NOTES

DETERMINATION OF COBALT IN SEAWATER BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY AFTER PRECONCENTRATION WITH DIETHYLDITHIOCARBAMATE EXTRACTION AND VACUUM EVAPORATION OF SOLVENT

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A simple and effective preconcentration method of cobalt from seawater is described. Cobalt is extracted as the diethyldithiocarbamate into carbon tetrachloride, then the solvent is evaporated by a rotary evaporator. The element is determined by graphite furnace atomic absorption spectrometry after dissolution of the residue with nitric acid and hydrogen peroxide. By using this method, cobalt in seawater with levels of ng dm^{-3} range could be determined.

The cobalt content of seawater is usually at ng dm^{-3} level, so that its determination, even by graphite furnace atomic absorption spectrometry (g.f.a.a.), requires about a thousand fold preconcentration. A number of preconcentration methods for cobalt from water, such as, solvent extraction^{1)~3)}, ion-exchange^{4)~6)}, coprecipitation⁷⁾⁸⁾, colloid flotation⁹⁾¹⁰⁾, electrodeposition on graphite tube¹¹⁾, adsorption on silica gel¹²⁾, and collection on polyurethane foam¹³⁾, have been reported. Of these preconcentration techniques, solvent extraction method appears to be the most convenient in view of simplicity and rapidity. Most of solvent extraction methods, however, lack the concentration efficiency, so that further concentration steps are needed. The effective preconcentration method based on the extraction of metal diethyldithiocarbamate and vacuum evaporation of the extract was described in the previous paper¹⁴⁾ for the determination of bismuth in seawater.

In this work, the preconcentration method is applied to the determination of cobalt in seawater by graphite furnace atomic absorption spectrometry. This preconcentration method is of advantage the other method on account of simplicity, high efficiency, and less contamination. Cobalt can be concentrated above a thousand fold over the original amount in seawater. The preconcentration step allows the determination of cobalt with levels of ng dm^{-3} range in seawater.

EXPERIMENTAL

Reagent

A $1000 \mu\text{g cm}^{-3}$ cobalt solution was prepared by dissolving a definite amount of cobalt ammonium sulfate in 0.1 mol dm^{-3} nitric acid. The solution was then diluted as required. A 4% sodium diethyldithiocarbamate (NaDDC) solution was prepared freshly in each case by dissolving a definite amount of NaDDC in distilled-deionized water. All the other chemicals used were of a guaranteed reagent quality.

Apparatus

A Hitachi HFA graphite furnace atomizer was used in conjunction with a Hitachi 170-50 atomic absorption spectrophotometer. A single-element cobalt hollow cathode lamp (Hitachi) was employed as the light source. A Hitachi Horiba F-7 pH meter was employed.

Procedure

A seawater sample acidified at 0.1 mol dm^{-3} hydrochloric acid was filtered through a $0.45 \mu\text{m}$ millipore filter. An aliquot (e.g. 2000 cm^3) of the solution was taken in a polypropylene beaker. To this solution, 4 cm^3 of 20% sodium citrate solution was added. The acidity of the solution was adjusted to pH 8 by addition of aqueous ammonia. The solution was transferred into a separatory funnel, then 20 cm^3 of 4% NaDDC solution was added. The extraction of cobalt diethyldithiocarbamate was carried out by 100 cm^3 of carbon tetrachloride for 10 min in the first step and by 10 cm^3 of the solvent for 10 s in the second step. The organic phases were transferred into a flask, then the flask was equipped with a rotary evaporator. The extract was evaporated to dryness under reduced pressure with an aspirator at 60°C for 10 min and 90°C more 5 min on a water bath. The flask was taken away from the rotary evaporator, then vapor in the flask was replaced with air. The residue in the flask with a polyethylene stopper was dissolved by 0.2 cm^3 of nitric acid at 90°C on a steam bath for 3 min. After cooling to room temperature, 1.8 cm^3 of 10% hydrogen peroxide solution was added, then the mixture was shaken to be homogeneous solution. The weight loss of the final solution was less than 0.2% of the total amount in the dissolution process. The solution was used for the determination of cobalt by g.f.a.a..

RESULTS AND DISCUSSION

Effect of experimental variables

Standard measurements of graphite furnace atomic absorption spectrometry were made on a $20\text{-}\mu\text{l}$ final solution containing about $0.02\text{--}0.2 \mu\text{g cm}^{-3}$ cobalt. This was dried at 150°C for 30 s, ashed for 50 s at 1000°C , and atomized during 5 s at 2500°C . The rate of argon flow was $3 \text{ dm}^3 \text{ min}^{-1}$.

Table 1 Effect of complexing reagents on the measurement of cobalt by g.f.a.a.

Reagents	Relative peak height
—	100 †
NaDDC	103
APDC	96
Dithizone	55
8-Quinolinol	n.d.
Cupferron	n.d.

Co: $0.2 \mu\text{g cm}^{-3}$

nitric acid: 1.3 mol dm^{-3}

hydrogen peroxide: 3 mol dm^{-3} , n.d.: no detectable

† complexing reagent: none

The excess of complexing reagent for extraction of cobalt remains partly in final solution after the preconcentration process. The effect of complexing reagents on g.f.a.a. of cobalt should be examined. Each 10 mg of complexing reagent, such as, sodium diethyldithiocarbamate (NaDDC), ammonium pyrrolidinedithiocarbamate (APDC), diphenylthiocarbazone (dithizone), 8-quinolinol, and cupferron was separately added in a test tube. To this contents, 0.4 μg of cobalt was added, then dissolved with 0.2 cm^3 of nitric acid and 1.8 cm^3 of 10% hydrogen peroxide solution by same way as the foregoing procedure. The result of the measurement by g.f.a.a. are shown in Table 1. The good results were obtained with NaDDC or APDC, but NaDDC was best. It can be presumed that NaDDC or APDC is readily decomposed than the other reagents by the action of nitric acid and hydrogen peroxide.

The artificial seawater containing cobalt were adjusted at various pH values. The extraction and preconcentration of cobalt were carried out by the foregoing procedure. The absorbance of cobalt was measured by g.f.a.a.. The quantitative extraction of cobalt into carbon tetrachloride was obtained at pH 4-11. The result was consistent with the paper by Bode¹⁵⁾. The extraction of cobalt diethyldithiocarbamate in basic media is preferable because the large portion of excess NaDDC remains in aqueous phase.

Recovery of 0.4 μg of cobalt from 2000 cm^3 of artificial seawater at pH 8 by the foregoing procedure was 95.7%.

Interference

A study of interference was made for the mixture of metal ions, about same contents of seawater, such as aluminum, arsenic, chromium, copper, iron, manganese, molybdenum, nickel, silver, tin, titanium, uranium, vanadium, and zinc. The mixture of metal ions tested are found not to cause relative error over 6% throughout the two steps of preconcentration and atomic absorption spectrometry.

Analysis of Seawater

The seawater samples of the Indian Ocean, the Pacific Ocean, and the Seashore of the Pacific Ocean (Oarai coast, Ibaraki, Japan) were analyzed for cobalt content by the foregoing procedure, using each 2000 cm^3 of seawater.

Table 2 Determination of cobalt in seawater

Samples	Cobalt found ($\mu\text{g dm}^{-3}$)	R.S.D.‡ (%)
The Indian Ocean(1000 m in depth)†	0.045	
The Pacific Ocean(1500 m in depth)‡	0.050	
Oarai coast, seashore of(surface)‡ the Pacific Ocean	0.082	6.5

† 12°01'02" S 93°58'03" E

‡ 29°56'04" N 133°08'06" E

‡ 36°19'09" N 140°35'29" E

‡ Relative standard deviation (five determinations)

The results are given in Table 2. The cobalt content of seashore sample was higher than that of an ocean sample because the seawater of seashore was contaminated with the metal from the land.

The authors wish to thank Professor Kunihiro Watanuki, Tokyo University, for the offer of the ocean seawater samples.

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Keyword phrases

cobalt determination in seawater; graphite furnace atomic absorption spectrometry of cobalt; diethyldithiocarbamate extraction; preconcentration of cobalt by vacuum evaporation of solvent.

(Received January 25, 1984)