Flameless Atomic-Absorption Spectrometric and Differential-Pulse Polarographic Determination of Cadmium after Coprecipitation with Hafnium Hydroxide

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Using the coprecipitation method with hafnium hydroxide, the flameless atomic-absorption spectrometric and the differential-pulse polarographic determinations of cadmium have been studied. The collecting ability of hafnium hydroxide for cadmium is excellent; from 0.01 to at least 1000 μg of cadmium in 50—400 cm^3 of a sample solution is coprecipitated quantitatively. The presence of hafnium hydroxide does not interfere with either method of determining cadmium. Of the diverse ions examined, there are no ions which interfere with the flameless atomic-absorption spectrometric determination, even if they are present in a concentration of at least 5000 times that of cadmium; as for the differential-pulse polarographic determination, only indium interferes when present in small amounts. The linear calibration curves through the point of origin were obtained over the range of 0.4—4 ng cm^{-3} of cadmium for the former method and 0.04—40 μg cm^{-3} for the latter method. In the proposed methods, the flameless atomic-absorption spectrometric determination was successfully applied to the analysis for trace amounts of cadmium in river-water samples.

The coprecipitation method is one of the most useful methods for the concentration of cadmium, and various techniques for the determination of trace cadmium, coupled with a preconcentration procedure by means of coprecipitation, have been proposed; inductively coupled plasma-atomic emission spectrometry using hydroxide of indium1) or lanthanum2) as a coprecipitant; X-Ray fluorescence using 1,3:2,4-di-*O*-benzylidene-D-glucitol3) and 1,10-phenanthroline-sodium tetraphenylborate;4) flame atomic-absorption spectrometry using naphthalene,5) soybean protein,6) strontium carbonate,7) aluminium hydroxide,8) and tris(1-pyrrolidinecarbodithioato)cobalt(III),9) and flameless atomic-absorption spectrometry using iron(III) hydroxide10) and cobalt 1-pyrrolidinecarbodithioate(cobalt–APDC).11) Moreover, tin(IV) hydroxide12) has also been proposed as a useful collector of cadmium as a result of investigation using the radiotracer method.

In a previous paper,13) the present authors suggested that hafnium hydroxide is effective as a collector of trace amounts of lead; it can be satisfactorily analyzed by means of differential-pulse polarography in the presence of large amounts of hafnium. This time, we have recognized that hafnium hydroxide also coprecipitates quantitatively over a wide concentration range of cadmium almost entirely without the coprecipitation of alkali and alkaline earth metals and that this concentration method can be successfully combined with the cadmium determination by means of flameless atomic-absorption spectrometry or differential-pulse polarography. Both methods proposed here are simple, fairly free from the effect of diverse ions, and give good reproducibilities. Cadmium determination by a combined coprecipitation-differential-pulse polarography has not yet been tried. Concerning combined coprecipitation-flameless atomic-absorption spectrometry, however, as has been mentioned above, several methods have been reported. Among those, though, the method using iron(III) hydroxide as a collector11) can not avoid the coprecipitation of large amounts of alkaline earth elements which may interfere with cadmium determination, and in the case of cobalt–APDC,12) it is troublesome to digest the precipitate in order to reduce the matrix effect because of the presence of cobalt–APDC itself. This paper will describe the fundamental conditions for the coprecipitation of cadmium with hafnium hydroxide and for the flameless atomic-absorption spectrometric and the differential-pulse polarographic determination of cadmium.

Experimental

Apparatus. All the atomic-absorption measurements were carried out with a Hitachi 170-70 Zeeman-effect atomic-absorption spectrometer with a hollow cadmium cathode lamp (Hitachi 2082008) and a cup-type graphite furnace (Hitachi 170-5104). A Yanagimoto voltammetric analyzer, model p-1000, was used for the differential-pulse polarographic measurements, operating in a three-electrode configuration with a dropping-mercury electrode, a saturated calomel reference electrode, and a platinum counter electrode. A Hitachi-Horiba model M-5 glass electrode pH meter was also used for the pH measurements.

Reagents. Standard Cadmium Solution: A solution containing about 1 mg cm^{-3} of cadmium was prepared by dissolving guaranteed reagent-grade cadmium nitrate in a small amount of nitric acid and by then diluting it with distilled water. The solution was subsequently standardized by complexometric titration.

Hafnium Solution: A solution containing about 5 mg cm^{-3} of hafnium was prepared by dissolving hafnium chloride (Nakarai Chemicals Co.) in 2 mol dm^{-3} of hydrochloric acid and standardized by complexometric back titration.

All the other reagents used were of a guaranteed reagent grade and were purified with a chelate resin when necessary.

Recommended Procedures. Flameless Atomic-Absorption Spectrometric Determination: To a sample solution (50—400 cm^3) containing 0.01—0.1 μg of cadmium, 10 mg of hafnium is added and the pH is adjusted to about 9.5

Table 1. Operating Conditions for Flameless Atomic-Absorption Spectrometry

Analytical wavelength	228.8 nm
Lamp current	8 mA
Slit width	No. 2 (1.1 nm)
Scale expantion	X2
Argon-gas flow rate	
Sheath gas	3 $\mathrm{l\,min^{-1}}$
Carrier gas	0 $\mathrm{l\,min^{-1}}$
Drying conditions	21A (ca. 100 °C), 70s
Ashing conditions	80A (ca. 700 °C), 30s
Atomizing conditions	250A (ca. 2250 °C), 5s
Injection volume	20 μl

Table 2. Operating Conditions for Differential-Pulse Polarography

Scan range	−0.3 to −0.9 V
Scan rate	10 $\mathrm{mV\,s^{-1}}$
Modulation amplitude	50 mV
Forced drop time	1s
Temp. of measurements	20±0.1 °C

with 1:1 aqueous ammonia in order to precipitate hafnium hydroxide. After the solution has then been allowed to stand for more than 20 min, the precipitate is filtered by suction using a 3G4 sintered-glass filter, washed with aqueous ammonia of pH 9.5, and dissolved with 1 $\mathrm{cm^3}$ of concd. nitric acid. After the solution is diluted to 25 $\mathrm{cm^3}$ with distilled water, measurements of the atomic absorbance are carried out under the optimum operating conditions, which are shown in Table 1.

Differential-Pulse Polarographic Determination: To a sample solution (50—400 $\mathrm{cm^3}$) containing 1—1000 μg of cadmium, 10 mg of hafnium is added and then precipitated as hafnium hydroxide at about pH 9.5 with 1:1 aqueous ammonia. After allowing the solution to stand for more than 20 min, the precipitate is filtered by suction using a 3G4 sintered-glass filter, washed with aqueous ammonia of pH 9.5, and dissolved with 2 $\mathrm{cm^3}$ of concd hydrochloric acid (with two 1-$\mathrm{cm^3}$ portions of concd hydrochloric acid at about a 5-min interval). The solution is then diluted to 25 $\mathrm{cm^3}$ with distilled water and deaerated with pure nitrogen for 5 min. Then, the polarogram is recorded under the operating conditions shown in Table 2 and the cadmium is determined by the current peak height at −0.64 V.

Results and Discussion

Study of Optimum Conditions for Coprecipitation. The effect of the pH on the coprecipitation of cadmium with hafnium hydroxide was examined by coprecipitating 0.1 or 30 μg of cadmium from 100 $\mathrm{cm^3}$ of the sample solution. As is shown in Fig. 1, almost 100% recoveries of cadmium were obtained over the pH range from 7.0 to 12.0 for 0.1 μg of cadmium and from 7.5 to 12.0 for 30 μg of cadmium. Hence, a pH of about 9.5 was used for the coprecipitation in the further experiments. The amount of hafnium which is required for the quantitative coprecipitation of cadmium increases gradually with an increase in the volume of the sample solution. As a result of the examinations for portions of the sample solution from 50 to 400 $\mathrm{cm^3}$, we found that more than 5 mg of hafnium was needed for 400 $\mathrm{cm^3}$. In this study, 10 mg of hafnium was used. The coexistence of a large amount of hafnium does not interfere with the determinations; that is, the presence of 0.08 to at least 2 $\mathrm{mg\,cm^{-3}}$ of hafnium does not affect the flameless atomic-absorption spectrometric determination, nor does the presence of from 0.08 to at least 1 $\mathrm{mg\,cm^{-3}}$ interfere with the differential-pulse polarographic determination. The investigation of the aging time of the precipitate for the cadmium recovery led to the result that standing for more than 20 min at room temperature was suitable for the quantitative collection of cadmium, because almost a 100% recovery was attained about 15 min after the precipitation of hafnium hydroxide and this percentage remained almost constant for at least 10 h.

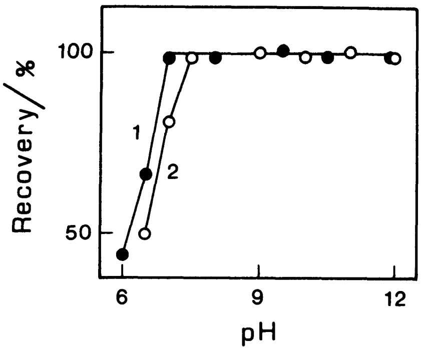

Fig. 1. Effect of pH on coprecipitation.
1: Measurements by flameless atomic absorption spectrometry, Cd 0.1 μg/25 $\mathrm{cm^3}$, Hf 10 mg/25 $\mathrm{cm^3}$, concd $\mathrm{HNO_3}$ 1 $\mathrm{cm^3}$/25 $\mathrm{cm^3}$.
2: Measurements by differential pulse polarography, Cd 30 μg/25 $\mathrm{cm^3}$, Hf 10 mg/25 $\mathrm{cm^3}$, concd HCl 2 $\mathrm{cm^3}$/25 $\mathrm{cm^3}$.

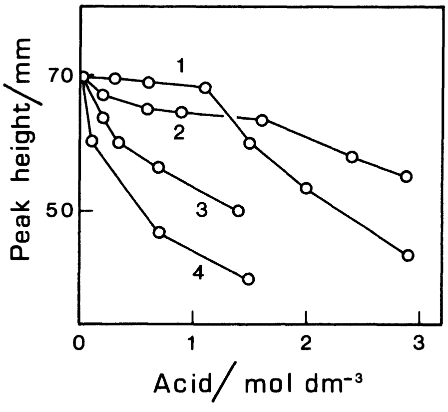

Fig. 2. Effect of acid concentration on peak height of cadmium.
Measurements by flameless atomic absorption spectrometry, Cd 0.1 μg/25 $\mathrm{cm^3}$, Hf 10 mg/25 $\mathrm{cm^3}$,
1: $\mathrm{HNO_3}$, 2: HCl, 3: $\mathrm{HClO_4}$, 4: $\mathrm{H_2SO_4}$.

Choice of Acids for Dissolution of Precipitate. For the dissolution of hafnium hydroxide, several acids,

Table 3. Influence of Diverse Ions

Ion	A		B		Ion	A		B	
	Amount added	Cadmium found	Amount added	Cadmium found		Amount added	Cadmium found	Amount added	Cadmium found
	mg	ng	mg	μg		mg	ng	mg	μg
$\mathrm{Li^+}$	1	100.0	5	30.3	$\mathrm{Bi^{3+}}$	0.5	99.0	0.1	30.6
$\mathrm{Na^+}$	10	99.5	—	—	$\mathrm{Cu^{2+}}$	0.5	98.5	1	28.5
$\mathrm{K^+}$	10	100.0	—	—	$\mathrm{Zn^{2+}}$	0.5	104.8	5	30.3
$\mathrm{Be^{2+}}$	0.5	105.0	5	29.6	$\mathrm{La^{3+}}$	1	100.5	5	30.5
$\mathrm{Mg^{2+}}$	10	102.0	5	30.0	$\mathrm{Zr^{4+}}$	1	100.5	5	30.3
$\mathrm{Ca^{2+}}$	10	102.5	5	30.8	$\mathrm{Th^{4+}}$	1	98.9	5	30.0
$\mathrm{Sr^{2+}}$	1	100.1	—	—	V(V)	—	—	0.1	29.1
$\mathrm{Ba^{2+}}$	1	100.0	5	30.3	$\mathrm{Cr^{3+}}$	0.5	104.5	0.1	29.1
$\mathrm{Al^{3+}}$	1	101.7	5	28.5	Mo(VI)	1	97.3	5	30.0
$\mathrm{Ga^{3+}}$	1	104.8	5	28.8	W(VI)	1	98.0	—	—
$\mathrm{In^{3+}}$	0.5	105.0	0.05	62.2	$\mathrm{Mn^{2+}}$	1	96.3[a)]	5	29.5
$\mathrm{Sn^{4+}}$	1	95.5	0.05	29.2	$\mathrm{Fe^{3+}}$	1	100.1	0.1	30.0
$\mathrm{Pb^{2+}}$	1	100.0	0.1	29.5	$\mathrm{Co^{2+}}$	1	99.0	1	30.1
$\mathrm{Sb^{3+}}$	1	101.5	1	30.0	$\mathrm{Ni^{2+}}$	1	99.5	1	29.7

A: The flameless atomic-absorption spectrometric determination (100 ng of cadmium was taken). B: The differential-pulse polarographic determination (30 μg of cadmium was taken). a) Hydrochloric acid was used to dissolve the precipitate.

such as nitric, hydrochloric, sulfuric, and perchloric acid, were examined. Hafnium hydroxide dissolves easily in nitric, hydrochloric, and perchloric acids, but not easily in sulfuric acid. The effects of these acids on the atomic absorbance or the polarogram of cadmium are diverse. In Fig. 2, the effects of the concentrations of these acids on the peak height on the flameless atomic-absorption spectrometric determination are shown. The addition of increasing amounts of these acids decreases the peak heights of cadmium. In the case of nitric acid, however, the magnitude of the decrease is small over the concentration range from about 0.3 to 1.1 mol dm^{-3}, and in this concentration range, the use of this acid gives the highest peak height. On the basis of these results, the nitric acid was used to dissolve the precipitate for the flameless atomic-absorption spectrometric determination. For the differential-pulse polarographic determination, it was found that the hydrochloric acid was adequate as a supporting electrolyte for the dissolution of hafnium hydroxide and for obtaining well-defined polarograms. Since the presence of this acid over the concentration range from 0.5 to at least 3 mol dm^{-3} did not affect the current peak height of cadmium, an acidity of about 1 mol dm^{-3} was adopted in this experiment.

Optimum Operating Conditions. According to the recommended procedure, the instrumental parameters, such as the drying, ashing, and atomizing conditions and the flow rate of argon gas, were examined using a solution which contained 0.1 μg/25 cm^3 of cadmium. An almost constant absorbance was obtained when the drying, ashing, and atomizing currents were within 19 to 22 A, 45 to 85 A, and 220 to 280 A respectively. The times of drying, ashing, and atomizing also did not affect the absorbance within the time ranges examined, that is, 50—90 s, 10—40 s, and 4—10 s respectively. The change in the flow rate of the sheath gas from 1 to 5 l min^{-1} had no effect on the cadmium absorbance, but the increase in the flow rate of the carrier gas made the absorbance decrease gradually. From these results and the results of the examinations of other instrumental conditions, such as the lamp current, the slit width, and the injection volume, the optimum conditions for the measurement of the cadmium absorbance were determined to be as shown in Table 1. For the differential-pulse polarography, the conditions which are summarized in Table 2 were adopted as the optimum operating conditions.

Calibration Curves. The straight lines through the point of origin were obtained over the concentration range from 0.4 to 4 ng cm^{-3} of cadmium for the flameless atomic-absorption spectrometry and from 0.04 to 40 μg cm^{-3} for the differential-pulse polarography. The reproducibility of the AAS method, expressed by the relative standard deviation obtained from five repeated determinations, was 2.8% for 4 ng cm^{-3} of cadmium, while that one of the polarographic method was 1.3% for 1.2 μg cm^{-3} of cadmium.

Influence of Diverse Ions. The results of the influence of the diverse ions examined by the recommended procedures are summarized in Table 3. For the flameless atomic-absorption spectrometry, large amounts of sodium, potassium, magnesium, and calcium were found not to interfere with the determination. Some ions, such as beryllium, indium, bismuth(III), copper(II), zinc, and chromium(III), can also coexist, at least up to 5000 times of the amount of cadmium, and there are no ions among the examined ones which have a serious influence on the determi-

Table 4. Amounts of Coprecipitation of Alkali and Alkaline Earth Metals

Ion*	Amount added	Recovery
	mg/100 cm^3	%
Na$^+$	5	2.0
K$^+$	5	5.0
Mg^{2+}	5	5.1
Ca^{2+}	5	6.1
Sr^{2+}	5	5.0
Ba^{2+}	5	15.0

* Coprecipitated at about pH 9.5 using 10 mg of hafnium. The final volume of the solutions was made up to 25 cm^3.

nation. For the differential-pulse polarographic determination, only indium interferes even present in only a small amount.

The Amounts of the Coprecipitation of Alkali and Alkaline Earth Metals. The amounts of the coprecipitation of alkali and alkaline earth metals were also studied. The amount of the coprecipitation of each ion was determined by measuring the amount of the ion remaining in the aqueous phase after the coprecipitation had been carried out and by subtracting this amount from the original amount of the ion. Flame photometry was used for the measurement of sodium, potassium, strontium, and barium, and the complexometric titration method, for magnesium and calcium. The results obtained are shown in Table 4. From this, it is obvious that alkali and alkaline earth metals hardly coprecipitate with hafnium hydroxide; this suggests that the use of hafnium hydroxide is effective for the separation of some kinds of elements from a sample solution containing large amounts of alkali and alkaline earth metals.

Application to River Water. Of the proposed methods, flameless atomic-absorption spectrometry was used for the determination of cadmium in the Kakehashi river system. The river-water samples were filtered through a membrane filter (Toyo Roshi TM-2p; pore size 0.45 µm) and acidified with hydrochloric acid to about pH 2 as soon as possible after sampling. Then cadmium was determined according to the recommended procedure. As is summarized in Table 5, the results which were obtained from the calibration and from the standard addition methods were in good agreement.

Table 5. Results for Cadmium in River Water

Kakehashi river system sampling point	Sample volume	A Cd found	B Cd found
	cm^3	ng cm^{-3}	ng cm^{-3}
Nunohashi	—$^{a)}$	0.79	0.82
Kanahira	—$^{a)}$	0.47	0.52
Shōrenji	100	0.22	0.20
Yūsenji	300	0.033	0.036
Kamonourahashi	300	0.035	0.034
Nomiōhashi	300	0.052	0.041
Kakehashiōhashi	300	0.043	0.039
Kakehashigawabashi	300	0.052	0.048

A: Determination by the calibration method. B: Determination by the standard addition method. a) Cadmium was determined without preconcentration.

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