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DETERMINATION OF COBALT IN NATURAL WATERS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY AFTER MICRO SOLVENT EXTRACTION WITH CAPRIQUAT

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Cobalt is extracted as the thiocyanato complex with trioctylmethylammonium chloride(Capriquat) in o-dichlorobenzene, and determined by graphite furnace atomic absorption spectrometry using pyrolytic graphite coated tube. At the sampling point, the proposed method was applied. The organic phase separated was stored in a refrigerator, and determined in the laboratory within a day.

A simple and rapid preconcentration method for the determination of trace elements in natural waters is required as a consequence of increased concern over environmental pollution. And there has been a growing demand for in situ and/or on site analysis for the speciation of trace elements because of the time delays involved in laboratory-based analysis, adsorption on sampling bottle at natural pH of sample or leaching from at pH 2 of acidified sample. The cobalt content of natural water is often below µg/l, and sometimes at ng/l level, so that its determination, even by graphite furnace atomic absorption spectrometry(GFAAS), requires about a thousand fold preconcentration. A thousand fold preconcentration was already achieved by diethyldithiocarbamate(DDTC) extraction and vacuum evaporation of solvent,1,2) however, consumed much of costly samples, 2 l per an extraction. Foe reducing the consumptions of sample and reagents the micro solvent, using only 50- or 100-µl, extraction method with DDTC was investigated to allow copper3) and nickel4) determinations in sea water, however this method can not be applied to the on site operation because of the pH adjustment step involved. The preconcentration method based on the extraction of thiocyanato complex with Capriquat in benzene[5,6] might be applied because the pH adjustment step is unnecessary. Therefore the micro solvent extraction with Capriquat method was studied to concentrate the cobalt species in natural waters at the sampling points. Furthermore to enhance the sensitivity in GFAAS the pyrolytic graphite(PG) coating[7] was performed, amd the detection limit for cobalt was improved about 4 times compared with untreated tube. Therefore the determination of cobalt at the ng/l level in natural waters was practicable by 200 fold preconcentration.

The recommended procedure for 200 fold preconcentration is as follows. After the pretreatments as described later, a 20 ml aliquot of the solution was taken in a stoppered centrifuge tube and acidified to 0.1 mol/l hydrochloric acid as required. One ml of 2 mol/l diammonium hydrogen citrate solution and 0.5 ml of 5 mol/l potassium thiocyanate solution were added. The solution was shaken with 0.1 ml of 0.01 mol/l Capriquat in o-dichlorobenzene for 5 min. To separate the phases the solution was centrifuged for 2 min by a hand driven centrifuge. The organic phase was transferred into a collection vial by Micro Pipette(Eppendorf 4780) and stored in a portable refrigerator. The cobalt content was determined by the standard addition method. In the laboratory, atomic absorption measurement was done using PG coated tube within a day after the phase separation.

All chemicals used were of reagent grade or the highest quality available. A Hitachi GA-2B graphite furnace atomizer was used in conjunction with a Hitachi 170-50 atomic absorption spectrophotometer. Working conditions were as follows: Analytical line; 240.7 nm, Drying; 160 °C-20 s, Ashing; 700 °C-40 s (ramp mode), Atomizing; 2800 °C-5 s, Injecting volume; 10 µl.

Matsuo et al.[8] studied an extraction system of tetradecyldimethylbenzylammonium chloride (Zephiramine)-thiocyanatocobalt(II)-chloroform, at the aqueous/organic phase volume ratio of 25 ml/5 ml. However, it is necessary to study the details of the optimum conditions for the micro solvent extraction with Capriquat. The choice of organic solvent is of great importance to the micro solvent extraction. A high boiling point, low miscibility with water and large specific gravity are desired, then chloroform and carbon tetrachloride were eliminated. Even for high salt content sample, sea water, o-dichlorobenzene was suitable. The organic phase was a little, so centrifuge tube was used instead of separatory funnel. To collect the organic phase on the bottom, the centrifugal separation step was necessary. In consideration of the field work, the hand driven centrifuge was used and modified so as to make use of 30 ml centrifuge tube. To take out the organic phase easily, Micro Pipette with 0.5 ml combitip was used with 0.1 ml comfortip.

The effect of experimental variables on the recovery of cobalt from artificial sea water was examined by the same preconcentration procedure, and decided as mentioned above. The acidity of 0.1 mol/l hydrochloric acid was chosen because natural water samples are commonly stored at this acidity. Diammonium hydrogen citrate solution was added as masking agent, mainly for iron. Details will be reported later.

The natural water samples, sea water and river water, were analyzed for cobalt content by foregoing procedure, 200 fold preconcentration, except the samples of Honzan mine carried out by 50 fold preconcentration. The results are given in Table 1. Before preconcentration, three methods of pretreatments were employed at the sampling points. Method A : The collected sample was acidified to 0.1 mol/l hydrochloric acid, boiled for an hour, and filtered through 0.45 μm Millipore filter. Method B : The collected sample was filtered, acidified to 0.1 mol/l hydrochloric acid, and boiled for an hour. Method C : The collected sample was filtered. Then these solutions were supplied to the micro solvent extraction.

Table 1. Comparison of the analytical results for natural waters obtained by the four pretreatment methods

Sample	Sampling Date	Cobalt found, μg/l			
		Method a)			
		A	B	C	D b)
Sea water	'85.9.6				
Hitachi		0.110	0.043	0.052	0.047 ± 0.003
Isozaki		0.043	0.021	0.023	0.023 ± 0.002
River water	'85.9.13				
Honzan mine		1.16	1.25	1.17	1.17 ± 0.08
Ashio dam		0.22	0.017	0.006	0.008 ± 0.003

Methods A-C : Micro solvent extraction was done at the sampling points. The organic phases were stored in a refrigerator, and determined in the laboratory within a day.

Method D : Micro solvent extraction and determination were done in the laboratory within 10 d.

a) Procedures are given in the text.

b) Mean ± standard deviation (n=3-4).

To test the precision and accuracy, the filtered and acidified samples were also stored in a refrigerator, and the results obtained in the laboratory are shown as Method D. The reagent blanks were obtained using high-purity water supplied from Milli-Q system(Millipore) at the sampling points and in the laboratory, and the apparent difference were not observed.

The results, though the values varied a little, show that there is no significant difference between the analytical values obtained from Method C and Method D, that is, the contents of labile or extractable species in the filtered sample do not vary so much by acidification and during the storage in a refrigerator. The analytical values obtained from Method B are the total contents in the filtered sample, so-called the dissolved species.9) And the analytical values obtained from Method A are seemed to be the absolute "total" concentrations involved in unfiltered portion, adsorbed on or incorporated into particulate matter retained by 0.45 μm filter. The detailed discussion about the individual results will be described after the carried back samples are analyzed minutely.

The trace metal speciation in natural waters is a difficult, but an important subject. This method will provide an epochal means to this field of study.

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