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Determination of Chromium, Copper and Lead in River Water by Graphite-Furnace Atomic Absorption Spectrometry after Coprecipitation with Terbium Hydroxide

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Coprecipitation with terbium hydroxide quantitatively recovered trace amounts of chromium(III), copper(II) and lead(II) at pH 8.4 - 10.8, 8.0 - 11.5 and 8.7 - 11.5, respectively. The precipitate was dissolved in 0.85 mol dm^{-3} nitric acid, and the analytes were determined by graphite-furnace atomic absorption spectrometry (GF-AAS). The presence of terbium (up to 7 g dm^{-3}) did not interfere with the determination. The detection limits were 0.3 μg dm^{-3} for chromium, 0.4 μg dm^{-3} for copper and 0.5 μg dm^{-3} for lead, when the analytes in 200 cm^3 of the sample solution were concentrated into 10 cm^3. The ions added to river or seawater were quantitatively recovered. Chromium and copper in a contaminated river water were successfully determined.

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Coprecipitation with metal hydroxides has been widely used for the concentration of trace metal ions in water, associated with a number of determination techniques.[1,2] Various coprecipitants have been used for the preconcentration of chromium,[3-5] copper[4,6,8] and lead[7] in natural water prior to determination by graphite-furnace atomic absorption spectrometry (GF-AAS). They include hydroxides of gallium,[3] indium,[4] or tin,[7,8] and iron hexamethylenedithiocarbamate.[5,6] Since most of these coprecipitants cause serious spectral interference, the separation of analytes from the coprecipitants is necessary.

We have been studying the systematics of coprecipitation with rare earth hydroxides. In previous studies,[9,10] we found that scandium hydroxide has a good collecting ability for many trace metals, and hardly coprecipitates matrix ions, such as alkali and alkaline earth metals. Since scandium does not cause serious interference, the analytes were determined by GF-AAS after the precipitate was simply dissolved in diluted nitric acid.

We focused on terbium as a middle rare earth element. Terbium hydroxide has been used for the coprecipitation of selenite[11] and indium.[12] Recently, we found that terbium hydroxide has a good collecting ability for chromium(III), copper(II) and lead(II), and hardly coprecipitates the matrix ions. Additionally, terbium does not interfere with the determination of the metals by GF-AAS, and is less expensive than scandium.

In this paper, we describe the conditions for the coprecipitation of trace amounts of chromium, copper and lead with terbium hydroxide and for the determination of these elements by GF-AAS, and the application of the present method to river water.

Experimental

Apparatus

A Shimadzu AA-660G atomic absorption spectrometer with a GFA-4A graphite furnace atomizer was used for GF-AAS measurements. The optimum operating conditions, which were studied using a 0.85 mol dm^{-3} nitric acid solution containing 2.5 g dm^{-3} of terbium and 0.1 mg dm^{-3} of chromium, copper and lead, are summarized in Table 1. A Hitachi-Horiba Model M-5 pH meter with a glass-electrode was used for pH measurements.

Reagents

Nitric acid and sodium hydroxide of guaranteed reagent grade (Nacalai Tesque Inc.) were used. Reagents of guaranteed reagent grade were used as long as they were available. Deionized water with a Milli-Q system (Elix-5-Guradient-A10, Millipore) was used to prepare of all solutions.

Chromium(III), copper(II) and lead(II) solutions. A stock solution containing 1 g dm^{-3} of chromium(III), copper(II) or lead(II) was prepared by dissolving their nitrates in a small amount of concentrated nitric acid and diluting with deionized water. The concentration of chromium and lead was determined by complexometric titration using Xylenol Orange (Dotite) as an indicator and that of copper using Murexide (Dotite).

Terbium solution. A terbium stock solution (8.5 g Tb^{3+} dm^{-3})

Table 1 Operating conditions for GF-AAS

	Cr	Cu	Pb
Sample volume/mm^3	20	20	20
Analytical wavelength/nm	357.9	324.7	283.3
Lamp current/mA	10	10	10
Slit width/nm	0.50	0.50	1.0
Argon gas flow rate			
Inner gas/dm^3 min^{-1}	1.5	1.5	1.5
Outer gas/dm^3 min^{-1}	1.5	1.5	1.5
Drying (Ramp)	150°C, 40 s	150°C, 40 s	150°C, 45 s
Ashing (Step)	700°C, 20 s	500°C, 20 s	250°C, 20 s
Atomizing (Step)[a]	2500°C, 4 s	2300°C, 4 s	1400°C, 3 s
Cleaning (Step)	2800°C, 2 s	2800°C, 2 s	2800°C, 2 s

a. Inner gas was stopped.

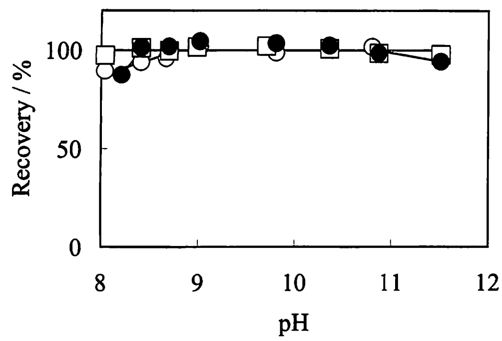

Fig. 1 Effect of the pH on the recovery of Cr^{3+} (●), Cu^{2+} (□) or Pb^{2+} (○).

Table 2 Tolerance ratio of diverse ions for the determination of Cr^{3+}, Cu^{2+} and Pb^{2+}

Tolerance ratio[a] Ion [mg]/Tb [mg]	Ion
10	Na^+, K^+, Mg^{2+}, Ca^{2+}
0.04	Li^+, Ba^{2+}, Al^{3+}, La^{3+}, Th^{4+}, Zr^{4+}, Cr^{3+},[b] MoO_4^{2-}, WO_4^{2-}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+},[c] Zn^{2+}, Cd^{2+}, In^{2+}, Sn^{4+}, Pb^{2+},[d] Sb^{3+}
0.02	Fe^{3+}

a. Errors in determination of Cr^{3+}, Cu^{2+} and Pb^{2+} were within ± 5%, when the ratio of the diverse ion was less than the value.
b. Influence on Cu^{2+} and Pb^{2+} was examined.
c. Influence on Cr^{3+} and Pb^{2+} was examined.
d. Influence on Cr^{3+} and Cu^{2+} was examined.

was prepared by dissolving terbium chloride (Nacalai Tesque Inc., extra pure reagent grade), and the concentration was determined by complexometric titration using Xylenol Orange as an indicator.

Recommended procedure

A sample solution (200 cm^3) placed in a Pyrex glass beaker was added to 3 cm^3 of the terbium stock solution, which contained 25 mg of terbium, and the pH was adjusted to 9 with a 0.1 mol dm^{-3} sodium hydroxide solution. After the solution was allowed to stand for several minutes, the precipitate was collected on a 3G4 sintered-glass filter (pore size 5 - 10 μm, diameter 30 mm), washed with a small amount of deionized water, and dissolved with 0.6 cm^3 of concentrated nitric acid. The solution was made up to 10 cm^3 with deionized water. The atomic absorbance of chromium, copper or lead in this solution was measured under the operating conditions given in Table 1.

It took some 15 min for filtration with a glass filter. The filter was easily cleaned with nitric acid and used repeatedly.

Results and Discussion

Optimum conditions for coprecipitation

In a preliminary experiment, we found that terbium hydroxide flocculated at pH above 7, giving a filterable precipitate. The effect of the pH on the coprecipitation of metal ions with terbium hydroxide was studied with a solution containing 5 μg dm^{-3} of chromium(III), copper(II) and lead(II). The results are shown in Fig. 1. Quantitative recoveries were obtained over pH ranges of 8.4 - 10.8 for chromium(III), 8.0 - 11.5 for copper(II) and 8.7 - 11.5 for lead(II). A pH of 9 was used for the coprecipitation of these ions in further experiments.

Among lanthanoide(III) hydroxides, lanthanum[13-15] and samarium[16] hydroxides have been used for the coprecipitation of chromium, copper and lead, as far as we know. When using these hydroxides, it is necessary that the pH of the sample solution is adjusted to higher than 9.8. Thus, the pH for the coprecipitation of these analytes with terbium hydroxide is lower than that with hydroxide of lanthanum or samarium. This is probably due to the lower solubility product of terbium hydroxide.[17] The lower pH for coprecipitation with terbium hydroxide is advantageous for the separation of the analytes from alkali and alkaline earth metals.

The necessary amount of terbium for the coprecipitation was examined with 200 cm^3 of the sample solution spiked with 5 μg dm^{-3} of chromium(III), copper(II) and lead(II). More than 14 mg of terbium was required for quantitative recoveries. Twenty five milligrams of terbium was used in further experiments.

The recoveries of the analytes reached 100% within several minutes after the formation of terbium hydroxide, and remained unchanged while standing for 3 h.

The precipitate of terbium hydroxide was readily dissolved with nitric or hydrochloric acid.

Determination of the analytes by GF-AAS

The conditions for the determination of the analytes by GF-AAS were normally examined in the presence of 2.5 g dm^{-3} of terbium. The atomic absorbance of the analytes did not depend on the concentration of nitric acid in a range of 0.5 - 2.0 mol dm^{-3}. However, the absorbance of chromium and lead gradually decreased with an increase in the hydrochloric acid concentration. The absorbance of lead was about 45% lower in 0.9 mol dm^{-3} hydrochloric acid than that in 0.85 mol dm^{-3} nitric acid. Thus, nitric acid was used in further experiments.

The absorbances and concentrations showed linear relationships, passing through the origin, up to 200 μg dm^{-3} for chromium and copper and 150 μg dm^{-3} for lead. The absorbances of the analytes did not change with the presence of terbium up to 7 g dm^{-3}.

The relative standard deviations for the absorbances obtained from five repeated determinations for 100 μg dm^{-3} of chromium(III), copper(II) and lead(II) were 3.2%, 3.7% and 4.6%, respectively. The detection limits, which were calculated as 3-times the standard deviation, were 0.3 μg dm^{-3} for chromium, 0.4 μg dm^{-3} for copper and 0.5 μg dm^{-3} for lead, when a 20-times concentration was applied.

Interferences of diverse ions

The effect of 23 diverse ions on the determinations of chromium(III), copper(II) and lead(II) was examined through the recommended procedure using 40 cm^3 of sample solution. The initial concentrations were 25 μg dm^{-3} for the analytes and 0.625 g dm^{-3} for terbium. Table 2 shows that large amounts of sodium, potassium, magnesium and calcium did not interfere with the determination. Other ions tested did not produce any serious interference effect up to 12.5 - 25 mg dm^{-3}.

Recoveries of spiked chromium(III), copper(II) and lead(II) from water samples

The recoveries of spiked chromium(III), copper(II) and lead(II) from river and seawater were examined. The water samples were collected from the upper reaches of the Asano River and the Kanaiwa Harbor, Ishikawa Prefecture, and acidified to 7.5×10^{-3} mol dm^{-3} nitric acid. As shown in Table 3, the obtained recoveries are satisfactory. Blank runs were

Table 3 Recovery of spiked Cr^{3+}, Cu^{2+} and Pb^{2+} from water samples

Sample, sampling date	Cr^{3+}			Cu^{2+}			Pb^{2+}		
	Found/ μg dm^{-3}	Added/ μg dm^{-3}	Recovery,[a] %	Found/ μg dm^{-3}	Added/ μg dm^{-3}	Recovery,[a] %	Found/ μg dm^{-3}	Added/ μg dm^{-3}	Recovery,[a] %
River water									
Feb. 8	0.35	0.5	101 ± 2.6	0.51	0.5	96.4 ± 4.7	ND	0.5	101 ± 10
Dec. 17	ND	5	100 ± 6.0	0.41	5	102 ± 6.8	ND	5	95.7 ± 3.3
Feb. 12	0.44	10	103 ± 3.0	0.47	10	95.0 ± 3.2	ND	7.5	96.0 ± 2.3
Sea water									
Feb. 19	0.41	0.5	99.0 ± 2.6	0.47	0.5	105 ± 11	0.95	0.5	101 ± 8.9
Dec. 14	ND	5	100 ± 1.9	0.73	5	96.1 ± 3.3	0.58	5	101 ± 2.1
Feb. 20	ND	10	99.8 ± 1.1	ND	10	99.1 ± 4.2	ND	7.5	96.7 ± 1.5

a. The recovery is the average and SD of three replicate determinations. ND: Not detected.

Table 4 Results of the determination of chromium, copper and lead in water of a tributary of the Gohtani River

Method	Cr/μg dm^{-3}	Cu/μg dm^{-3}	Pb/μg dm^{-3}
Calibration curve method	0.72 ± 0.09	206[a] ± 16	ND
Standard addition method	0.98 ± 0.17	222[a] ± 12	—

The results are the average and SD for three replicate determinations.
ND: Not detected.
—: Not determined.
a. The final solution was diluted 30 times with 0.85 mol dm^{-3} nitric acid prior to the determination.

carried out using 200 cm^3 of deionized water as a sample. The blank values were 0.3 μg dm^{-3} for chromium, 0.4 μg dm^{-3} for copper and 0.5 μg dm^{-3} for lead, which were almost the same as the detection limits discussed above. Thus, it seems that the proposed method is applicable to the analysis of these water samples containing above 0.3 - 0.5 μg dm^{-3} of chromium(III), copper(II) and lead(II).

Application to the determinations of chromium, copper and lead in river water

The present method was applied to a river water sample that was collected from a tributary of the Gohtani River flowing in Komatsu City, Ishikawa Prefecture. There is a copper mine, the Ogoya Mine, in the drainage area of the tributary. The mine had been worked for some 300 years and shut down in 1962.

This sample was filtered through Advantec quantitative filter paper (No. 5C, diameter 300 mm), and acidified to 0.12 mol dm^{-3} hydrochloric acid. Prior to coprecipitation, 200 cm^3 of the sample was spiked with 0.5 g of hydroxylammonium chloride, and left standing for 3 h in order to reduce chromium(VI) to chromium(III). The determined concentration is, therefore, for the sum of chromium(III) and chromium(VI).

The results are given in Table 4. The data for chromium and copper were corrected for the blank values. The concentrations of chromium and copper in the sample solution were determined by a calibration curve method and a standard addition method. The results of copper were in good agreement with the two methods. The data of chromium by the standard addition method gave, however, slightly higher values and variations than those by the calibration curve method. Lead was not detected, since the found values were not significantly higher than the blank values.

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