Determination of Chromium(III) and Chromium(VI) by Electrothermal Atomization Atomic-Absorption Spectrometry Following Coprecipitation with Gallium(III) Phosphate

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Gallium(III) phosphate coprecipitates quantitatively 0.2—7.5 μg of chromium(III) from 100 to 500 cm^3 of a sample solution at pH 4.5—6.0. Although chromium(VI) is hardly coprecipitated with gallium(III) phosphate, it can be collected as chromium(III) after reduction by hydroxylamine. The calibration curve is linear from 8 to 300 $ng\,cm^{-3}$ for chromium. The detection limit (signal/noise=2) is 0.11 $ng\,cm^{-3}$ of chromium(III) or chromium(VI) in 500 cm^3 of the initial sample solution.

The coprecipitation method is one of the most useful ways to concentrate trace metal ions. A large number of coprecipitants have been investigated.1—3) Previously, we suggested that gallium(III) phosphate is useful as a collector of trace amounts of lead(II),4) tin(IV),5) and indium(III).6) This time, we report that gallium(III) phosphate also coprecipitates chromium(III) quantitatively, and that the coprecipitated chromium(III) could be determined by electrothermal atomization atomic absorption spectrometry without any influence of gallium(III) phosphate. In this method, although chromium(VI) is hardly coprecipitated with gallium(III) phosphate, it can be done as chromium(III) after reduction using hydroxylamine.7—9) By utilizing this method, consecutive determinations of chromium(III) and chromium(VI) were also studied. The methods proposed here are simple and have good reproducibilities.

For the preconcentration of chromium(III) and/or chromium(VI) prior to an electrothermal atomization atomic absorption spectrometric determination, the following coprecipitants have been proposed: manganese diethyldithiocarbamate (manganese DDTC)10,11) and hydroxides of iron(III),12—20) magnesium,21) indium,22) and aluminium23) for chromium(III), manganese DDTC,10,11) lead sulfate,24,25) cobalt 1-pyrrolidinecarbodithioate (cobalt APDC),26) and zinc diethyldithiocarbamate (zinc DDTC)27) for chromium(VI), hydroxides of bismuth15,16) and iron(II)19—21) for both chromium(III) and chromium(VI), and hydroxides of lanthanum28,29) and zirconium30) for chromium. However, some of these coprecipitants have their own disadvantages. The presence of iron,15—19) bismuth,15,16) and magnesium,21) used as coprecipitants, is prone to influence the atomic absorbance of chromium. In the cases of cobalt APDC26) and lanthanum hydroxide,28,29) the recoveries of chromium(VI) and chromium are incomplete, respectively. The dissolution of manganese DDTC10,11) requires heating, and that of zinc DDTC27) and zirconium hydroxide30) is slow. A method using gallium(III) phosphate as a coprecipitant overcomes these weak points.

This paper describes the fundamental conditions for the coprecipitation of trace amounts of chromium(III) and chromium(VI) with gallium(III) phosphate and for their determination using electrothermal atomization atomic absorption spectrometry.

Experimental

Apparatus. All of the equipment employed in this work has been described previously.5)

Reagents. The reagents were the same as those described previously,5) except for those mentioned below.

Standard Chromium(III) Solution: A solution containing about 1000 $\mu g\,cm^{-3}$ of chromium(III) was prepared by dissolving chromium(III) nitrate in a small amount of nitric acid and diluting with distilled water. The concentration of this solution was determined by complexometric back titration.

Standard Chromium(VI) Solution: A solution containing 1000 $\mu g\,cm^{-3}$ of chromium(VI) was prepared by dissolving potassium dichromate (99.99%) in distilled water.

Recommended Procedures. Determination of Chromium(III): To a sample solution (100—500 cm^3) containing 0.2—7.5 μg of chromium(III), 15 mg of gallium(III) and 3 cm^3 of 0.5 $mol\,dm^{-3}$ phosphoric acid are added. Gallium(III) phosphate is then precipitated at a pH of about 5 using 7 $mol\,dm^{-3}$ and 1 $mol\,dm^{-3}$ ammonia solution.

After the precipitate is allowed to settle, the solution is filtered by suction using a 3G4 glass filter. After the collected precipitate is dissolved in 1 cm^3 of concentrated nitric

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acid, the solution is diluted to 25 cm^3 with distilled water. The atomic absorbance of chromium(III) is then measured at 359.3 nm.

Determination of Chromium(VI): A sample solution (100—500 cm^3) containing 0.2—7.5 μg of chromium(VI) is acidified with hydrochloric acid at a concentration of about 0.1 mol dm^{-3}. After adding 0.5 g of hydroxylamine hydrochloride, the sample is allowed to stand for about 1 h in order to reduce chromium(VI) to chromium(III). Then, the obtained chromium(III) is determined using the same procedure as that for chromium(III). If the sample solution contains both chromium(III) and chromium(VI), their total amount is obtained. In this case, the amount of chromium(VI) can be calculated by subtracting the content of chromium(III) from the total amount.

Results and Discussion

Composition of the Precipitate of Gallium(III) Phosphate. The contents of gallium(III) and phosphate in the precipitate formed at pH 5 were measured by electrothermal atomization atomic absorption spectrometry and by the molybdenum blue method spectrophotometrically, respectively. The mole ratio of gallium(III) and phosphate in it was estimated to be about 1 : 1. The X-ray diffraction analysis suggested that the precipitate was amorphous.

Optimum Conditions for Coprecipitation of Chromium(III) and Chromium(VI). Gallium(III) phosphate coprecipitated chromium(III) quantitatively at pH 4.5—6.0 (Fig. 1). In Fig. 1, the results of examinations concerning some metal ions are also appended. Almost 100% recovery of chromium(III) was obtained within a few minutes after the formation of gallium(III) phosphate; it remained almost constant upon standing for at least 24 h. On the other hand, chromium(VI) was hardly coprecipitated with gallium(III) phosphate at pH 3.0—6.0 (Fig. 1). By adding 0.5 g of hydroxylamine hydrochloride[7—9] into 100—500 cm^3 of a sample solution acidified with hydrochloric acid in concentrations to about 0.1 mol dm^{-3}, however, it could be completely reduced to chromium(III), and could then be quantitatively coprecipitated without any interference from hydroxylamine.

The required amount of gallium(III) for the quantitative recovery of chromium(III) was more than 5 mg for both 100 and 500 cm^3 of the sample solution. The presence of gallium(III) did not affect the determination of chromium(III) over the range of 0.1—1.2 mg cm^{-3} of gallium(III) in the final sample solution. The necessary amount of phosphoric acid for the quantitative coprecipitation of chromium(III) was more than 0.1×10^{-3} mol for 100 cm^3 of the sample solution and 0.5×10^{-3} mol for 500 cm^3. The presence of phosphate also did not influence the determination of chromium(III).

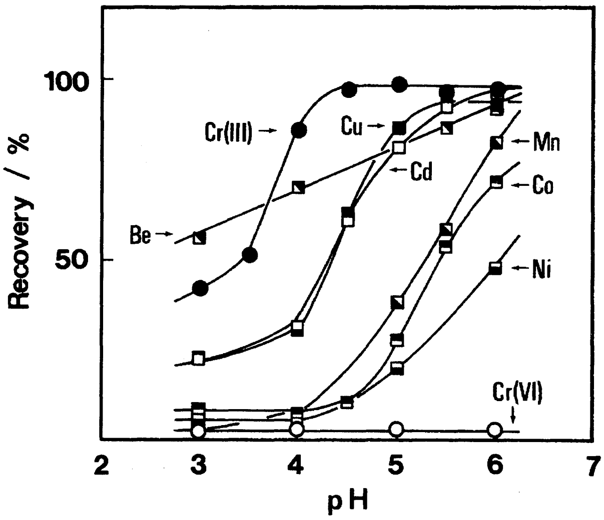

Fig. 1. Effect of the pH on the recoveries of chromium(III), chromium(VI), and some metal ions. Ga(III), 15 mg (Cr(III)(●) and Cr(VI)(○)) or 10 mg (Be(II)(◪), Mn(II)(◩), Co(II)(⬒), Ni(II)(⬓), Cu(II)(■), and Cd(II)(□)); 0.5 mol dm^{-3} H_3PO_4, 3 cm^3; concd HNO_3, 1 cm^3; final volume, 25 cm^3. ●) Cr(III), 4 μg. ○) Cr(VI), 4 μg. ◪) Be(II), 0.2 μg. ◩) Mn(II), 0.25 μg. ⬒) Co(II), 25 μg. ⬓) Ni(II), 25 μg. ■) Cu(II), 12.5 μg. □) Cd(II), 0.25 μg.

For the dissolution of gallium(III) phosphate, nitric acid was preferred to hydrochloric acid, because the former acid gave a slightly higher absorbance of chromium than did the latter acid, although gallium(III) phosphate dissolved readily in either acid. In this procedure, 1 cm^3 of concentrated nitric acid was used.

The Relation between the Coprecipitated Amount of Chromium(III) and the Remained Amount of Chromium(III) in the Solution. Using 2.5 mg of gallium(III) and 3 cm^3 of 0.5 mol dm^{-3} phosphoric acid, the 0.05—2.0 mg range of chromium(III) was coprecipitated at pH 5.0 from 60 cm^3 of aqueous solution and; the solution was then stood for 5 h at 25.0±0.1 °C. According to the results shown in Fig. 2, the relation between the coprecipitated amount of chromium(III) and its remaining amount in the solution followed the Freundlich adsorption isotherm,[31,32]

$$\log (x/m) = (1/n)\log C + \log k, \tag{1}$$

where x is the coprecipitated amount of chromium(III) (mol), m is the amount of gallium(III) phosphate used for the coprecipitation (mol), C is the concentration of the remaining chromium(III) in the solution (mol per 60 cm^3), and n and k are constants. From this, the coprecipitation of chromium(III) with gallium(III) phosphate seems to be governed mainly by adsorption. In this experiment, the recovery of chromium(III) was more than 95% when a 0.05—0.2 mg range was coprecipitated; however, its recovery decreased along with an increase in the amount of chromium(III) from 0.2—2.0 mg. Thus, for the initial amount range from 0.05—0.2 mg of chromium(III), n and $\log k$ were 1.30 and 4.23 and for 0.2—2.0 mg of chromium(III), 2.64 and 1.58, respectively. In Fig. 2, the results of beryllium(II), copper(II),

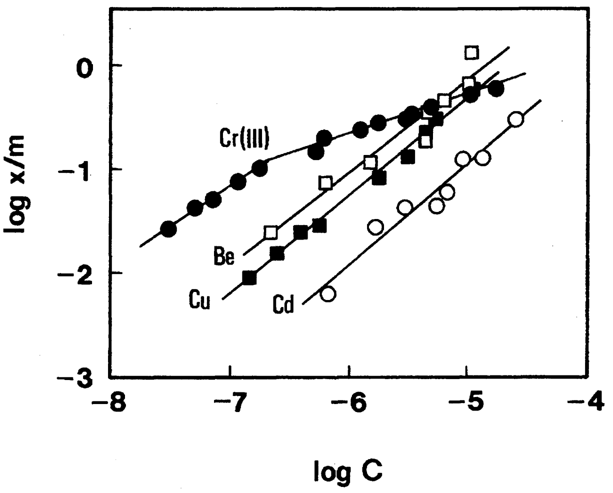

Fig. 2. Relations between the coprecipitated amounts of some metal ions and the remained amounts of them in the solution after the coprecipitation. ●) Cr(III). □) Be(II). ■) Cu(II). ○) Cd(II). Ga(III), 2.5 mg; 0.5 mol dm^{-3} H_3PO_4, 3 cm^3; pH, 5.0; temperature, 25.0±0.1 °C. x: The coprecipitated amount of metal ion (mol). m: The amount of gallium(III) phosphate used for the coprecipitation (mol). C: The concentration of metal ion remaining in the solution after the coprecipitation (mol per 60 cm^3).

and cadmium(II) which can be recovered more than 80% at pH 5 (Fig. 1) are also appended.

Optimization of Operating Conditions. Almost constant peak heights were obtained with 27—30 A of heating current and a heating time of 20—40 s during the drying stage, and with 80—140 A and 20—60 s during the ashing stage, respectively. In the atomizing stage, the peak height became higher along with an increase of the heating current, and reached a maximum at 310 A, which is the highest current obtainable in this apparatus. This peak height remained almost constant for a heating time of 5—10 s. For an atomizing time of 5—7.5 s, however, a memory effect was observed.

Calibration Curves. Straight lines through the point of origin were obtained over the concentration range from 8 to 300 ng cm^{-3} of both chromium(III) and chromium(VI). The reproducibilities of these procedures (relative standard deviation) for the peak heights obtained from five repeated determinations were 1.56% for 4 μg of chromium(III) in 100 cm^3 of the sample solution and 0.61% for 5 μg of chromium(VI), respectively. The detection limit (signal to noise ratio=2) was 0.11 ng cm^{-3} of chromium(III) or chromium(VI) in 500 cm^3 of the initial sample solution.

Interference. The influence of each of 32 diverse ions on the determination of 4 μg of chromium(III) in 100 cm^3 of a sample solution was examined according to the recommended procedure. Chromium(III) could be determined within a ±5% error in the presence of each of 100 mg of potassium(I) and magnesium(II), 25 mg of calcium(II), 1 mg of lithium(I), beryllium(II), strontium(II), barium(II), indium(III), thallium(I), thallium(III), germanium(IV), tin(IV), lead(II), antimony(III), bismuth(III), selenium(IV), tellurium(IV), zinc(II), lanthanum(III), titanium(IV), vanadium(V), manganese(II), iron(III), cobalt(II), and nickel(II), and 0.1 mg of molybdenum(VI). Although 1200 mg of sodium(I) and 1 mg of aluminium(III), arsenic(V), copper(II), cadmium(II), and tungsten(VI) interfered with the determination when a non-impregnated graphite furnace was used, their interferences could be remarkably reduced by using a graphite furnace impregnated with hafnium.[33)]

Recoveries of Chromium(III) and Chromium(VI) from Spiked Water Samples. Using the recommended procedures, the recoveries of 0.25—5.0 μg

Table 1. Results of the Determination of Chromium(III) and Chromium(VI) in River Water

Location in Gohtani river	Calibration method			Standard addition method	
	Cr(III) found	Cr(III)+Cr(VI) found	RSD	Cr(III)+Cr(VI) found	RSD
	μg dm^{-3}	μg dm^{-3}	%	μg dm^{-3}	%
Upper stream of Kuratani bridge	—	N.D.	—	—	—
Branch around Kuratani bridge[a)]	T.	0.49_3	3.0	—	—
	T.	0.40_1	8.3	0.44_2	4.7
Lower stream of Kuratani bridge	T.	(0.14_1)[b)]	10.9	0.14_8	7.2
Nodani bridge	T.	(0.14_8)[b)]	20.1	0.13_3	20.6

The results obtained are the average of three replicate determinations. a) Sampled on separate days. b) The result was estimated by the extrapolation of the calibration curve. N. D. : Not detected. T. : Trace. RSD: Relative standard deviation.

of chromium(III) and chromium(VI) in 100—500 cm^3 of sample solutions were examined; 95—105% recoveries were obtained within the relative standard deviation range of 0.7—13.8% from distilled, tap, and river water samples.

Determination of Chromium(III) and Chromium(VI) in River Water. Based on the results mentioned above, the determination of chromium(III) and chromium(VI) in river water (located in Ishikawa prefecture) was tried. For the total amount of chromium(III) and chromium(VI), the results obtained by the calibration and the standard addition methods were in good agreement with each other (Table 1). However, chromium(III) could not be determined. Its concentration seems to have been around, or less than, the detection limit of the proposed method.

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