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Coprecipitation of Trace Metal Ions in Water with Bismuth(III) Diethyldithiocarbamate for an Electrothermal Atomic Absorption Spectrometric Determination

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Electrothermal atomic absorption spectrometry combined with preconcentration techniques has been widely used for the determination of trace metal ions. Among the preconcentration techniques, the coprecipitation method is a useful means of enrichment, and various coprecipitants have been proposed. We have been investigating a new coprecipitant of trace metals in water for the electrothermal atomic absorption spectrometric determination, and have found that bismuth(III) diethyldithiocarbamate (bismuth(III) DDTC) has a good collecting ability for lead, copper, cadmium, cobalt, and nickel. However, it hardly coprecipitates matrix ions, such as sodium, potassium, magnesium, and calcium. It is thus applicable to the determination of the above-mentioned five metals. Also, bismuth(III) DDTC can be easily dissolved with nitric acid. In previous papers,^{1,2} we suggested that nickel DDTC is a convenient coprecipitant to handle, because it can be dissolved in about 8 M nitric acid and acetone without any digestion or heating, which is sometimes required for the dissolution of organic precipitates. The bismuth(III) DDTC proposed here is dissolved more easily than nickel DDTC, and has not been reported as a coprecipitant for the concentration of trace ions, although DDTC complexes of various metal ions, such as aluminium(III),³ iron(II),⁴ iron(III),⁵ zinc(II),^{6,7} nickel(II),⁸ manganese(II),⁹ and copper(II)¹⁰ have been previously proposed.

In this note, the fundamental conditions for the coprecipitation of trace amounts of cobalt in water with bismuth(III) DDTC and for an electrothermal atomic absorption spectrometric determination of cobalt are described, appending that some other metal ions, such as copper and cadmium, may also be determined with the method proposed here.

Experimental

Apparatus

A Hitachi 170-70 Zeeman atomic absorption spectrometer was used for the atomic absorption measurements, and a Toa Model HM-5BS glass electrode pH meter for pH measurements.

Reagents

All reagents used were of guaranteed reagent grade. A solution containing about 1 mg cm⁻³ of cobalt or bismuth(III) was prepared by dissolving metal nitrate in a small amount of concentrated nitric acid and diluting with distilled water. The

concentrations of cobalt and bismuth(III) were determined by complexometric titration using Murexide and Xylenol Orange as indicators, respectively. About a 2% DDTC solution was prepared by dissolving sodium salt of DDTC (Wako Pure Chemicals) in distilled water and filtering out any insoluble material.

Results and Discussion

Recoveries of some metal ions by bismuth(III) DDTC

The usefulness of bismuth(III) DDTC as a coprecipitant was investigated according to the coprecipitation procedure indicated in the recommended procedure described below, determining the recovery percentages of some metal ions. The recovery of each metal ion was determined by electrothermal atomic absorption spectrometry. For sodium, potassium, magnesium, and calcium, however, flame atomic absorption spectrometry was used. As shown in Table 1, lead, copper, cadmium, cobalt, and nickel could be coprecipitated quantitatively, which indicates that bismuth(III) DDTC is applicable to the concentration of those ions. Other ions, especially sodium, potassium, magnesium, and calcium, were hardly collected.

Determination of cobalt

Recommended procedure. An aqueous solution containing 5 mg of bismuth(III) and 2 cm³ of a 2% DDTC solution is added

Table 1 Recoveries of some ions by bismuth(III) DDTC

Ion	Added/ µg	Recovery, %	Ion	Added/ µg	Recovery, %
Na ⁺	5000	0.41	Cr ³⁺	1	16.7
K ⁺	5000	0.49	Cr(VI)	1	68.9
Mg ²⁺	5000	0.33	Mo(VI)	1	68.8
Ca ²⁺	5000	0.20	Mn ²⁺	0.1	80.5
Sn ⁴⁺	1	32.5	Co ²⁺	1	100.8
Pb ²⁺	0.2	101.5	Ni ²⁺	10	99.0
Sb ³⁺	5	56.2	Au ³⁺	0.5	65.7
Cu ²⁺	2	99.4	Ag ⁺	2	71.8
Cd ²⁺	0.02	100.7			

Ions were coprecipitated at pH about 9 from about 100 cm³ of aqueous solution.

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Table 2 Operating conditions for atomic absorption spectrometry

Analytical wavelength	240.7 nm
Lamp current	7.5 mA
Slit width	No. 2 (1.1 nm)
Argon gas flow rate	
Sheath gas	3 dm ³ min ⁻¹
Carrier gas	0 dm ³ min ⁻¹
Injection volume	10 mm ³
Cuvette	uncoated tube type graphite furnace
Drying conditions	24 A (ca. 170°C), 45 s
Ashing conditions	80 A (ca. 780°C), 40 s
Atomizing conditions	290 A (ca. 2750°C), 5 s

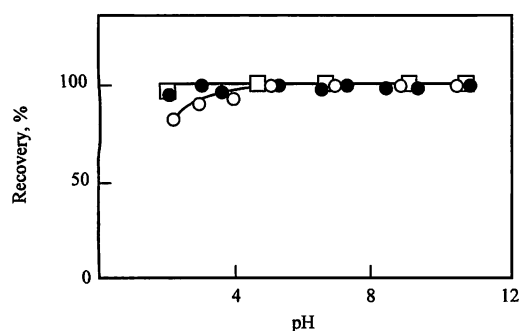


Fig. 1 Effect of the pH on the recovery of cobalt, copper, or cadmium from about 100 cm³ of a sample solution containing 1 µg of cobalt (●), 2 µg of copper (□), or 0.02 µg of cadmium (○).

with stirring to a sample solution (up to 500 cm³) containing 0.1 – 1.5 µg of cobalt, and the pH is adjusted to about 9 with about 5 M aqueous ammonia. After the precipitate has settled, the solution is filtered through a 3G4 sintered-glass filter. The precipitate is washed with a small amount of distilled water and dissolved in 1 cm³ of concentrated nitric acid. Then, a 0.5 cm³ volume of acetone is added and the solution is made up to 5 cm³ with distilled water. The atomic absorbance of cobalt is measured under the operating conditions given in Table 2. A blank is also run, using distilled water as a sample solution.

Study of the optimum conditions for coprecipitation. The effect of the pH on the coprecipitation with bismuth(III) DDTC was studied with a solution containing 1 µg of cobalt. The maximum and almost constant recoveries were obtained over a pH range from 2.0 to 11.2 (Fig. 1). A pH of about 9 was used for the coprecipitation of cobalt in further experiments, because the precipitate of bismuth(III) DDTC obtained above a pH of about 8 was bulky, and hence easy to handle. In Fig. 1, the results of copper and cadmium are also appended. The necessary amount of bismuth(III) DDTC for coprecipitation was examined with a sample solution (50 – 500 cm³) containing 1 µg of cobalt. The required amount of bismuth(III) DDTC for the quantitative coprecipitation increased along with increasing the sample volume, and the complexation of 4 mg of bismuth(III) with DDTC was necessary for up to 500 cm³ of sample solution. Since the atomic absorption of cobalt was not affected, even if 10 mg of bismuth(III) was added, 5 mg was used in further experiments. Because the addition of up to 10 cm³ of a 2% DDTC solution also did not interfere with the cobalt determination, 2 cm³, corresponding to about 11-times (as a molar ratio) 5 mg of bismuth(III), was used for coprecipitation,

Table 3 Effect of diverse ions on the determination of 1 µg of cobalt

Mass ratio ^a [Ion]/[Cobalt]	Ion
925000	Cl ⁻
600000	Na ⁺
250000	K ⁺
125000	Ca ²⁺
100000	Mg ²⁺
50000	Br ⁻ , I ⁻ , SO ₄ ²⁻
5000	F ⁻
1000	PO ₄ ³⁻
500	Li ⁺ , Be ²⁺ , Sr ²⁺ , Ba ²⁺ , Al ³⁺ , Ga ³⁺ , In ³⁺ , Sn ⁴⁺ , Pb ²⁺ , Sb ³⁺ , Bi ³⁺ , Zn ²⁺ , La ³⁺ , Ce ³⁺ , Zr ⁴⁺ , Th ⁴⁺ , Cr ³⁺ , Mo ^{VI} , W ^{VI} , Mn ²⁺ , Fe ³⁺ , Cu ²⁺ , Cd ²⁺

Coprecipitation was carried out from about 80 cm³ of the sample solution at pH about 9.

a. The errors are within ±5%.

because the molar ratio of bismuth(III) to DDTC in the complex was confirmed to be 1:3 by an elemental analysis. The recovery of cobalt reached almost 100% within a few minutes after the formation of bismuth(III) DDTC, and remained almost unchanged while standing for 5 h. Hence, the precipitate was filtered after some settlement had occurred.

Dissolution of the coprecipitant. For the dissolution of bismuth(III) DDTC, several common concentrated mineral acids were examined. As a result, it was found that bismuth(III) DDTC dissolved easily in nitric acid. Although the resulting clear solution sometimes became turbid upon dilution with distilled water, it was possible to prevent the solution from turbidity by the addition of a small amount of acetone. Thus, in this experiment, 1 cm³ of concentrated nitric acid was used to dissolve the precipitate and 0.5 cm³ of acetone was added into the resultant solution, since the addition of 0.25 – 2.5 cm³ of concentrated nitric acid and up to 2.5 cm³ of acetone did not affect the cobalt absorption.

Calibration curve. A linear relationship, passing through the origin, between the peak height and concentration was obtained from 0.1 – 1.5 µg of cobalt in the final solution (5 cm³). The relative standard deviation for the peak heights obtained from five repeated determinations was 0.89% for 1 µg of cobalt in about 300 cm³ of the sample solution. The detection limit (signal to noise = 2) was 0.04 ng cm⁻³ of cobalt in 500 cm³ of the initial sample solution.

Interferences of diverse ions. The effect of 33 diverse ions on the determination of cobalt was examined using about 80 cm³ of a sample solution by the recommended procedure. Table 3 shows that large amounts of sodium, potassium, magnesium, calcium, fluoride, chloride, bromide, iodide, sulfate, and phosphate did not interfere with the determination. No other ions tested produced any serious interference effect, even at a concentration 500-times the mass of the cobalt present.

Recovery of cobalt from spiked water samples. To evaluate the usefulness of this method, the recoveries of cobalt from river, tap, and sea water samples spiked with cobalt were examined. As shown in Table 4, the obtained results were satisfactory, and it seems that the proposed method is applicable to analyses of these water samples which contain down to 0.2 ng cm⁻³ of cobalt. The recoveries of copper and cadmium were also examined and the good results were obtained (Table 4).

Based on the results obtained from the above-mentioned experiments, the determinations of cobalt in river, tap, and sea

Table 4 Recovery from spiked water samples

Sample	Added/ μg	Found/ μg	RSD, %
River water			
Co	0.1	0.1	2.37
Cu	0.1	0.1	3.77
Cd	0.015	0.015	9.61
Tap water			
Co	0.1	0.1 ₀₁	6.66
Cu	0.1	0.1	3.26
Cd	0.015	0.015	9.76
Sea water			
Co	0.1	0.1	6.19
Cu	0.1	0.09 ₆	7.05
Cd	0.015	0.015 ₆	5.00

The obtained results are the average of three replicate determinations. The sample volume taken was 500 cm³.

water (located in Ishikawa prefecture) were tried. The samples were filtered through a Fuji Photo Film FR-40 membrane filter (pore size 0.4 μm) as soon as possible after sampling and adjusted to pH 2.5 - 3.0 with concentrated nitric acid. Table 5 summarizes the analytical results. In this Table, the results of analyses of copper and cadmium are also appended, indicating that the results obtained by the calibration and standard addition methods are in good agreement.

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Table 5 Results of the determination in water samples

Sample	Found/ ng cm^{-3}	
	Calibration method	Standard addition method
River water		
Co	N.D.	N.D.
Cu	0.32	0.32
Cd	0.009	0.009
Tap water		
Co	N.D.	N.D.
Cu	2.30	2.34
Cd	0.007	0.007
Sea water		
Co	0.22	0.24
Cu	1.16	1.06
Cd	0.015	0.016

The obtained results are the average of three replicate determinations. The sample volume taken was 500 cm³. N.D.: not detected.

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