Coprecipitation of Trace Metal Ions with Scandium Hydroxide for Graphite Furnace Atomic Absorption Spectrometry

Joichi Ueda* and Tomoharu Minami
Department of Chemistry, Faculty of Education, Kanazawa University, Kakumamachi, Kanazawa 920-11

(Received March 31, 1997; CL-970240)

Scandium hydroxide is a useful coprecipitant for the preconcentration of copper, tin(IV), lead, antimony(III), bismuth(III), cadmium, chromium(III), cobalt, and nickel on the graphite furnace atomic absorption spectrometry. The determination of trace amount of copper in water was demonstrated.

Coprecipitation has been widely used for the preconcentration of trace elements in water, connecting to various determination techniques, and a variety of coprecipitants have been proposed.[1-5] In the combination with the graphite furnace atomic absorption spectrometry which is prone to suffer from matrix effect, it is desirable to use such a coprecipitant that the separation factor for alkali and alkaline earth metals is sufficient and the presence of the coprecipitant itself does not cause of background absorption. We have been investigating a new coprecipitant of trace metals in water samples for the graphite furnace atomic absorption spectrometric determination and have found that scandium hydroxide has a good collecting ability for copper, tin(IV), lead, antimony(III), bismuth(III), cadmium, chromium(III), cobalt, and nickel and hardly coprecipitates matrix ions such as alkali and alkaline earth metals, and the presence of scandium does not interfere in the determinations of those nine metals. The coprecipitant proposed here may also be applicable for the preconcentration of those trace metals on other determination techniques than the graphite furnace atomic absorption spectrometry.

Measurements were carried out with Shimadzu AA-660G atomic absorption spectrometer with GFA-4A graphite furnace atomizer. A solution containing 5 mg cm^{-3} of scandium was prepared by dissolving scandium nitrate (99.9%) with distilled water. All the other reagents used were of guaranteed reagent grade.

Scandium precipitates almost completely as hydroxide at above pH about 8 by the addition of aqueous ammonia. The usefulness of this hydroxide as a coprecipitant was investigated according to the following coprecipitation procedure, determining the recovery percentages of various metal ions. To an aqueous solution (ca.100 cm^3) containing a metal ion and 10 mg of scandium, an aqueous ammonia was added. The precipitate formed was filtered and dissolved with nitric acid. After the solution was diluted adequately with distilled water, the recovery of each metal ion was determined by the graphite furnace atomic absorption spectrometry. For sodium, potassium, magnesium, and calcium, however, flame atomic absorption spectrometry was used. As the results are shown in Table 1, copper, tin(IV), lead, antimony(III), bismuth(III), cadmium, chromium(III), cobalt, and nickel could be coprecipitated satisfactorily, but the others were hardly collected. In addition, scandium hydroxide coprecipitated quantitatively those nine ions over the wide pH range around 8-10.4. In Figure 1, the cases of copper, lead, and cadmium are shown.

Table 1. Recoveries of some ions by scandium hydroxide

Ion	Added/ mg	Recovery/ %	Ion	Added/ mg	Recovery/ %
Na^+	50	0.3	Cu^{2+}	0.5	100.1
K^+	50	2.8	Cd^{2+}	0.5	99.2
Mg^{2+}	50	0.8	Cr^{3+}	0.5	98.8
Ca^{2+}	50	0.8	Cr(VI)	0.5	42.2
Sr^{2+}	50	1.5	Mo(VI)	0.05	8.1
Ba^{2+}	50	5.2	Mn^{2+}	0.05	7.5
Sn^{4+}	0.5	98.5	Co^{2+}	0.05	98.2
Pb^{2+}	0.5	100.3	Ni^{2+}	0.05	98.5
Sb^{3+}	0.5	99.1	Au^{3+}	0.05	21.3
Bi^{3+}	0.5	97.8			

Ions were coprecipitated at pH about 9.5 using 10 mg of Sc from about 100 cm^3 of aqueous solution.

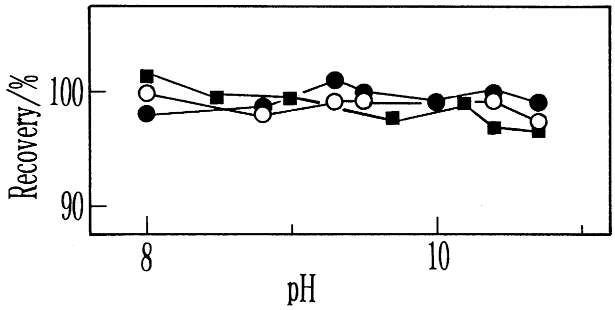

Figure 1. Effect of pH on the recovery of copper, lead, or cadmium. Each ion was coprecipitated from about 100 cm^3 sample solution. Sc 10 mg, (1+1)HNO_3 1cm^3, final volume 25 cm^3. Cu 2.5 μg (●), Pb 2.5 μg (■), Cd 0.12 μg (○). Wavelength(nm) —— Cu 324.7, Pb 283.3, Cd 228.8.

The results examined about the fundamental conditions for the copper determination were described below.

A pH of about 9.5 was chosen for the copper coprecipitation. The recovery of copper reached the maximum value at a few minutes after scandium hydroxide was formed and this value remained almost constant for at least 6h. Although the precipitate dissolves easily in all common mineral acids, nitric acid was used in this experiment because this acid gave the highest atomic absorbance of copper. The presence of up to 1.4 mg cm^{-3} of scandium did not interfere with the copper determination and the calibration curve was linear over the concentration range 2-200 ng cm^{-3} of copper, passing through the point of origin.

From these results, the following procedure for copper determination can be recommended. To a sample solution (100-400 cm^3) containing 0.05-5 μg of copper, 10 mg of

Table 2. Recovery of copper from spiked water samples

Sample	Sample volume/ cm^3	Cu added/ ng cm^{-3}	Cu found/ ng cm^{-3}	RSD, %
Tap water	400	0.5	0.48	5.5
	400	10.0	9.75	1.3
River water	400	0.5	0.48$_5$	6.1
	400	10.0	10.03	2.1
Sea water	400	0.5	0.47$_5$	9.2
	400	10.0	9.70	5.1

The recoveries obtained are the average of four replicate determinations.

scandium is added and the pH of the solution is adjusted to about 9.5 with aqueous ammonia (1+1). After the precipitate has settled, the solution is filtered through a 3G4 sintered-glass filter. The precipitate is washed with a small amount of aqueous ammonia (pH 9.5) and dissolved in 1 cm^3 of nitric acid (1+1). Then the solution is made up to 25 cm^3 with distilled water and the atomic absorbance of copper is measured. The relative standard deviation of this method obtained from five repeat determinations was 1.8% for 1 μg of copper in 100 cm^3 of sample solution and the detection limit (signal to noise ratio = 2) was 0.02 ng cm^{-3} of copper in 400 cm^3 of the initial sample solution. The influence of each of 28 diverse ions on the determination of 1 μg copper was examined by coprecipitating it from about 100 cm^3 of sample solution. Any ions did not give the serious effects on the determination and copper can be determined within 5% error in the presence of ca. 12 mg cm^{-3} of Na^+, ca. 5.2 mg cm^{-3} of K^+, ca. 2.5 mg cm^{-3} each of Mg^{2+} and Ca^{2+}, and ca. 0.01 mg cm^{-3} each of Li^+, Sr^{2+}, Ba^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sn^{4+}, Pb^{2+}, Sb^{3+}, Bi^{3+}, Zn^{2+}, Cd^{2+}, La^{3+}, Zr^{4+}, Th^{4+}, Cr^{3+}, Mo(VI), W(VI), Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Pt(IV), and Au^{3+}. To evaluate the potential of this method, the recoveries of copper from tap, river, and sea water samples spiked with copper were examined. As shown in Table 2, the good results were obtained.

From these results, it can be seen that scandium hydroxide has an excellent collecting ability for copper. Lanthanum which is similar in chemical behavior to scandium has been used widely as a matrix modifier in graphite furnace atomic absorption spectrometry and a coprecipitant of metal ions. So, scandium is also expected to be a good matrix modifier and a coprecipitant as lanthanum be, but there is a disadvantage of scandium that it is more expensive than lanthanum. However, scandium hydroxide can coprecipitate copper from lower pH range, 8-10.4, than lanthanum hydroxide[6] can, 10-12, hardly coprecipitating magnesium which is prone to influence the graphite furnace atomic absorption spectrometry, even if the sample solution contains a large amount of magnesium like sea water. Scandium hydroxide was also recognized to be the effective coprecipitant for tin(IV), lead, antimony(III), bismuth (III), cadmium, chromium(III), cobalt, and nickel on the graphite furnace atomic absorption spectrometric determination. It seems that scandium hydroxide may be applicable for the preconcentration of these nine metal ions on the other various determination techniques.

References and Notes

1 T. R. Crompton, "The Analysis of Natural Waters," Oxford University Press, New York(1993), Vol. 2, pp. 92-123.

2 Yu. A. Zolotov and N. M. Kuz'min, in "Comprehensive Analytical Chemistry," ed by G. Svehla, Elsevier, New York(1990), Vol. 25, pp. 79-94.

3 A. Mizuike, "Enrichment Techniques for Inorganic Trace Analysis," Springer-Verlag, Berlin(1983), pp. 61-66.

4 K. Fuwa, S. Shimomura, S. Toda, and T. Kumamaru, "Saishin Genshikyuko Bunseki (in Japanese)," Hirokawa Pub., Tokyo(1989), pp. 1035-1045.

5 T. Takahashi and H. Daidouji, "Furnace Genshikyuko Bunseki (in Japanese)," Gakkai Shuppan Center, Tokyo (1984), pp. 95, 143.

6 K. Himeno, K. Yanagisawa, T. Yuki, and Y. Nakamura, *Bunseki Kagaku*, **33**, T43(1984).