Coprecipitation of Scandium with Calcium Oxalate

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The coprecipitation of scandium with calcium as oxalate was studied. Precipitation of calcium was carried out in homogeneous precipitation system, in which dimethyl oxalate was decomposed to form oxalate ion. Homogeneous and logarithmic distribution coefficients were obtained by measuring radioactivity of Sc-46 used as a tracer, and by the chelatometric titration of calcium. Logarithmic distribution was followed at pH 2.0~3.5, whereas near pH 4 homogeneous distribution was obeyed. It was optimum for the enrichment of scandium, that calcium was precipitated at about 80°C in the pH range between 2.5 and 3.0, and precipitate was filtered after 2 or 3 hours.

INTRODUCTION

In the previous communication[1], the determination of scandium in several rocks and natural water was investigated, and it was observed that calcium oxalate was successfully used as a carrier for concentrating a very small amount of scandium like as in the case of rare earths[2]. It is therefore interested to study the coprecipitation of scandium with calcium oxalate.

Calcium oxalate forms mainly as the monohydrate, $CaC_2O_4 \cdot H_2O$ when it is precipitated in hot solution, whereas at room temperature unstable di- and trihydrate precipitate[3]. For this reason and also for the detailed stuty on the coprecipitation behaviour of scandium, the homogeneous precipitation technique[4] at relatively high temperature, seems to be convenient. The homogeneous precipitation of calcium oxalate was performed through the slow hydrolysis of ester of oxalic acid and the effects of several variables such as precipitation rate, temperature, amount of scandium and particularly the pH value of the solution, on the distribution coefficients were investigated in detail by using scandium-46 as a tracer.

EXPERIMENTAL

Apparatus and Reagents

A Kobe Kogyo's NaI(Tl) (1 3/4′×2′) Well Type Scintillation Counter, Model PS 300, connected to a Transistorized Scaler, Model SA-230 was used for counting radioactivity, and the measurements of pH value were made with a Hitachi-Horiba's Glass Electrode pH Meter, Model M-3.

Scandium-46 was supplied as chloride in hydrochloric acid by the Radiochemical Center, Amersham. It was diluted to make the solution of ~1μc/ml.

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Reagent grade dimethyl oxalate was purified by recrystallizing from methyl alcohol and was stored in a dry atmosphere, because it hydrolyses upon contact with moisture.

Scandium solution of $10^{-2}M$ was prepared by dissolving 0.691 g. of scandium oxide in hydrochloric acid and diluted to 1 litre.

Calcium solution was prepared by dissolving calcium acetate in water and standardised by EDTA titration using Eriochrome Black T as an indicator.

Other chemicals used were chemically pure or reagent grade materials.

Procedure

The following procedure was adopted in the homogeneous precipitation. To an aliquot of the calcium acetate stock solution taken in 250 ml Erlenmayer's flask, scandium-46 activity with the appropriate inactive element is added. Dry dimethyl oxalate of known weight is added and dissolved. The solution is made 1N with respect to acetic acid or formic acid, pH is adjusted to a desired value and the resulting solution is diluted to 200 ml. The flask connected with an Allihn's condenser is placed in a thermostatic bath and the solution is stirred continuously with mechanical stirrer to prevent supersaturation.

At appropriate intervals of time, exactly 2.0 ml of aliquot is pipetted out through a sintered glass filter from the reacting solution, in which calcium is precipitating by oxalate ion formed from dimethyl oxalate.

Scandium present in the solution is estimated by gamma counting. Calcium remaining in the filtrate is determined by Mg-EDTA titration using Eriochrome Black T as a metallochromic indicator, after the above aliquot is ashed by digestion with concentrated sulphuric acid and hydrogen peroxide on a regulated hot plate.

Homogeneous and logarithmic distribution coefficients[5][6], D and λ, were calculated from the following equations:

$$\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{solid}} = D\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{solution}} \tag{1}$$

$$\log\frac{\text{initial tracer}}{\text{tracer in solution}} = \lambda \log\frac{\text{initial carrier}}{\text{carrier in solution}} \tag{2}$$

RESULTS AND DISCUSSION

The percentages of scandium coprecipitated and of calcium precipitated in the fractionation of calcium oxalate at different pH were plotted in Fig. 1. The experimental conditions were as follows, the concentration of scandium, calcium and dimethyl oxalate were $2.67 \times 10^{-6}M$, $2.5 \times 10^{-2}M$ and $5.0 \times 10^{-2}M$, respectively, total volume of the reacting solution was 200 ml which was buffered with $1M$ acetate or formate, and the temperature was $81.0 \pm 0.2°C$.

Figure 1 showed that the relation between scandium coprecipitated and calcium precipitated varied considerably with the pH value of the solution. The rate of the coprecipitation shows a large increase with the decrease of the pH in the region from pH 4.67 to 2.43.

From the curves in the figure, percentages of scandium coprecipitated was obtained at 10 and 20 percent precipitation of calcium, and the results were plot-
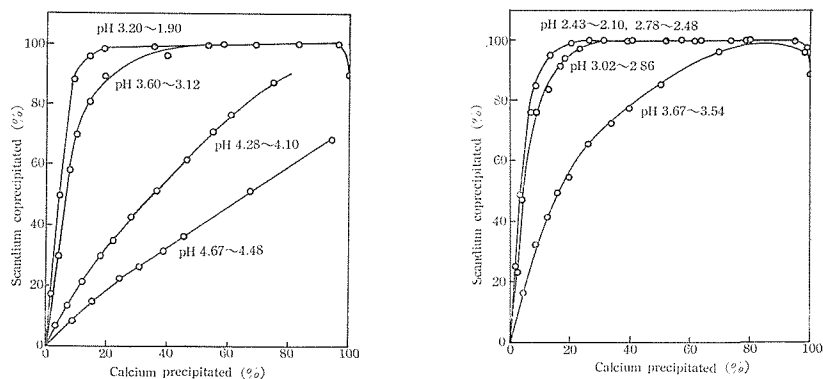
Fig. 1. Coprecipitation of scandium with calcium oxalate at different pH.
Sc: $2.67 \times 10^{-6} M$, Ca: $2.5 \times 10^{-2} M$, dimethyl oxalate: $5.0 \times 10^{-2} M$,
temperature: $81.0 \pm 0.2°C$.
left; $1M$ acetate solution. right; $1M$ formate solution.

ted against pH in Fig. 2. As indicated in the figure, the coprecipitation re-
covery of scandium has a maximum value, 90 and 98 percent respectively, between
pH 2 and 3. However the final percent coprecipitation becomes constant (mean
value 89.3%) independent of pH value, after the reacting solution is digested at
81°C for 20 hours. The homogeneous and the logarithmic distribution coefficients,
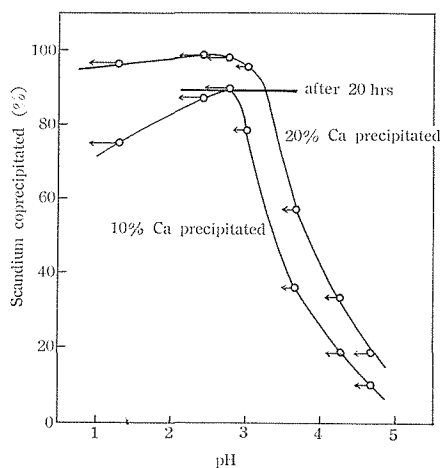D and λ, were calculated from these experimental data.

Fig. 2. Effect of pH on Sc-coprecipitation.

The logarithmic distribution coefficient, λ obtained at lower pH was shown
in Fig. 3, and the logarithmic and the homogeneous distribution coefficient, D at
relatively high pH were shown in Fig. 4. At lower pH region, the logarithmic
distribution coefficient is constant, although it decreases gradually with the lapse
of time, that may be due to the recrystallization and diffusion process by prolonged
digestion. Figure 4 indicated that the homogeneous distribution coefficient D
was constant near the pH 4 rather than the logarithmic one. The distribution
coefficient extrapolated to zero percent of calcium precipitated decreases contin-
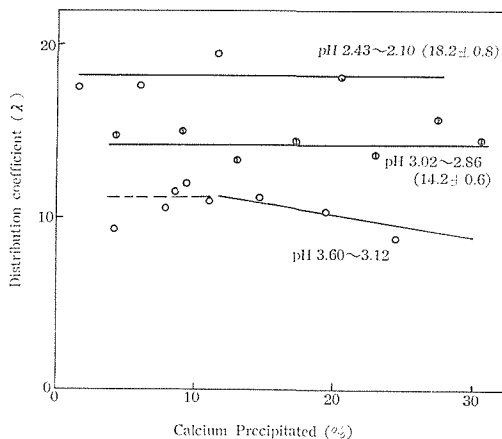
Fig. 3. Effect of pH on distribution coefficient.
  Sc : $2.67 \times 10^{-6} M$, Ca : $2.5 \times 10^{-2} M$,
  dimethyl oxalate : $5.0 \times 10^{-2} M$,
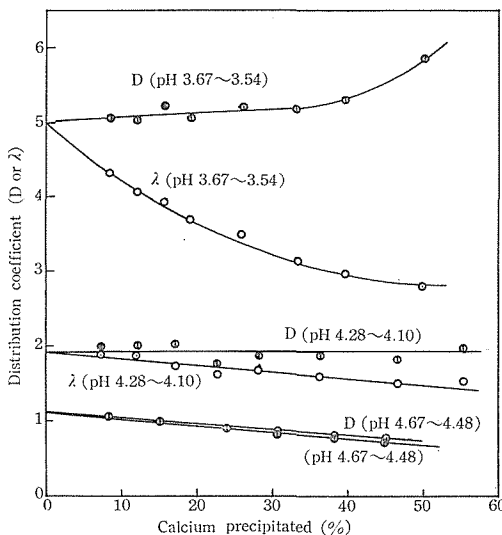 temperature : $81.0 \pm 0.2^{\circ}$C.

Fig. 4. Effect of pH on distribution coefficient
  Sc : $2.67 \times 10^{-6} M$, Ca : $2.5 \times 10^{-2} M$,
  dimethyl oxalate : $5.0 \times 10^{-2} M$,
  temperature : $81.0 \pm 0.2^{\circ}$C.

-uously as the pH rises.

As illustrated in these figures, the nature of the coprecipitation process changes from the logarithmic distribution to the homogeneous one as pH rises. These facts are much interested not only in the significance for the enrichment of scandium, but also in the coprecipitation behaviour of the element in this homogeneous precipitation system.

Figures 5 and 6 express the effect of the concentration of scandium at pH 3.67 and 4.08. The distribution coefficient somewhat decreased with the increase of
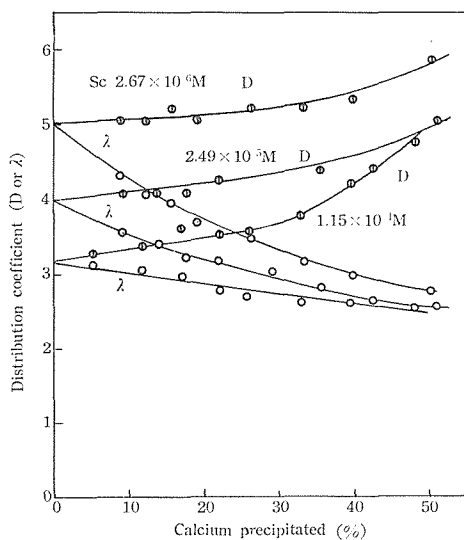
Fig. 5. Effect of scandium concentration on distribution
coefficient at pH 3.67.
Ca : $2.50 \times 10^{-2}M$, dimethyl oxalate : $5.0 \times 10^{-2}M$,
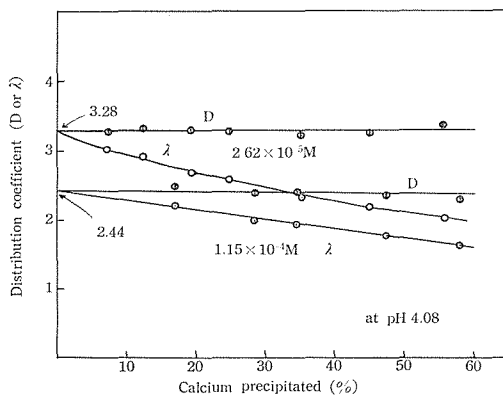temperature : $81.0 \pm 0.2°C$.

Fig. 6. Effect of scandium concentration on distribution
coefficient at pH 4.08.
Ca : $2.50 \times 10^{-2}M$, dimethyl oxalate : $5.0 \times 10^{-2}M$,
temperature : $81.0 \pm 0.2°C$.

concentration of scandium even in the condition obeying the homogeneous distribution law.

The effect of temperature was examined at pH 3.67 where the partly occlusion occurs. Figure 7 shows the distribution coefficients are nearly constant within the limit of errors over the range of temperature between 60 and 81°C. It is evident that the distribution coefficients are not affected by temperature in the range studied.

The effect of dimethyl oxalate concentration was shown in Fig. 8. The distribution coefficients obtained at the same percent precipitation of calcium increases,
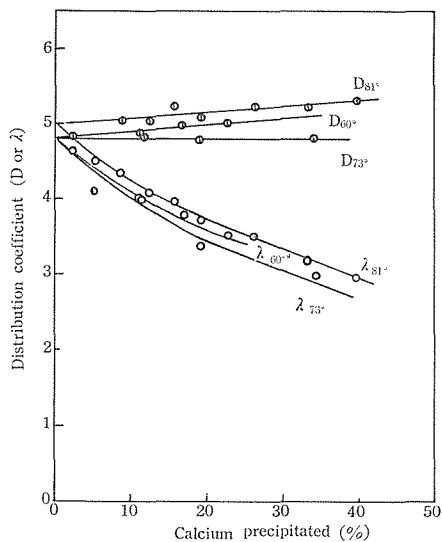
Fig. 7. Effect of temperature on distribution coefficient.
Sc : $2.67 \times 10^{-6} M$, Ca : $2.5 \times 10^{-2} M$,
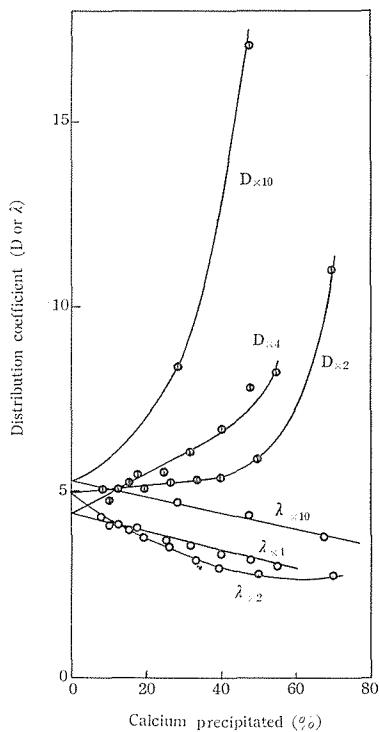dimethyl oxalate : $5.0 \times 10^{-2} M$.

Fig. 8. Effect of dimethyl oxalate concentration.
Sc : $2.67 \times 10^{-6} M$, Ca : $2.5 \times 10^{-2} M$,
temperature : $81.0 \pm 0.2°C$.

as the stoichiometric quantity necessary for complete precipitation of calcium rises from 2.0 times to 10, but the system tends to obey the logarithmic distribution law. However it is interested that the distrbution coefficients extrapolated to zero percent of calcium are nearly constant.

Table 1 represented the time required for 20 and 50 percent precipitation of calcium under various conditions. From the table and the results in Figs. 7 and 8, the effect of precipitation rate of calcium oxalate on distribution coefficients becomes evident; when the time required for 20 percent precipitation is decreased from 548 to 93 min. the distribution coefficients almost remain constant, but when that is decreased from 50 to 21 min. the precipitation rate gives considerable influence to distribution coefficients.

Table 1. Time required for the precipitation of calcium oxalate.

pH	Temp. °C	Mol. ratio $C_2O_4^{--}/Ca^{++}$	Medium	Conc. of Sc mol.	Time required, min.	
					20% ppt.	50% ppt.
3.67 (~3.54)	60.2	2	1M-acetate	2.67×10^{-6}	548	—
//	73.0	//	//	//	181	—
//	81.0	//	//	//	93	239
// (~3.40)	//	4	//	//	50	123
// (~3.12)	//	10	//	//	21	47
2.43 (~2.10)	//	2	1M-formate	//	39	73
2.78 (~2.48)	//	//	//	//	50	97
3.20 (~2.86)	//	//	//	//	67	144
// (~1.90)	//	//	1M-acetate	//	56	85
3.60 (~3.12)	//	//	//	//	93	227
4.28 (~4.10)	//	//	//	//	105	323
3.67 (~3.54)	//	//	1M-formate	2.49×10^{-5}	83	232
//	//	//	//	1.15×10^{-4}	69	189
4.08 (~3.92)	//	//	1M-acetate	2.62×10^{-5}	93	280
//	//	//	//	1.15×10^{-4}	58	205

The fundamental conditions in concentrating scandium ion with calcium oxalate had been studied in this investigation. The pH value and the time of reaction is important, because the percentages of scandium precipitated increased with the pH risen, but decreased with the lapse of time because of the digestion. For the enrichment of scandium, the optimum condition is as follows. The calcium is precipitated by hydrolysing dimethyl oxalate at about 80°C in the pH range between 2.5 and 3.0, and calcium oxalate formed is filtered after 2 or 3 hours from the beginning of the reaction.

REFERENCES

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