyl)phosphate

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The gravimetric determination of scandium by di-(2-ethylhexyl)phosphate(DEHPA) as a precipitant and the mole ratio of Sc-DEHPA precipitation obtained in ethanol medium have been investigated. Scandium can be determined by gravimetric method of precipitation of Sc-DEHPA and the mole ratio of Sc-DEHPA is found as 1 : 2 in ethanol medium.

### Introduction

Scandium is pseudo-rare earth element and its chemical and physical properties are similar to those of rare earth elements. The considerable application of scandium in recent years has presented a challenge to analytical chemists.<sup>1,2</sup> The application areas<sup>3</sup> of scandium include laser crystals, surface coatings, scandium-sodium lamps, solid electrolytes, advanced ceramics, high temperature superconductors, nuclear materials, cathode material for color cathode-ray tubes, anode material for x-ray spectrometers and catalysts for automobiles. Scandium bearing ores are few and the element occurs in extremely low concentrations.

Scandium ores are wolframite<sup>4</sup>, titanous magnetite, xenotime and monazite and are also in tin slag<sup>5</sup> and uranium ore.<sup>6</sup> The possible separation methods of scandium from these ores are solvent extraction<sup>7</sup> and ion exchange chromatography.<sup>8</sup> The determination methods of scandium are gravimetric,<sup>9</sup> volumetric<sup>10</sup>, spectrophotometric<sup>11</sup> and gas chromatographic methods<sup>12</sup>. These methods suffer interferences due to matrix effects. The precipitants for gravimetric determination of scandium are mainly hydroxide,<sup>13</sup> borate,<sup>14</sup> carbonate<sup>14</sup>, oxalate,<sup>15</sup> tartrate,<sup>16</sup> phosphate<sup>14</sup> and fluoride,<sup>14</sup> but, they also have possible interferences from other ions present and the procedures are tedious.

Authors<sup>17</sup> have studied the separation of scandium from in slag by a solvent extraction method using DEHPA<sup>18-21</sup> as an extractant. DEHPA is a monovalent acid and does not dissolve in water but dissolves in basic solutions or organic solvents. DEHPA has a good extraction efficiency for Sc<sup>3+</sup> by a selective complex formation. Authors also found that the precipitation of scandium-DEHPA was formed in ethanol medium and the mole ratio of Sc-DEHPA was 1 : 2.4 using mole ratio method.<sup>22</sup> In this paper, we have studied the determination for scandium using Sc-DEHPA precipitation in ethanol and have calculated the mole ratio of Sc-DEHPA precipitation.

### Experimental

**Reagents and Apparatus.** For a standard 0.2224 M scandium solution (10 mg/ml), 2.5690 grams of 99.9% Sc

(NO<sub>3</sub>)<sub>3</sub> was dissolved in 1 ml of concentrated nitric acid and evaporated the excess nitric acid and the volume of the solution was diluted to 50 ml with water. DEHPA stock solution (3.040 × 10<sup>-2</sup> M) was prepared by dissolving 1.0 ml of 99.7% DEHPA purchased from Sigma Co. with 99.9% ethanol. The solutions of other ions for studying interference effects were made as 0.2495 M, 0.3706 M, 0.1791 M and 0.4115 M for Ca<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup> and Mg<sup>2+</sup>, respectively.

**Procedure.** A 1 ml of 0.2224 M scandium standard solution was transferred to a 100 ml beaker and 36.57 ml of 3.040 × 10<sup>-2</sup> M DEHPA solution dissolved in ethanol was added. The mole ratio of Sc<sup>3+</sup> and DEHPA was 1 : 5. Then the solution was diluted to 50 ml with ethanol and was stirred thoroughly. Approximately 4 hours standing the solution was filtered using 1G4 glass filter crucible under 40 mm Hg pressure. The precipitate was washed with 20 ml ethanol three times and transferred to oven at 105°C for drying. The precipitate was cooled to room temperature and weighed. The precipitate was transferred to an aluminum crucible, and ignited for about 4 hours at 900°C. The residue was weighed after cooling.

### Results and Discussion

In order to study the mole ratio of Sc-DEHPA precipitation, scandium solutions containing 10 mg, 20 mg, 30 mg and 40 mg were placed in each 10 ml beakers and excess DEHPA was added. The samples were diluted to 50 ml with ethanol and stirred. The precipitate was filtered using the filter crucible connected to a continuous vacuum line. The precipitate was dried at 105°C and weighed. These data were compared with the calculated weights from the expectant mole ratio of scandium and DEHPA. This results were as shown in Table 1. As can be seen in Table 1, we found that the precision of the precipitate weights formed at each scandium concentration solution in ethanol medium and dried at 105°C had estimated standard deviation (ESD) of 1.7-5.6%. Table 1 also shows that the differences between the experimental and calculated data based on the Sc-DEHPA ratio of 1 : 2 or 1 : 2.4 were -4.72~+0.48% and -15.1~18.8%, respectively. From the results, the mole ratio of scandium and DEHPA in Sc-DEHPA precipitate formed in

**Table 1.** Analytical Data of Sc-DEHPA precipitate dried at 105°C using various amounts of Scandium

Sc taken (mg)	Run no	ppt. wt(mg) (dried at 105°C)	Calculated values at Sc(DEHPA) <sub>2</sub> (mg)		Calculated values at Sc(DEHPA) <sub>2.4</sub> (mg)	
				difference		difference
10	1	151.0	153.0	-2.0	181.0	-30.0
	2	153.2	∕	+0.2	∕	-28.2
	3	157.0	∕	+4.0	∕	-24.0
		m.v 153.7	m.d	+0.7	m.d	-27.4
		esd 3.0	m.d%	+0.48	m.d%	-15.1
				difference		difference
20	1	301.0	306.0	-5.0	363.0	-62.0
	2	290.1	∕	-15.9	∕	-73.0
	3	293.1	∕	-12.9	∕	-70.0
		m.v 295.0	m.d	-11.0	m.d	-68.0
		esd 5.6	m.d%	-4.72	m.d%	-18.8
				difference		difference
30	1	457.0	459.0	-2.0	544.0	-87.0
	2	464.1	∕	+4.9	∕	-80.0
	3	458.8	∕	-0.2	∕	-85.2
		m.v 459.8	m.d	+0.9	m.d	-84.1
		esd 3.7	m.d%	+0.20	m.d%	-15.5
				difference		difference
40	1	609.3	612.0	-2.7	727.0	-111.7
	2	612.2	∕	+0.2	∕	-114.8
	3	610.1	∕	-2.0	∕	-116.9
		m.v 611.2	m.d	+0.8	m.d	-116.2
		esd 1.7	m.d%	-0.13	m.d%	-16.1

m.v=mean value, esd=estimated standard deviation, m.d=mean difference, m.d%=mean difference percent.

ethanol medium was considered as 1:2. In a previous paper,<sup>22</sup> we reported that the mole ratio of scandium and DEHPA of Sc-DEHPA precipitate in ethanol medium was 1:2.4. The mole ratio was estimated using mole ratio method by determining the scandium amount remaining in the supernatant solution after the precipitate was formed. In this method as can be seen in Table 1, the ratio is estimated by comparing the experimental data with calculated values assuming the Sc-DEHPA ratio of 1:2. Further, the data of precipitate weights ignited at 900°C are shown in Table 2. In Table 2, the experimental data and the calculated weights from 1:2 and 1:2.4 mole ratio are compared. The calculated values from 1:2 and 1:2.4 are calculated from the formula of Sc<sub>2</sub>O<sub>3</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>2</sub> and Sc<sub>2</sub>O<sub>3</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>2.4</sub>. In this results, the calculated values from 1:2 mole ratio agree almost with experimental data. The difference of calculated value from 1:2 mole ratio and experimental values are -3.40~17.1%. This difference is larger than that of Table 1, -4.72~+0.48%. As can be seen in Table 2, the experimental data are less than the calculated value. This is ascribable to a loss of vaporization of precipitate in igniting precipitate at 900°C.

**Effects of nitric acid concentration in sample solution for scandium precipitation formation.** In order to investigate the effect of apparent pH of the sample solution on the formation of precipitation of Sc-DEHPA, each of 1, 2 and 3 ml of 10 mg/ml Sc<sup>3+</sup> solution was taken in

each 100 ml beaker and each of 1, 2 and 3 ml of concentrated HNO<sub>3</sub> added each beaker, respectively, and adjusted to 50 ml with ethanol and the above procedure was followed. The amounts of precipitate obtained here at 105°C and 900°C were weighed. The results are shown in Table 3.

Table 3 shows the precipitate weights are slightly different in each scandium solution according to nitric acid concentration. Therefore, we think that acidity of the solution effects slightly the formation of precipitation of Sc-DEHPA. We only found that the particle size of the precipitate was smaller in the concentrated nitric acid and the effects of other acid, such as HCl, H<sub>2</sub>SO<sub>4</sub> are as same as HNO<sub>3</sub>. It is preferable to perform the formation of Sc-DEHPA in neutral sample solution.

**Scandium precipitation in aqueous solution.** In the above procedure, the formation of Sc-DEHPA precipitation is established in ethanol medium including 1-3 ml water. In order to study the Sc-DEHPA precipitation in aqueous sample solution, each of 1 and 2 ml of 10 mg/ml Sc<sup>3+</sup> solution was taken in 100 ml beaker and added 1 ml of nitric acid, 3.65 ml of 0.304 M DEHPA solution and 10, 20 and 30 ml of water in each beaker and diluted to 50 ml with ethanol. After precipitation of Sc-DEHPA was made, it is filtered using glass filter and weighed after drying at 105°C and igniting at 900°C. The results are shown in Table 4.

Table 4 shows precipitate weights obtained in the water

**Table 2.** Analytical Data of Sc-DEHPA precipitate obtained at 900°C using various amounts of Scandium

Sc taken (mg)	Run no	ppt. wt(mg) (dried at 900°C)		Calculated values at Sc <sub>2</sub> O <sub>3</sub> (P <sub>2</sub> O <sub>5</sub> ) <sub>2</sub> (mg)			Calculated values at Sc <sub>2</sub> O <sub>3</sub> (P <sub>2</sub> O <sub>5</sub> ) <sub>2.4</sub> (mg)		
					difference		difference		difference
10	1		39.2	46.9	-7.7	53.2	-14.0		
	2		38.1	∕	-8.7	∕	-15.1		
	3		39.2	∕	-7.7	∕	-14.0		
		m.v	38.8	m.d	-0.03	m.d	-14.4		
		esd	0.6	m.d%	-17.1	m.d%	-27.0		
20	1		91.0	93.0	-2.0	106	-15.0		
	2		90.0	∕	-3.0	∕	-16.0		
	3		87.0	∕	-6.0	∕	-19.0		
		m.v	89.3	m.d	-3.67	m.d	-16.7		
		esd	2.1	m.d%	-3.94	m.d%	-15.7		
30	1		120.2	141.0	-20.8	159.0	-38.8		
	2		120.1	∕	-20.9	∕	-38.9		
	3		121.1	∕	-19.9	∕	-37.9		
		m.v	120.5	m.d	-20.5	m.d	-38.5		
		esd	0.5	m.d%	-14.61	m.d%	-24.2		
40	1		177.1	182.1	-5.0	212.2	-35.1		
	2		176.0	∕	-6.1	∕	-36.2		
	3		176.2	∕	-5.9	∕	-36.0		
		m.v	176.1	m.d	-6.0	m.d	-36.1		
		esd	0.7	m.d%	-3.40	m.d%	-16.7		

m.v=mean value, esd=estimated standard deviation, m.d=mean difference, m.d%=mean difference percent.

**Table 3.** Effect of concentration of HNO<sub>3</sub> on Sc-DEHPA precipitation

Sc(mg)	Free acid		0.3 N HNO <sub>3</sub>		0.6 N HNO <sub>3</sub>		0.9 N HNO <sub>3</sub>	
	ppt. wt(mg)		ppt. wt(mg)		ppt. wt(mg)		ppt. wt(mg)	
	105°C	900°C	105°C	900°C	105°C	900°C	105°C	900°C
10	153.7	38.8	152.5	33.0	150.3	36.7	148.9	38.1
20	295.0	89.3	294.3	86.5	291.7	85.4	293.6	84.3
30	459.8	120.5	457.6	119.2	457.0	119.5	454.9	118.2

**Table 4.** Effects of amount of H<sub>2</sub>O on Sc-DEHPA precipitation

Sc(mg)	ppt. wt in ethanol medium		ppt wt in amount of H <sub>2</sub> O					
			10 ml H <sub>2</sub> O		20 ml H <sub>2</sub> O		30 ml H <sub>2</sub> O	
	105°C	900°C	105°C	900°C	105°C	900°C	105°C	900°C
10	<sup>b</sup> 153.7	38.8	<sup>a</sup> 202.1	34.0	<sup>a</sup> 285.5	34.0	<sup>a</sup> 286.4	34.0
10	<sup>a</sup> 153.7	38.8	<sup>b</sup> 154.3	34.0	<sup>b</sup> 161.4	34.0	<sup>b</sup> 160.3	34.0
20	<sup>b</sup> 295.0	89.3	<sup>b</sup> 302.6	86.0	<sup>b</sup> 302.3	89.0	<sup>b</sup> 295.4	85.0

<sup>a</sup>no ethanol washing, <sup>b</sup>ethanol washing.

rich medium was increased with increasing the amount of water (a in the Table 4). The state of precipitate in water phase is gel and not same shape of precipitate as obtained in ethanol medium. The reason of increasing weights is due to weights of insoluble DEHPA in water. In order to remove the insoluble DEHPA, after filtering precipitate with glass filter, washed completely with about 20 ml ethanol three times for dissolving DEHPA included in the precipitate (b in Table 4). The weights were the same as the values obtained in ethanol medium. This indicates that the insoluble DEHPA in water is removed by washing with ethanol. But, when the precipitate obtained in the water rich medium was filtered, it took a long time to filter it. Consequently, we found that it was easy to make precipitation of Sc-DEHPA in ethanol medium. In the case of aqueous sample solution, it prefers to reduce the volume of sample solution to minimum for preventing co-precipitation of insoluble DEHPA in aqueous medium.

**Sc-DEHPA precipitation ignited at 900°C.** As can be seen in Table 2, the precipitate weights ignited at 900°C were compared with the values calculated from the formation of Sc<sub>2</sub>O<sub>3</sub>(P<sub>2</sub>O<sub>5</sub>) and Sc<sub>2</sub>O<sub>3</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>2.4</sub>. When Sc-(DEHPA)<sub>2</sub> and Sc-(DEHPA)<sub>2.4</sub> are ignited at 900°C, we think that Sc<sup>3+</sup> converted to Sc<sub>2</sub>O<sub>3</sub> and PO<sub>4</sub><sup>3-</sup> converted to P<sub>2</sub>O<sub>5</sub>. In order to identify the results, we determined the mole ratio of P and Sc in the precipitate ignited at 900°C. It is found that the mole

**Table 5.** Tolerance limits in the determination of Sc<sup>3+</sup> (5 mg/l)

Foreign ions	Amount added(mg/L)	ppt. wt obtained at 104°C (cm)	ppt. wt obtained at 900°C (cm)
Sc <sup>3+</sup> only	5.00(0.111 M)	76.9	19.5
Al <sup>3+</sup> added	100(3.70 M)	76.9	19.7
Mg <sup>2+</sup> added	100(4.11 M)	77.1	20.1
Ca <sup>2+</sup> added	100(2.49 M)	78.8	20.1
Fe <sup>3+</sup> added	10.0(0.179 M)	82.3	20.3
	50.0(0.899 M)	88.1	23.5
	100(1.79 M)	93.6	30.4

ratio between Sc and P is 1 : 2.

**Effects of foreign ions.** The effects of foreign ions co-existing in tin slag solution were investigated in the procedure of precipitation of scandium and DEHPA. The result is Table 5.

This data show that iron ion among the ions influence the gravimetric determination of scandium using Sc-DEHPA precipitation method and other ions have no interference.

### Conclusion

(1) The gravimetric determination of scandium with DEHPA as a precipitant in ethanol medium has been investigated.

(2) The mole ratio of Sc-DEHPA precipitate is 1 : 2 in ethanol medium.

(3) The formula of precipitate ignited at 900°C is Sc<sub>2</sub>O<sub>3</sub>(PO<sub>3</sub>)<sub>2</sub>.

(4) The gravimetric determination of scandium dried at 105°C was better than the method ignited at 900°C.

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## $\pi$ -Participation in Bicyclo[3.2.1]oct-6-en-2-yl Cation. <sup>19</sup>F NMR Spectroscopy as a Probe

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*p*-Fluorophenyl bicyclo[3.2.1]oct-6-en-2-yl cation (**3**) prepared in FSO<sub>3</sub>H-SO<sub>2</sub>-ClF solution at -90°C and examined by fluorine-19 nmr spectroscopy. The nmr data give a clear evidence for the formation of a stabilized  $\pi$ -bridging cation species in superacids. The degree of  $\pi$  delocalization in this cation is found to be inferior to the onset of nonclassical stabilization in 2-norbornenyl cation.

### Introduction

Ever since the  $\pi$ -bridged formulation of the 2-arylnorbor-

nenyl 2-brosylate in solvolytic media by Brown<sup>1</sup>, various approaches have been made by physical organic chemists to confirm the existence of such cationic species. Using the tool