

Selective Coprecipitation of Chromium(III) in Water with Scandium Hydroxide Prior to Graphite Furnace Atomic Absorption Spectrometric Determination

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Abstract

Chromium(III) was separated from chromium(VI) by the coprecipitation with scandium hydroxide and determined by graphite furnace atomic absorption spectrometry (GF-AAS). In the presence of 0.28 mol dm^{-3} sodium sulfate and $0.28 \times 10^{-3} \text{ mol dm}^{-3}$ disodium hydrogen phosphate, chromium(III) up to $10 \mu\text{g dm}^{-3}$ was quantitatively coprecipitated with scandium hydroxide at pH 9.8, while $50 \mu\text{g dm}^{-3}$ of chromium(VI) was hardly coprecipitated. Under this condition, chromium(III) was separated from chromium(VI) when the concentration of chromium(VI) was less than five times that of chromium(III). The sum of chromium(III) and chromium(VI) was determined in a similar way after the reduction of chromium(VI) to chromium(III) with 2.5 g dm^{-3} of hydroxylammonium chloride at 0.12 mol dm^{-3} of hydrochloric acid. This coprecipitation method was applied to the determination of chromium(III) and chromium(VI) in a water sample collected from an urban river.

Introduction

There is substantial interest in speciation of chromium in water. Chromium(III) and chromium(VI) are found in aqueous media. The chromium(III) species are chiefly present as hydroxo complexes. The chromium(VI) species are dominated by chromate and are highly toxic. Speciation of chromium(III) and chromium(VI) on the basis of coprecipitation has been widely investigated because of its simplicity. Selective coprecipitation of chromium(III) was studied using iron hydroxide,¹⁻⁵ aluminium hydroxide,⁶ gallium hydroxide,⁷ gallium phosphate,⁸ hafnium hydroxide⁹ and yttrium

hydroxide.¹⁰ For selective coprecipitation of chromium(VI), reagents employed were lead sulfate^{11,12} and zinc-diethyldithiocarbamate.¹³ In some cases, since the presence of a coprecipitant affects the determination of chromium, it is necessary to remove the coprecipitant⁵ or to add a chemical modifier⁷ prior to the determination.

Although rare earth hydroxides such as lanthanum hydroxide,^{14,15} terbium hydroxide¹⁶ and erbium hydroxide¹⁷ were also applied to the coprecipitation of chromium, speciation of chromium(III) and chromium(VI) has not been achieved except for yttrium hydroxide. We have been studying the systematics of coprecipitation

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with rare earth hydroxides. In a previous study, we found that scandium hydroxide is promising for the coprecipitation of trace metals prior to graphite furnace atomic absorption spectrometry (GF-AAS),^{18,19} since scandium did not interfere with the GF-AAS determinations of some metals. In addition, we found in preliminary experiments that the coprecipitated percentage of chromium(VI) was lower for heavy lanthanoid and scandium hydroxides, while chromium(III) was quantitatively coprecipitated.

In this paper, we describe the conditions of coprecipitation with scandium hydroxide for the separation of chromium(III) and chromium(VI) and the determination of chromium(III) and chromium(VI) in water samples.

Experimental

Apparatus

A Shimadzu AA-660G atomic absorption spectrometer with a GFA-4A graphite furnace atomizer was used for the chromium determinations. The graphite tube used was a high density graphite tube (not pyrolyzed). The optimum operating conditions for chromium are summarized in Table 1. The background was corrected using a D₂ lamp throughout the experiments. A Perkin Elmer Optima 2000DV inductively-coupled plasma atomic emission spectrometer was used for preliminary experiments. A Hitachi-Horiba Model M-5 pH meter with a glass-electrode was used for

pH measurements.

Reagents

Reagents of guaranteed reagent grade were used except for scandium oxide. Deionized water (Elix-5-Gradient-A10, Millipore) was used for the preparation of all solutions.

Chromium solutions. Chromium(III) solution (1 g dm⁻³) was prepared by dissolving 770 mg of chromium(III) nitrate nonahydrate (Nacalai Tesque Inc.) with a small amount of concentrated nitric acid and diluting to 100 cm³ with deionized water. Chromium(VI) solution (1 g dm⁻³) was prepared by dissolving 283 mg of potassium dichromate (Wako Pure Chemical Industries, Ltd.) in 100 cm³ of 0.1 mol dm⁻³ nitric acid.

Phosphate solution. Phosphate solution (0.28 mol dm⁻³) was prepared by dissolving 1.246 g of disodium hydrogen phosphate dihydrate in 25 cm³ of deionized water.

Scandium solution. Scandium solution

Table 1 Operating conditions of GF-AAS for chromium

Sample volume/ mm ³	20
Analytical wavelength/ nm	357.9
Lamp current/ mA	10
Slit width/ nm	0.50
Argon gas flow rate	
Inner gas/ dm ³ min ⁻¹	1.5
Outer gas/ dm ³ min ⁻¹	1.5
Drying	Ramp, 150°C, 50 s
Ashing	Step, 600°C, 30 s
Atomizing	Step, 2500°C, 4 s ^a
Cleaning	Step, 2800°C, 2 s

a. Inner gas was stopped.

(1.5 g dm⁻³) was prepared by dissolving 230 mg of scandium oxide (99.9%, Wako Pure Chemical Industries, Ltd.) in 8 cm³ of concentrated nitric acid on heating and diluting to 100 cm³ with deionized water.

Recommended Procedure

Determination of chromium(III)

An aliquot of sample solution (200 cm³) was placed in a Pyrex glass beaker, and 8 g of sodium sulfate anhydrous (0.056 mol as sulfate ion), 0.2 cm³ of phosphate solution (0.056 × 10⁻³ mol as phosphate ion) and 2.7 cm³ of scandium solution (4 mg as scandium ion) were added. The pH was adjusted to 9.8 with sodium hydroxide solution to form scandium hydroxide. Fresh water samples were kept for several minutes and seawater samples were kept for ten minutes. The precipitate was collected on a 3G4 sintered-glass filter, washed with a small amount of deionized water, and dissolved with 0.8 cm³ of concentrated nitric acid. The solution was made up to 10 cm³ with deionized water and the atomic absorbance of chromium in this solution was measured under the operating conditions given in Table 1. The calibration curve for chromium(III) was prepared by using an aqueous solution containing 1.2 mol dm⁻³ nitric acid and 0.4 g dm⁻³ of scandium.

Determination of chromium(VI)

Another aliquot of the sample solution (200 cm³) was placed in a Pyrex glass beaker, 0.5 g of hydroxylammonium chloride and 2 cm³ of concentrated hydrochloric acid were

added, and it was left to stand for an hour in order to reduce chromium(VI) to chromium(III). The coprecipitation method for chromium was the same as that for chromium(III) mentioned above. Chromium in the final solution was determined by GF-AAS, giving the concentration for the sum of chromium(III) and chromium(VI). The concentration for chromium(VI) was obtained by subtracting chromium(III) from the sum of chromium(III) and chromium(VI).

Results and Discussion

Determination of chromium by GF-AAS

In these experiments, solutions were prepared by mixing the solutions of scandium, chromium and nitric or hydrochloric acid without a coprecipitation procedure.

The conditions for the determination of chromium by GF-AAS were examined in the presence of scandium. The presence of scandium (up to 7.4 g dm⁻³) did not interfere with the determination of chromium. The background absorbance at 357.9 nm was not affected by scandium. Therefore, the presence of scandium does not cause spectral interference for chromium. It is thought that scandium does not cause any interference in the ashing or atomizing steps such as loss of chromium or changes in the atomizing efficiency.

The effect of the concentration of nitric and hydrochloric acids on the chromium absorbance was examined. Although the

absorbance decreased with increases in the acid concentration, it was almost constant in the range of 1-2 mol dm⁻³ for nitric acid and 1.5-2 mol dm⁻³ for hydrochloric acid. Thus, 1.2 mol dm⁻³ of nitric acid was used in the subsequent experiments.

The absorbance and concentration of chromium showed a linear relationship, passing through the origin, up to 200 μg dm⁻³. The relative standard deviation was 4.1% for the five replicate measurements of 100 μg dm⁻³ chromium. The detection limit, which was calculated as three times the standard deviation for the blank (containing 0.4 g dm⁻³ of scandium and 1.2 mol dm⁻³ of nitric acid), was 0.2 μg dm⁻³.

The optimum conditions for coprecipitation of chromium(III)

As reported in a previous paper,¹⁸ scandium hydroxide quantitatively precipitates above pH 8. The precipitate is readily filterable and dissolves easily in diluted mineral acids.

In these experiments, sulfate and phosphate ions were not added to the aqueous solution containing chromium(III) or chromium(VI) before either chromium was coprecipitated with scandium hydroxide.

The effect of pH on the coprecipitation of chromium(III) or chromium(VI) was examined with 200 cm³ of the solution containing 4 mg of scandium and 1 μg of the analyte. The results are shown in Fig. 1. Chromium(III) was quantitatively coprecipitated with scandium hydroxide in a

pH range of 8.3-11.3. The coprecipitated percentage of chromium(VI) was 11% at pH 8 and decreased at higher pH values. On the other hand, it is possible for water samples that precipitates such as magnesium hydroxide are formed at higher pH values. Thus, we determined the optimum pH to be 9.8 for selective coprecipitation of chromium(III).

The effect of the scandium amount (1-80 mg dm⁻³) on coprecipitation of 5 μg dm⁻³ chromium(III) was examined. More than 1 mg dm⁻³ of scandium was necessary for quantitative coprecipitation of chromium(III). Thus, 20 mg dm⁻³ of scandium was adopted as the optimum condition.

Interference of diverse ions

The effect of 28 diverse ions on the coprecipitation and determination of chromium(III) was examined using a sample solution (50 cm³) containing 1 μg of chromium(III) and 4 mg of scandium. Table 2 shows that large amounts of sodium,

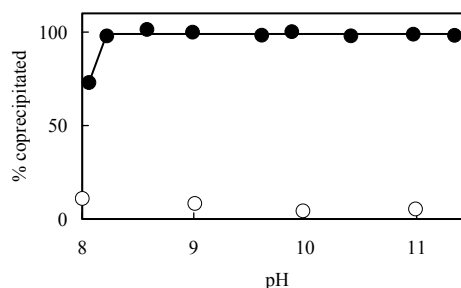


Fig. 1 Effect of pH on coprecipitation of 1 μg/200 cm³ of chromium(III) (●) and chromium(VI) (○) with 4 mg of scandium.

potassium, magnesium and calcium did not interfere with the coprecipitation. It was found that the other ions tested did not interfere when the ion (mg)/scandium (mg) ratio was less than 0.25.

Table 2 Tolerance ratio of diverse ions to scandium for the coprecipitation and determination of 1 μg of Cr(III)

Tolerance ratio ^a Ion [mg]/Sc [mg]	Ion
600	Na ^{+b}
260	K ^{+b}
250	Ca ^{2+c}
50	Mg ^{2+c}
0.25	Li ^{+ b} , Sr ^{2+ c} , Ba ^{2+ b} , Al ^{3+ c} , La ^{3+ b} , Th ^{4+ c} , Zr ^{4+ b} , MoO ₄ ^{2- d} , WO ₄ ^{2- e} , Mn ^{2+ c} , Fe ^{3+ c} , Co ^{2+ c} , Ni ^{2+ c} , PtCl ₆ ^{2- f} , Cu ^{2+ c} , AuCl ₄ ^{- f} , Zn ^{2+ c} , Cd ^{2+ c} , Ga ^{3+ b} , In ^{3+ c} , Sn ^{4+ b} , Pb ^{2+ c} , Sb ^{3+ b} , Bi ^{3+c}

Coprecipitation was carried out with 4 mg of scandium in 50 cm³ of the sample solution at pH 9.8.

- The errors in the determination of chromium were within $\pm 5\%$, when the ratio of the diverse ions was less than the value.
- Counter ion was a chloride ion.
- Counter ion was a nitrate ion.
- Counter ion was an ammonium ion.
- Counter ion was a sodium ion.
- Counter ion was a hydrogen ion.

Table 3 Coprecipitation of chromium(VI) in the presence of anions

Species	Anion		Cr(VI)	
	Added mol dm ⁻³		Added $\mu\text{g dm}^{-3}$	Coprecipitated %
None	0		50	20.6 \pm 4.8
Cl ⁻	0.028		50	18.8 \pm 1.4
NO ₃ ⁻	0.028		50	16.3 \pm 2.2
SO ₄ ²⁻	0.028		50	4.3 \pm 0.6
SO ₄ ²⁻	0.28		50	3.2 \pm 0.1
CO ₃ ²⁻	0.70 \times 10 ⁻³		50	6.0 \pm 0.5
PO ₄ ³⁻	0.28 \times 10 ⁻³		50	3.7 \pm 0.0
SO ₄ ²⁻ +PO ₄ ³⁻	0.28+0.28 \times 10 ⁻³		50	0.9 \pm 0.1
SO ₄ ²⁻ +PO ₄ ³⁻	0.28+0.28 \times 10 ⁻³		5	1.6 \pm 1.2

The results are the average and standard deviation for three replicate experiments. ICP-AES was used for the determination.

Coprecipitation was carried out with 4 mg of scandium in 200 cm³ of the sample solution at pH 9.8. The anions were added as sodium salts.

Separation of chromium(III) and chromium(VI)

In order to find the best condition for separating chromium(III) from chromium(VI), the coprecipitation of chromium(VI) with scandium hydroxide was investigated in the presence of a variety of anions. The anions such as sulfate, phosphate, carbonate, nitrate and chloride were added as sodium salts. The results are shown in Table 3. Twenty one percent of chromium(VI) was coprecipitated in the absence of anions. The coprecipitated percentage was suppressed in the presence of anions. The suppression effect increased in the order of $\text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{PO}_4^{3-} \cong \text{CO}_3^{2-}$. In the experiments, phosphate and carbonate ions were examined at 0.28×10^{-3} and 0.70×10^{-3} mol dm^{-3} , respectively, because the recovery of scandium decreased when the concentrations of these anions were higher than these values. Adding both sulfate and phosphate ions was the most effective in suppressing the coprecipitation of chromium(VI).

In the presence of both sulfate (0.28 mol dm^{-3}) and phosphate ions (0.28×10^{-3} mol dm^{-3}), coprecipitation of $5 \mu\text{g dm}^{-3}$ chromium(III) with scandium hydroxide was tested. The average recovery and standard deviation were $96.3 \pm 5.0\%$ ($n = 3$). Thus, this condition was adopted as the recommended procedure.

The separation of $5 \mu\text{g dm}^{-3}$ chromium(III) from chromium(VI) was tried following the recommended procedure. The results are shown in Table 4. Four ratios of chromium(VI)/chromium(III), namely, 0, 1, 5 and 10, were tested. The observed concentrations of chromium did not show a significant difference when the ratio was less than 5. Thus, it can be concluded that chromium(VI) does not show significant interference for the determination of chromium(III) when the chromium(VI)/chromium(III) ratio is less than 5.

Table 4 Separation of chromium(III) from chromium(VI) following the recommended procedure

Added		Found	
Cr(III) $\mu\text{g dm}^{-3}$	Cr(VI) $\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	Percentage of added Cr(III)
5	0	4.81 ± 0.25	96.3 ± 5.0
5	5	4.83 ± 0.13	96.7 ± 2.5
5	25	5.05 ± 0.05	101 ± 1
5	50	5.35 ± 0.32	107 ± 6

The results are the average and standard deviation for three replicate experiments. ICP-AES was used for the determination.

Coprecipitation was carried out with 4 mg of scandium in 200 cm^3 of the sample solution at pH 9.8.

Recoveries of spiked chromium(III) and chromium(VI) from water samples

The recoveries of spiked chromium(III) from river and sea water samples were examined. The river and sea waters were collected from the Uji River, Kyoto Prefecture and Nanao Bay, Ishikawa Prefecture, respectively. These samples were filtered through an Advantec quantitative

filter paper (No. 5C, diameter 300 mm) and acidified with 0.12 mol dm⁻³ of hydrochloric acid. This was done to dissolve colloidal chromium adsorbed on manganese and/or iron oxide. The coprecipitation of chromium(III) was carried out just after the addition of hydrochloric acid. As shown in Table 5, spiked chromium(III) was quantitatively recovered.

Table 5 Recoveries of chromium from spiked water samples

Sample	Cr(III)			Cr(VI)		
	Found $\mu\text{g dm}^{-3}$	Added $\mu\text{g dm}^{-3}$	Recovery %	Found $\mu\text{g dm}^{-3}$	Added $\mu\text{g dm}^{-3}$	Recovery %
River water						
Jul. 19	0.15			0.37		
		5	105±2		5	103±9
		10	101±4		10	101±3
Seawater						
Aug. 6	0.20			0.09		
		5	105±8		5	102±1
		10	102±8			
Jul. 24	—			0.91*		
					10	97.2±1.8

The obtained recoveries are the average of three replicate experiments.

Chromium was determined by a calibration curve method.

The river and sea waters were collected from the Uji River, Kyoto Prefecture, and Nanao Bay, Ishikawa Prefecture, respectively.

*The sum of chromium(III) and chromium(VI).

Table 6 Determination of chromium in the Kaname River water

	Cr(III) $\mu\text{g dm}^{-3}$	Cr(III)+Cr(VI) $\mu\text{g dm}^{-3}$	Cr(VI) $\mu\text{g dm}^{-3}$
Calibration curve method	26.0±1.8	29.4±0.2	3.4±2.2
Standard addition method	23.2±1.9	29.0±0.8	5.8±2.5

The results for Cr(III) and Cr(III)+Cr(VI) are the average and standard deviation for three replicate samples.

The concentration for chromium(VI) was obtained by subtracting chromium(III) from the sum of chromium(III) and chromium(VI).

The procedure for the determination of chromium(VI) was also investigated using the reduction of chromium(VI) to chromium(III) prior to the coprecipitation. The reduction condition was designed on the basis of the paper of Kagaya *et al.*⁸ To the sample solution (200 cm³) containing hydrochloric acid (0.12 mol dm⁻³), 0.5 g of hydroxylammonium chloride as a reducing agent was added and it was left to stand for an hour. Chromium(VI) added to the river and sea water samples was reduced to chromium(III) and quantitatively coprecipitated with scandium hydroxide (Table 5).

Blank runs were carried out using 200 cm³ of deionized water as a sample. The blank value was $0.22 \pm 0.03 \mu\text{g dm}^{-3}$ for chromium ($n = 3$).

Application to the determination of chromium in river water

The recommended procedure was applied to the determination of chromium in river water. The river water sample was collected from the Kaname River, Ishikawa Prefecture on 17 August 2005. The Kaname River is a tributary flowing in a northwest residential area of Kanazawa City, where there are a few factories including a metal plating factory. The pretreatment of the river water sample was similar to that mentioned above. The final solution of the recommended procedure was diluted ten times with 1.2 mol dm⁻³ of nitric acid, since the concentration of chromium was very high. The results are

shown in Table 6. The determination was carried out by a calibration curve method and a standard addition method. For both chromium(III) and chromium(III) + chromium(VI), the concentrations obtained with the two methods did not show a statistically significant difference on the basis of a t-test ($p = 0.05$).

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