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Effect of Organic Coprecipitants on the Coprecipitation of Metal Chelates.

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Coprecipitation behavior of some metal oxinates with organic coprecipitants such as naphthalene and its derivatives, substituted diphenyls, phenolphtalein and acridine is studied. Organic compounds which can be employed as an effective collector for metal oxinates, possesses the low solubility in water and has one or more functional group such as OH, NO_2 or NH_2 which may interact with metal oxinates. Among the coprecipitants studied, α-naphthol, o-phenylphenol and o,o'-diphenol are favorable to collect metal oxinates, but oxine is useful only for rare earth oxinates. The application of the organic coprecipitant to the photometric determination of trace metals in a diluted solution is also examined, and the procedure for the determination of ferric iron is presented.

INTRODUCTION

The coprecipitation technique has been widely employed for collecting and concentrating trace amount of substances from very large volume of sample solution. Colloidal inorganic precipitates such as metal hydroxides are commonly utilized as effective carriers for metal ions. However, since such compounds carry down many ions by the occlusion, the technique is not selective so that it is sometimes followed by other procedures for the separation of the metal ion of interest from other ions and/or the carrier materials. Thus the use of organic reagent and organic coprecipitant become much favorable, especially for the carrier-free separation of radioactive tracer or the radioactive waste disposal, because besides its selectivity, carrier compound is easily, rapidly and completely destroyed by burning.

Since Kuznetsov[1] proposed the coprecipitation with organic compounds and introduced concept of *"extraction by solid extractant"*, some reports have been published. Weiss and Lai investigated the coprecipitation of ultramicro quantities of elements with α-benzoinoxime[2], α-nitroso-β-naphthol[3] and thionalid[4]. These compounds were homogeneously precipitated by adding as acetone solution and then evaporating acetone, but the constant distribution coefficient was not obtained[4]. Weiss and Slipman[5] used oxine which was also homogeneously produced by hydrolysis of 8-acetoxyquinoline. They showed the ferric-oxine system obeyed the logarithmic distribution. Similar research was carried by using macro amounts of aluminium oxinates as carrier[6]. For comparing the coprecipitation with the liquid-liquid extraction, that had been already suggested by Kuznetsov[1], Tappmeyer and Pickett studied the effect of oxine concentration on the coprecipitation behavior

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of metal oxinates by employing various organic coprecipitants other than the chelating agent[7]. They concluded that "the factors that influenced the copre-cipitation of metal chelats could be combined into one unified representation, which was identical in form to be quantitative expression used for extraction of metal chelates by organic solvent".

The authors have been deeply interested in the problem. In this research, the coprecipitation behavior of some metal oxinates with organic coprecipitants such as naphthalene and its derivatives, substituted diphenyls, phenolphthalein and acridine, was investigated principally from the practical stand point. Among the compounds, α-naphthol, o-phenylphenol and o,o'-diphenol were favorable to coprecipitate metal oxinates, but oxine was useful only for rare earth oxinates. The application of this technique to the photometric determination of metals present in diluted solution was also examined, and the procedure for the determi-nation of iron was described. The general procedure consists of the following steps: The metal ion is allowed to react with oxine; the chelate is coprecipitated with an organic coprecipitant; and the precipitate is dissolved in an organic sol-vent, followed by the absorption measurement. By this procedure, micro amount of metal can be simply determined without removing the organic coprecipitant.

EXPERIMENTAL

Apparatus and Reagents

A TEN well-type NaI(Tl) (2in. $\times 1\frac{3}{4}$in. dia.) scintillation counter PS-300, con-nected to a transistorized scaler, SA-230 was used for the radioactivity countings; a Hitachi-Horiba glass electode pH meter, model M-3 was used for the pH meas-urements: and a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer was employed for the measurements of light absorption.

Standard stock solutions of $FeCl_3$, $ScCl_3$, $CoCl_2$, $ZnCl_2$ $EuCl_3$ and $LuCl_3$ were prepared by dissolving the reagent grade salts, oxides, or metal in distilled water and/ or hydrochloric acid, followed by diluting to make each $5\times10^{-5}M$ solution. Oxine (8-Hydroxyquinoline) solution $(1\times10^{-2}M)$ was prepared by dissolving the reagent grade substance in hydrochloric acid and diluting with water. Organic coprecipitants investigated were the reagent grade materials and were used as acetone solution. Radioactive isotopes, cobalt-60, zinc-65 and scadium-46 were supplied from the Radiochemical Centre, Amersham, England; europium-152, 154 and lutetium-177 were produced in the Research Reactor of Kyoto University. All isotopes were used as chloride in hydrochloric acid solution.

Procedure

To a sample solution containing 1 ml of $5\times10^{-5}M$ metal stock solution with its radioactive tracer (about 5×10^5c.p.m.), 1 ml of 1 M acetic acid and appropriate amount of oxine are added. The solution is diluted to 50 ml and the pH is adjusted to a desired value with dilute sodium hydroxide or hydrochloric acid solutions. After 2 ml of the aliquot is pipetted out into a counting polyethylene tube, 2 ml of the organic coprecipitant acetone solution (0.25 g/ml) is then added to the remain-der, while stirring. After the solution is continuously mixed with a mechanical stirrer until it reaches the equilibrium, 2 ml of the supernatant solution was pi-

petted out through a sintered glass filter into another counting polyethylene capsule. The per cent coprecipitation is calculated from the gamma activities of these two counting samples.

The coprecipitation recovery of ferric iron, of which radioactive isotope could not be obtained, was photometrically determined. The detailed procedure will be described later in this paper.

RESULTS AND DISCUSSION

The effect of the concentration of the chelating reagent, oxine, was investigated on the cobalt-oxine-α-naphthol system. The typical per cent coprecipitation vs. pH curves are shown in Fig. 1, which were obtained in the presence 4×10^{-3}M, 4×10^{-4}M and 4×10^{-5}M oxine. The curve shifts to the higher pH region with the decrease in oxine concentration, in similar manner as the extractability vs. pH curve in the liquid-liquid extraction of metal chelates. However, in such a copre-
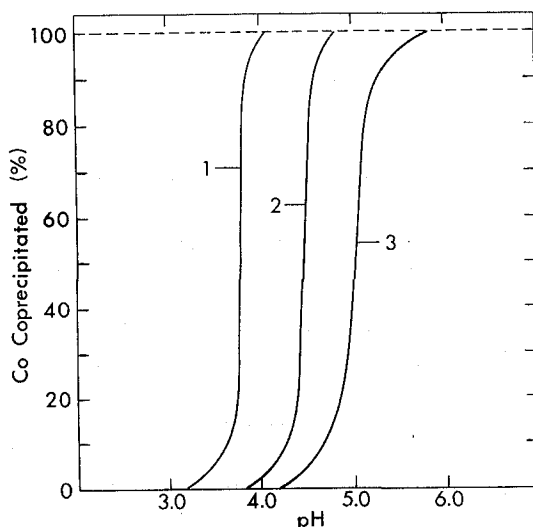

Fig. 1. Effect of concentration of oxine on coprecipitation of cobalt oxinate.
Oxine 1 : 4×10^{-3}M, 2 : 4×10^{-4}M, 3 : 4×10^{-5}M,
Co : 10^{-6}M, α-naphthol : 500 mg., sample solution : 50 ml,

cipitation system, the equilibrium may take place only between the solution and the surface of the solid, in contrast with that the liquid-liquid extraction is a thermodynamically equilibrated state. Therefore, although the effect of the concentration of chelating agent macroscopically resembles each other, it can not be considered that both the effects are completely identical. Although it is a very fundamental problem to reveal the similarity or the difference between the two partition system, the question can not be answered in the present time, because the knowledge of the distribution of metal chelates within the solid phase remains poor so far as the heterogeneous precipitation procedure is adopted like in this research.

Figures 2～6 show the coprecipitation behavior of cobalt, scandium, zinc, lute-
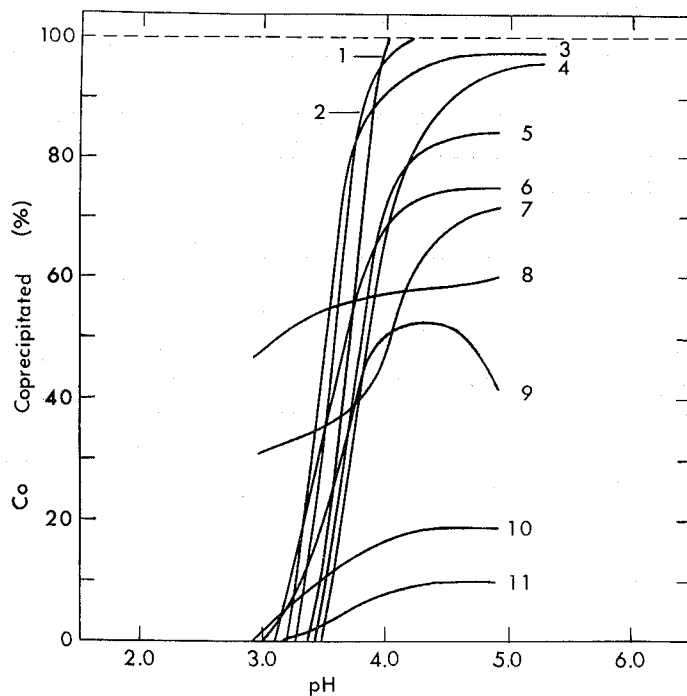
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Fig. 2. Coprecipitation of cobalt oxinate.

coprecipitants (500 mg.),
  1 : α-naphthol ; 2 : o-phenylphenol ; 3 : o,o'-diphenol ;
  4 : phenolphthalein ; 5 : β-naphthol ; 6 : α-nitronaphthalene ;
  7 : α-aminonaphthalene ; 8 : oxine ; 9 : naphthalene ;
  10 : β-aminonaphthalene ; 11 : acridine

Co : 10^{-6}M, oxine : 4×10^{-3}M and sample solution : 50 ml.

tium and europium oxinates with various organic coprecipitants. In all cases, the following precipitating condition was chosen : The final concentrations of the metal ion and oxine were 10^{-6}M and 4×10^{-3}M, respectively ; the added amount to the coprecipitant is 500 mg ; and the total volume of sample solution is 50 ml.

The ability of the organic coprecipitant to carry the oxinate is related to the functional group of the coprecipitant such as OH, NO_2 or NH_2 and its position of aromatic substitution. α-Naphthol, o-phenylphenol and o,o'-diphenol are excellent coprecipitant, and α-nitronapthalene is also favorable, except for cobalt ; β-naphthol or phenolphthalein is better rather than α-nitronaphthalene. Oxine is useful for europium and lutetium, but not for cobalt. This peculiar phenomena might be explained by the fact that the rare earth oxinate is extracted as the addition compound formed with fourth molecule of oxine in liquid-liquid extraction. In general the coprecipitants with hydroxy group are better in carrying the oxinates than the others, and α- or o-substitued compounds are more effective than β- or the other substituted one, but the substitution of amine is not so valid. The interaction between the oxinate and the coprecipitant with the functional groups such as OH, NO_2 or NH_2 is considered to be a kind of the solvation, but not the adduct-formation, since the per cent coprecipitation $vs.$ pH curves never shifted by the change in the amount of coprecipitant within the range studied (100 mg to 1 g).
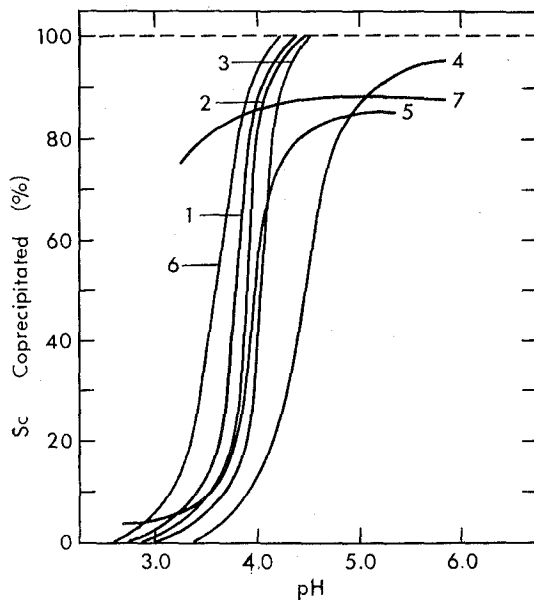
Fig. 3.　Coprecipitation of scandium oxinate.
　　coprecipitants (500 mg.),
　　　1 : α-naphthol ; 2 : o-phenylphenol ; 3 : o,o'-diphenol ;
　　　4 : phenolphthalein ; 5 : β-naphthol ; 6 : α-nitronaphthalene ;
　　　7 : oxine.
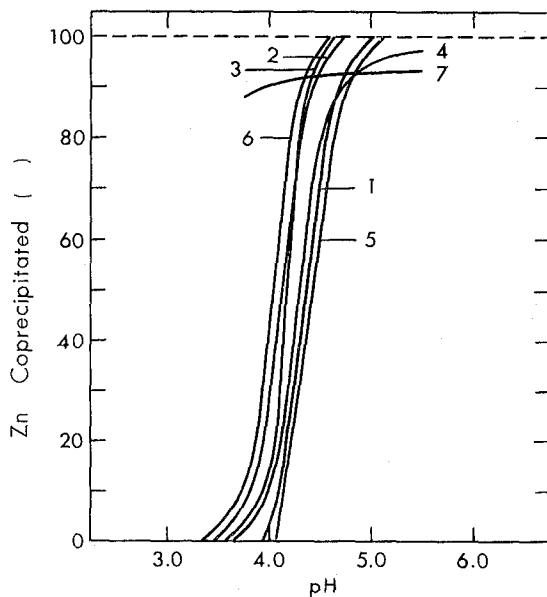Sc : 10^{-6}M, oxine : 4×10^{-3}M and sample solution : 50 ml.

Fig. 4.　Coprecipitation of zinc oxinate.
　　coprecipitants (500 mg.)
　　　1 : α-naphthol ; 2 : o-phenylphenol ; 3 : o,o'-diphenol ;
　　　4 : phenolphthalein ; 5 : β-naphthol ; 6 : α-nitronaphthalene ;
　　　7 : oxine.
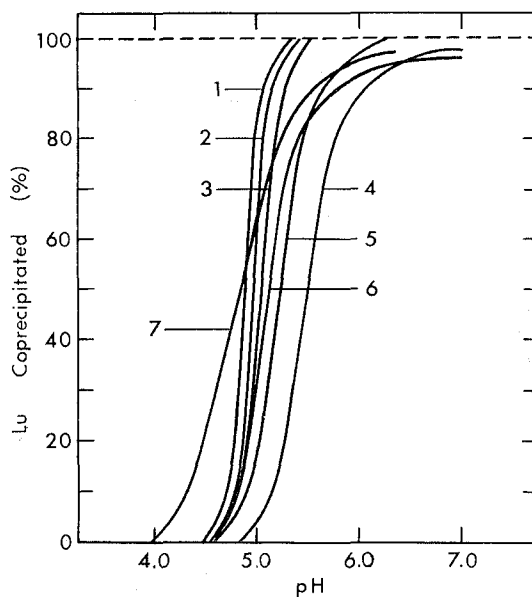Zn : 10^{-6}M, oxine : 4×10^{-3}M and sample solution : 50 ml,

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Fig. 5. Coprecipitation of lutetium oxinate.
  coprecipitants (500 mg.),
    1 : α-naphthol ; 2 : o-phenylphenol ; 3 : o,o'-diphenol ;
    4 : phenolphthalein ; 5 : β-naphthol ; 6 : α-nitronaphthalene ;
    7 : oxine.
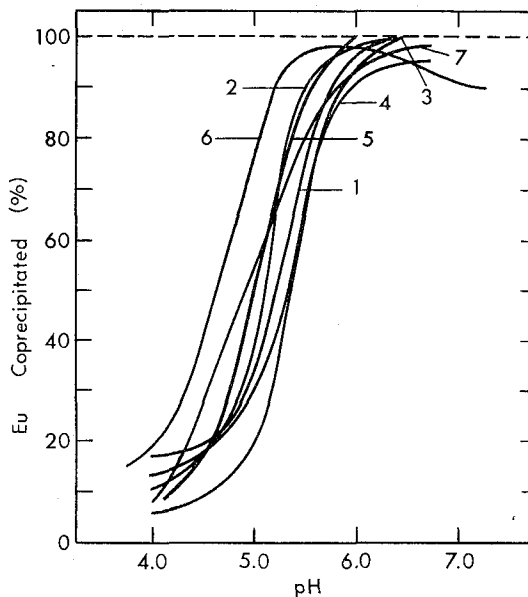Lu : 10^{-6}M, oxine : 4×10^{-3}M and sample solution : 50 ml.

Fig. 6. Coprecipitation of europium oxinate.
  coprecipitants (500 mg.),
    1 : α-naphthol ; 2 : o-phenylphenol ; 3 : o,o'-diphenol ;
    4 : phenolphthalein ; 5 : β-naphthol ; 6 : α-nitronapthalene ;
    7 : oxine.
Eu : 8×10^{-6}M, oxine : 4×10^{-3}M and sample solution : 50 ml.

The coprecipitation behavior of ferric oxinate was also examined by using o-phenylphenol and α-naphthol as coprecipitant. The per cent coprecipitation was determined photometrically as desbribed later, and the result is shown in Fig. 7.
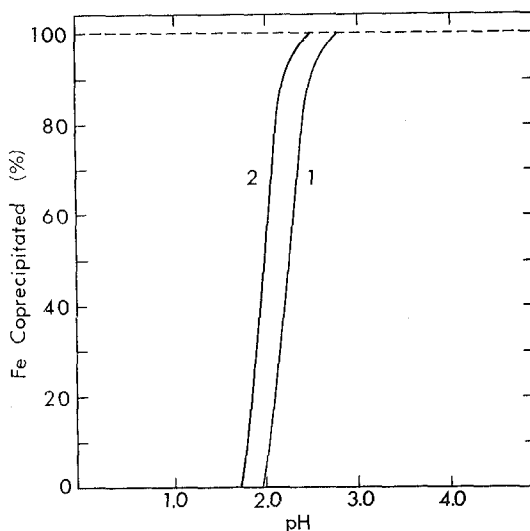

Fig. 7. Coprecipitation of ferric oxinate.
coprecipitants (250mg.),
1 : α-naphthol ; 2 : o-phenylphenol.
Fe : 2×10^{-5}M, oxine : 4×10^{-3}M, and sample solution : 50 ml.

At pH above 3, ferric oxinate can be quantitatively coprecipitated with these coprecipitants.

Ferric iron, cobalt, scandium and europium were recovered from 500 ml of sample solution. The concentrations of each metal ion and oxine were 10^{-6}M and 4×10^{-3}M, and 5 g of organic coprecipitant was used. The pH of the solution is adjusted to a definite value which is chosen from the curves in Figs. 2, 3, 6, and 7, that is, pH 4.5 for ferric iron and cobalt, pH 5.0 for scandium, and pH 6.5 for europium. The results are summerized in Table 1. α-Naphthol and o-phenylphenol

Table 1. Recovery of metal ions from 500 ml of solution.

Carrier (5g)	Element of Coprecipitated (%)			
	Co (II) pH=4.5	Sc(III) pH=5.0	Eu(III) pH=6.5	Fe(III) pH=4.5
α-naphthol	98.5	99.5	98.7	99.6
o-phenylphenol	98.4	99.2	98.6	99.0
o,o'-diphenol	—	99.0	99.6	—
α-nitro-naphthalene	—	98.5	98.1	—
phenolphthalein	85.3	87.7	95.7	—
β-naphthol	75.4	89.0	98.2	—
oxine	—	73.8	97.9	—

Conditions : Volume 500 ml : Metal ion 10^{-6}M ; Oxine 4×10^{-3}M

are superior, α-nitronaphthalene and β-naphthol are also useful, and oxine is again favorable for europium chelate.

The per cent coprecipitation of iron was determined photometrically as follows: Ferric iron is coprecipitated as the oxinate at pH 4.5 with 250 mg of o-phenylphenol or α-naphthol from a 50 ml of sample solution containing 4×10^{-3}M oxine. The precipitate is filtered through a glass filter (No.3) and then dissolved in small amount of benzene. The benzene solution is made transparent by filtering through a filter paper, which is washed several times with fresh benzene. The solution and washings are combined in a 10 ml measuring flask and after diluted to the mark, the absorbance is obtained at 470mμ.

Figure 8 shows the typical calibration curve of ferric iron which is in good agreement with that obtained by liquid-liquid extraction technique, obeying Beer's law up to about 10 ppm. This fact indicates that the coprecipitation recovery
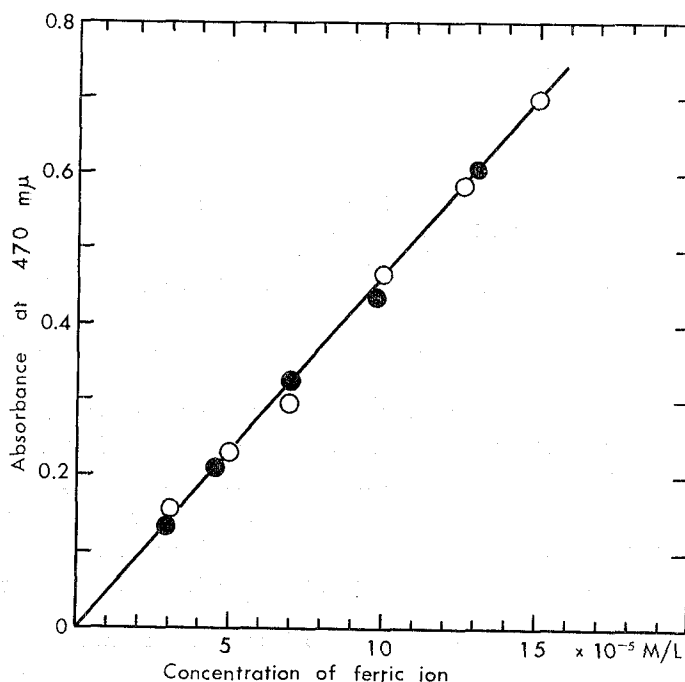

Fig. 8. Calibration curve of ferric ion.

○ : coprecipitation ; oxine : 4×10^{-3}M,   OPP : 250 mg,
      sample solution : 50 ml.

● : solvent extraction ; oxine : 4×10^{-3}M, OPP : 250 mg,
      solvent : benzene, sample solution : 10 ml.

is quantitative, and suggests that the coprecipitation technique can be successfully applied to the direct-spectrophotometric determination of iron: When the organic coprecipitate carrying metal chelate can be ready dissolved in an adequate organic solvent and the organic coprecipitant does not affect the light absorption of the chelate, micro amount of metal present in a much low concentration will be easily and rapidly determined, photometrically. As mentioned above, it is desirable that organic coprecipitant does not exhibit absorption at the wave length, at which the

absorbance of the metal chelate is obtained. Fortunately, o-phenylphenol and α-naphthol does not show any absorption in the region of the wave length which is used for the determination of ferric oxinate. The details of the new spectro-photometry as ferric oxinate will be reported in the near future[8].

SUMMARY

Metal chelates such as ferric iron, cobalt, zinc, scandium, and rare earth oxinates can be quantitatively coprecipitated with some organic coprecipitant at appropriate pH. Organic compound which can be employed as an effective copre-cipitant for metal chelates, has one or more functional group such as OH or NO_2 which may interact with the metal oxinates.

It is desired that the coprecipitant does not show light absorption which affects the absorption of the metal chelates coprecipitated. If the demand is satisfied, the coprecipitation technique will be adopted as a pre-treatment for the photometric determination of micro amount of metal ion present in a very dilute solution.

Among the organic compounds studied, o-phenylphenol and α-naphthol were excellent, and it was suggested that they could be utilized for the direct-spectro-photometric determination of iron as ferric oxinate.

Investigation on the coprecipitation mechanism and on the similarity to the liqiud-liquid extraction is very important problem. The authors will deal with the problem of interest, although it was not concerned in this research.

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