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Coprecipitation Technique for Preconcentration of Some Metal Ions prior to Graphite Furnace Atomic Absorption Spectrometric Determination

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Abstract

Summary—For the preconcentration of trace metal ions in the graphite furnace atomic absorption spectrometric determination (GFAAS), a rapid and simple coprecipitation method which does not need the filtration and the complete collection of the precipitate has been examined, using a known amount of hafnium as a coprecipitant and measuring the concentrations of both hafnium and the trace metal ions in the final sample solution prepared for the determination. The method is applicable to the preconcentration of cadmium, copper, beryllium, tin(IV), gallium, indium and bismuth(III) in water samples prior to GFAAS.

Introduction

Coprecipitation method is widely used for the concentration of trace metal ions and a variety of coprecipitants have been proposed.¹⁻³ In the graphite furnace atomic absorption spectrometric determination (GFAAS), this concentration method has sometimes been used for the preconcentration of trace metal ions, but it is somewhat troublesome and time-consuming in the filtration, especially for large volume sample. To shorten the filtration time, the filtration by suction, the centrifugation and the flotation technique¹ have been utilized for the collection of the precipitate.

Previously, we suggested that hafnium hydroxide is a suitable coprecipitant for the preconcentration of cadmium,⁴ copper,⁵ beryllium,⁶ tin(IV),⁷ gallium,⁸ indium⁸ and bismuth(III)⁹ in GFAAS. This time, we recognized that, by the use of hafnium as a coprecipitant, it becomes possible to concentrate the trace metal ions⁴⁻⁹ with simple and rapid coprecipitation procedure which does not require the filtration and the complete collection of the precipitate. This is done in a similar manner as the case of the atomic absorption determination of arsenic by the hydride evolution method¹⁰: a known amount of hafnium is used as a coprecipitant and the concentrations of both hafnium and the trace metal ions in the final sample solution prepared for the determination are measured. In this method, the decantation instead of the filtration can be used conveniently for the separation of the precipitate from mother liquor and the time

required for the concentration is remarkably shortened.

In this work, we evaluated the potential of this rapid coprecipitation method for GFAAS, recovering of cadmium, copper, beryllium, tin(IV), gallium, indium and bismuth(III) from distilled, river or tap water spiked with these metal ions and determining cadmium and copper in river water.

Experimental

Apparatus and Reagents

The atomic absorption measurements were carried out with Hitachi 170-70 Zeeman atomic absorption spectrometer with a tube (for Cu, Be, Ga, Sn and Bi) or cup (for Cd and In) type of graphite furnace. These furnaces were impregnated with hafnium as described in the previous paper,⁷ because the peak heights of beryllium, tin(IV), gallium and indium are enhanced with the presence of hafnium when non-impregnated graphite furnace was used. By the use of the impregnated furnace, the peak heights of those ions are enhanced and less affected anymore even if the solution containing up to 5.0mg ml⁻¹ of hafnium is injected. The peak heights of cadmium, copper and bismuth(III) are not affected whether the furnace is impregnated with hafnium or not.

A hafnium solution (5.0mg ml⁻¹) was prepared by dissolving hafnium chloride (Nacalai Tesque Co.) with distilled water. Its concentration was determined by the complexometric

titration (at about 90°C and in about 1 mol l⁻¹ nitric acid) using Xylenol Orange as an indicator. The standard solutions of cadmium,⁴ copper,⁵ beryllium,⁶ tin(IV),⁷ gallium,⁸ indium⁸ and bismuth(III)⁹ were prepared as mentioned in the previous papers. All the other reagents used were of analytical-reagent grade.

Table 1. Operating conditions for the atomic absorption spectrometry

	Cd	Cu	Be	Sn	Ga	In	Bi
Wave-length/nm	228.8	324.7	234.9	286.3	294.4	303.9	223.1
Lamp current/mA	8	10	15	15	12.5	10	12.5
Slit width	No. 2	No. 3	No. 3	No. 2	No. 2	No. 2	No. 3
Argon gas flow-rate/l min ⁻¹							
Sheath gas	3	3	3	3	3	3	3
Carrier gas	0	0	0	0	0	0	0
Injection volume/ μ l	20	10	10	10	10	20	10
Cuvette type	cup	tube	tube	tube	tube	cup	tube
Conditions for drying	21A 70s	23A 60s	24A 45s	24A 60s	24A 40s	24A 50s	24A 45s
ashing	80A 30s	95A 40s	110A 30s	110A 30s	100A 30s	100A 30s	92A 40s
atomizing	250A 5s	310A 5s	310A 5s	310A 5s	310A 5s	310A 5s	310A 5s

Recommended Procedure

To a sample solution (100-300ml) containing 10-100ng of cadmium, 0.5-10 μ g of copper, 20-200ng of beryllium, 0.1-10 μ g of tin(IV), 0.2-3 μ g of gallium, 0.2-4 μ g of indium or 0.02-3 μ g of bismuth(III), a known amount of hafnium (20mg) is added and the pH of the solution is adjusted to about 9.5 with aqueous ammonia (1+1). To settle down hafnium hydroxide produced, the solution is allowed to stand for more than

Table 2. Recovery of trace elements from spiked water samples

Element	Amount spiked/ μg	Sample volume/ml	Number of replicate	Ion recovery/%	RSD, %
<i>Distilled water</i>					
Cd	0.01	100	3	101.1	2.10
	0.01	300	3	96.8	9.98
	0.03	300	4	98.6	9.51
Cu	0.5	100	5	99.0	3.10
	0.5	300	3	98.1	3.00
	2.0	300	3	100.1	2.02
Be	0.02	300	4	105.7	6.20
	0.05	300	3	104.7	3.61
Sn	0.1	300	3	99.0	4.73
	2.0	300	3	103.1	2.04
Ga	0.2	300	3	97.1	2.66
	2.0	300	3	96.7	3.00
In	0.2	300	3	106.4	5.18
	2.0	300	3	104.0	4.43
Bi	0.02	300	3	97.0	5.00
	0.5	300	3	99.9	2.33
<i>Tap water</i>					
Cd	0.02	200	3	97.9	4.28
	0.1	300	3	99.5	3.09
Cu	0.5	300	3	99.8	3.03
	10.0	300	3	99.8	1.08
Be	0.05	300	3	104.8	3.85
Sn	0.1	300	3	102.2	4.51
	10.0	300	3	103.5	2.81
Ga	2.0	300	3	102.0	3.89
In	4.0	300	3	101.0	3.21
Bi	0.5	200	3	98.7	2.91
<i>River water</i>					
Cd	0.01	200	2	94.1	—
	0.1	300	3	98.4	3.99
Cu	0.5	300	3	96.0	4.01
	10.0	300	3	99.8	1.50
Be	0.02	200	3	102.3	5.77
	0.2	300	3	104.1	2.26
Sn	0.1	300	3	95.7	7.44
	10.0	300	3	102.2	2.91
Ga	0.2	300	3	97.1	5.69
	3.0	300	3	97.9	5.18
In	0.2	300	3	108.8	4.95
	4.0	300	3	105.2	3.06
Bi	0.02	200	3	96.7	4.11
	0.5	300	3	102.5	2.42
	3.0	300	3	98.8	3.04

Table 3. Result of the determination of cadmium and copper in river water

Location in Kakehashi river system	Sample volume/ ml	Proposed method				Previous method ^{4,5}	
		Calibration method		Standard addition method		Calibration method	Standard addition method
		Found*/ ng ml ⁻¹	RSD, %	Found*/ ng ml ⁻¹	RSD, %	Found+/ ng ml ⁻¹	Found+/ ng ml ⁻¹
<i>Cadmium</i>							
Shorenji	300	0.18	4.9	0.19	5.5	0.18	0.17
Yusenji	300	0.072	5.4	0.074	5.0	0.070	0.074
Nomiohashi	300	0.052	5.1	0.049	4.1	0.056	0.054
<i>Copper</i>							
Shorenji	200	16.3	2.4	15.9	2.0	16.1	16.6
Yusenji	200	15.2	1.9	15.1	2.8	14.3	14.8
Nomiohashi	300	5.6	4.2	5.9	3.8	5.3	5.5

* Average of four replicate determinations.

+ Average of duplicate determinations.

15min, then supernatant solution is discarded by decantation, permitting a little precipitate to escape. The precipitate remained is washed with a small amount of aqueous ammonia (pH about 9.5) and dissolved with such adequate amount of concentrated acid that the final acid concentration becomes about 1 mol l^{-1} (hydrochloric acid is used for tin(IV) determination and nitric acid for the others). Then the solution is diluted to about 10ml with distilled water. Taking a portion of this final sample solution ($20\mu\text{l}$ for cadmium or indium and $10\mu\text{l}$ for the others), the amount of the desired metal ion in the portion is measured by the graphite furnace atomic absorption spectrometry using the optimum operating conditions described in the previous papers⁴⁻⁹ (Table 1). Taking another portion (2ml) of the solution, the amount of hafnium in it (H_1 mg) is also measured by the complexometric titration (at about 90°C) with Xylenol Orange as an indicator. As the amount of the desired metal ion coprecipitated with H_1 mg of hafnium can be calculated from these measurements, the content of the desired ion in the original sample solution can be determined from the ratio of the quantity of added hafnium (20mg) to H_1 mg.

Results and Discussion

Optimum Conditions for Coprecipitation

The fundamental conditions for the coprecipitation of trace metal ions were examined in detail previously.⁴⁻⁹ Cadmium, copper, beryllium, tin(IV), gallium, indium and bismuth(III) can be coprecipitated quantitatively with hafnium hydroxide over the wide pH range of approximately 7-11. For the dissolution of the precipitate, hydrochloric acid is suitable for the tin(IV) determination and nitric acid for the others. The amount of acids used here is not necessary to be fixed strictly since the peak heights of the metal ions are little affected with the change of the final acid concentration around 1 mol l^{-1} . We also confirmed that the metal ions can be coprecipitated quantitatively from 300ml of sample solution by the use of 20mg of hafnium and the atomic absorbances of them were slightly affected by the presence of up to 5 mg ml^{-1} of hafnium.

Recovery of Hafnium Hydroxide

In this method, a part of the precipitate is allowed to escape in the decantation step. So, recoveries of hafnium hydroxide by the decantation were examined, measuring the amount of hafnium after the decantation by the complexometric titration. As a result, more than 80% of hafnium hydroxide could be always recovered by the use of 20mg of hafnium.

In the proposed method, furthermore, the amount of hafnium in the original sample solution must be negligibly small and the added hafnium as a coprecipitant must precipitate completely, because the content of the trace metal ion is calculated using the ratio of added amount of hafnium to precipitated amount of it. So, recoveries of hafnium from various sample volumes were examined, collecting hafnium hydroxide by the filtration method and then

measuring the amount of hafnium by the complexometric titration. Hafnium was precipitated almost completely in 1000ml of distilled water. Generally, the content of hafnium in natural water is negligibly small (it is 7×10^{-3} ng ml⁻¹ of hafnium in the sea water,¹¹ for example), so it seems that hafnium is a satisfactory coprecipitant for the rapid coprecipitation technique.

Recoveries of Metal Ions from Spiked Water Samples

According to the recommended procedure, the recoveries of cadmium, copper, berllium, tin(IV), gallium, indium and bismuth(III) from distilled, river or tap water spiked with them were examined. As shown in Table 2, the satisfactory results were obtained. The time required for the determination, moreover, was reduced to about one-half that of the previous methods⁴⁻⁹ in which the filtration technique was used, indicating that the proposed method is useful to the analyses of these metal ions in the water samples.

Application to River Water

The proposed method was applied to the determinations of cadmium and copper in the Kakehashi river system, located in the south of Ishikawa prefecture, flowing through Komatsu city into Japan sea. The samples were filtered through a Toyo Roshi TM-2p membrane filter (pore size $0.45 \mu\text{m}$) as soon as possible after sampling, and acidified with nitric acid to pH about 2 for storage. As shown in Table 3, the results obtained by the calibration method and the standard addition method were in good agreement with each other. These results also agreed well with the results obtained by the previous methods.^{4,5}

Conclusions

The coprecipitation procedure proposed here is easier and more rapid in operation than the conventional coprecipitation procedure in which the filtration is used for the separation of the precipitate. Hafnium hydroxide is recommended as a useful coprecipitant for the rapid preconcentration of the metal ions prior to GFAAS. Although a part of the precipitate escapes at a decantation step, the loss of the desired metal ions is not serious: more than 80% of hafnium hydroxide can be always recovered, and the final sample volume can be reduced easily, giving higher concentration factor (about 2 times) than the previous methods,⁴⁻⁹ since it is not necessary to fix the final volume strictly.

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