

DETERMINATION OF DISSOLVED TRACE METALS IN SEA WATER BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AFTER CONCENTRATION BY Fe (III)-APDC COPRECIPITATION

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ABSTRACT

A method for the determination of dissolved species of Cd, Co, Cu, Ni, Pb and Zn in sea water by flame atomic absorption spectrophotometry (AAS) is described.

Prior to analysis by AAS, these elements are concentrated by coprecipitation with iron pyrrolidinedithiocarbamate at pH 3 because of matrix effects and their low concentration levels in sea water.

The detection limits are 0.01, 0.04, 0.02, 0.05, 0.08, and 0.03 μ g/l, and the relative standard deviations are 1.0, 2.4, 1.3, 2.9, 2.0 and 2.9% for Cd, Co, Cu, Ni, Pb and Zn, respectively.

The method is shown to be satisfactory in terms of recovery and precision for the determination of these metals in sea water.

INTRODUCTION

Quantitative analysis of trace metals in sea water is important from environmental and geochemical viewpoints. However, it is difficult to determine trace metals directly by atomic absorption spectrophotometry (AAS) because of matrix effects and their low concentration levels in sea water.

Most analytical methods have detection limits which require sample preconcentration or separation of the trace metals from the major constituents in sea water. Commonly used techniques for preconcentration of trace metals include ion-exchange (Riley and Taylor, 1968; Smith, 1974), solvent extraction (Brooks et al., 1967; Danielsson *et al.*, 1978; Smith and Windom, 1980) and coprecipitation (Boyle and Edmond, 1977; Hudnik *et al.*, 1978; Yamazaki, 1980).

In coprecipitation method, ammonium pyrrolidinedithiocarbamate (APDC) is often used as an organic reagent which forms insoluble compounds with trace metals and a carrier element

that has to be added to the sample in order to obtain an adequate amount of precipitate for trapping trace elements.

Boyle and Edmond (1977) determined Cu, Ni and Cd in sea water by Co-APDC coprecipitation coupled with flameless AAS. Hudnik *et al.* (1979) reported a method for the determination of Cd, Co, Cr, Cu, Ni, and Pb in mineral water by flameless AAS with Fe-APDC coprecipitation.

For routine analysis dealing with a number of samples at one time, flameless AAS technique is often tedious and time consuming compared with flame AAS.

The present paper reports the modified procedure of the Fe-APDC coprecipitation (Hudnik *et al.*, 1978) for the determination of dissolved Cd, Co, Cu, Ni, Pb and Zn in coastal sea water by flame AAS.

MATERIALS AND METHODS

1. Reagents

A mixed stock solution of the metals was

prepared from Merck reagent grade chemicals.

An APDC solution (5%, w/v) was purified by multiple extractions with chloroform and n-hexane.

The citrate buffer solution was adjusted to pH 3.0 with hydrochloric acid and ammonium hydroxide. The solution was purified by repeated dithizone extraction with chloroform until no metals were found in the extract.

The Millipore membrane filters (pore size $0.45\mu\text{m}$, diameter 47mm) were used in filtering the samples and precipitates. The filters were purified by soaking in dil. HNO_3 (1 : 5) for two weeks and 0.1% APDC solution for overnight.

All other chemicals were of Merck reagent grade and used without further purification.

Distilled and deionized water was used throughout the study.

2. Instrument

Measurements were made with an Instrumentation Laboratory(IL) Model 251 atomic absorption spectrophotometer. IL hollow-cathode lamps (Cd, Co, Cu, Ni, Pb and Zn) and deuterium

lamp for background correction were used as light sources.

3. Recommended procedure

Samples should be filtered on Millipore membrane filters immediately after collection, if possible.

Pour 800ml of the filtered seawater sample into an one-liter round-bottom flask, add two drops of methyl orange and 5ml of Fe (III) solution (1,000mg/l), and adjust the pH approximately to 3. Add 15ml of the citrate buffer and finally 5ml of APDC solution. Shake the flask for one min., let stand for half an hour, and filter.

The precipitate is collected on a filter and transferred into a 10-ml test tube with stopper.

Dissolve the precipitate in 5ml of 1 : 5 HNO_3 in a water bath at 60°C . The sample solution is then aspirated into the burner for the absorption measurement.

The instrumental conditions for measurement are given in Table 1.

Table 1. Instrumental conditions for the flame AA measurement.

elements	Cd	Co	Cu	Ni	Pb	Zn
Wave length(nm)	228.8	240.7	324.7	232.0	283.3	213.9
Slit width(um)	320	80	320	40	320	320
Lamp current(mA)	5	10	5	5	5	5
Air flow rate(l/min)	8.1	8.1	8.1	8.1	8.1	7.2
Acetylene flow rate(l/min)	1.6	1.6	1.6	1.6	1.6	2.3
Scale expansion	X5	X5	X2	X5	X10	1

RESULTS AND DISCUSSION

1. Effect of pH on coprecipitation coefficient

A large batch of synthetic sea water was prepared and used for all experiments in the present study.

The pH was adjusted with only HCl and

ammonium hydroxide, and monitored with a pH meter. Fig.1 shows that pH in the range of 1~6 has no influence on the coprecipitation efficiency for these metals except for Zn and Cd.

The coprecipitation efficiency for Zn decreases sharply below pH 2.5. On the other hand, Cd has a tendency to decrease in the efficiency above pH 5.

In general, the coprecipitation efficiency declines

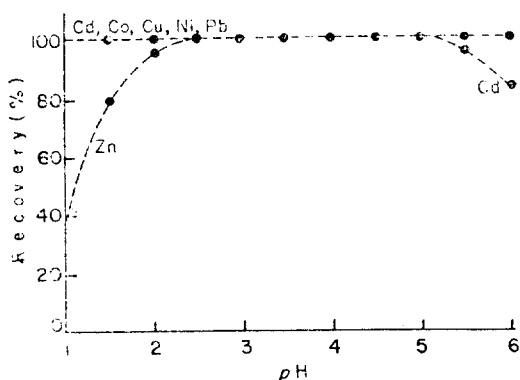


Fig. 1. Effect of pH on coprecipitation efficiency.

below pH 1 due to decomposition of APDC. And above pH 7 it decreases probably because of precipitation of $\text{Fe}(\text{OH})_3$.

2. Time-dependence of the coprecipitates

Metal complexes with APDC are generally known to have poor stability in the organic phase. Although they are stable in an aqueous solution, they have the time-limit. Fig. 2 shows the stability of APDC coprecipitates with time for metals such as Cd, Co, Cu, Ni, Pb and Zn in a synthetic sea water. Except for Zn, all metal coprecipitates are stable within 6hr. The stability of Zn coprecipitate decreases after 3.5 hr. Therefore, it is desirable to filter the metal

3. Recovery, precision and detection limits

The recovery, precision and detection limits of the present method were tested for the syn-

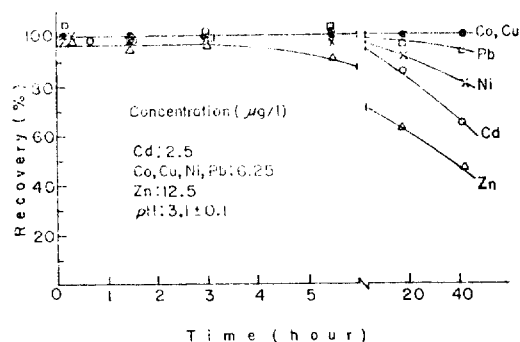


Fig. 2. Time-dependence of the coprecipitates.

coprecipitates with APDC within 3hr.

thetic sea water containing the known amounts of Cd, Co, Cu, Ni, Pb and Zn to see if this technique could be employed in analysis of the coastal sea water. The results shown in Table 2 were obtained from the eleven determinations. Table 2 shows that, in the formation of Fe-APDC precipitate, Cd, Co, Cu, Ni, Pb and Zn are coprecipitated quantitatively. The percent recovery and precision of these elements are quite high and acceptable.

4. Calibration curves

Calibration curves were studied for the conditions under which an actual multielement analysis might be performed. In order to make calibration curves, standards containing six cations were prepared in a synthetic sea water and concentrated by the coprecipitation method mentioned above. Calibration curves for various elements are given in Fig. 3.

Table 2. Recover, precision and detection limits

Element	Conc. ($\mu\text{g}/\text{l}$)		Recovery (%)	RSD (%)	Detection limit ($\mu\text{g}/\text{l}$)
	added	found			
Cd	1.25	1.22 \pm 0.01	98	1.0	0.01
Co	2.5	2.51 \pm 0.06	100	2.4	0.04
Cu	2.5	2.48 \pm 0.03	99	1.3	0.02
Ni	2.5	2.50 \pm 0.07	100	2.9	0.05
Pb	2.5	2.56 \pm 0.05	102	2.0	0.08
Zn	5.0	4.76 \pm 0.14	96	2.9	0.03

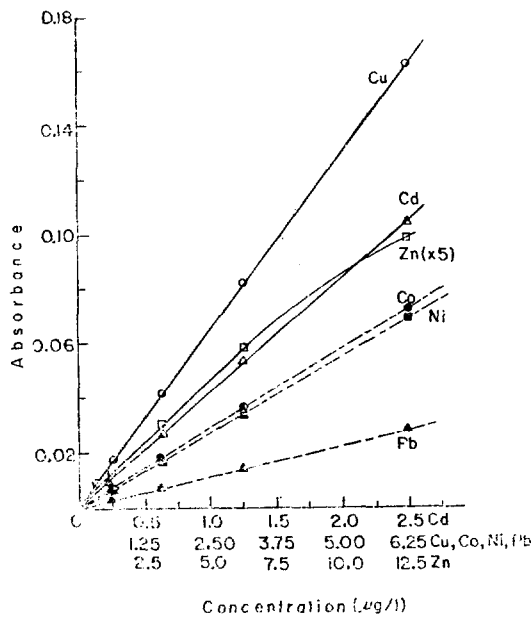


Fig. 3. Calibration curves for various elements.

5. Analysis of the coastal sea water

These experiments were carried out to determine if the method could be applied to natural waters such as coastal sea water where very low concentrations of various cations are often encountered. However, it should be emphasized that the samples were not checked by another independent analytical method. The results are shown in Table 3 for Cd, Cu, Pb and Zn in the Nagdong Estuary (Lee *et al.*, 1979).

The concentrations are reasonable levels for this type of water.

Table 3. Annual averages of dissolved Cd, Cu, Pb and Zn at sampling stations of the Nagdong Estuary ($\mu\text{g/l}$).

Element	Sampling stations	1	3	5	7	9
Cd		0.80	0.28	0.50	0.32	0.12
Cu		2.1	1.0	1.3	1.5	1.0
Pb		2.5	1.9	1.3	0.9	1.1
Zn		26.0	8.7	11.0	15.0	9.3

6. Interferences

In the absence of a buffer, the coprecipitation of Cd was inconsistent, due to shift in pH during coprecipitation process. In fact, the pH of the sample increased during this process. Maintaining the appropriate pH throughout the process was, therefore, quite important and accomplished by the use of ammonium citrate buffer.

Major constituents of sea water and large amount of iron introduced during the sample concentration could give molecular absorption interferences. This was excluded with the use of deuterium background corrector. There were no detectable changes in sensitivity due to the presence of small amounts of sea salt in the coprecipitates.

7. Comparison with other techniques

The present coprecipitation technique can be compared with chelation and solvent extraction, and ion-exchange techniques. Table 4 shows a

Table 4. Comparison of concentration methods.

METHOD	Solvent Extraction	Ion-Exchange Resin	Coprecipitation
	APDC-MIBK ^{a, b, c}	Chelex-100 ^d	APDC-Fe
Concentration factor	20	1000	160
Recovery(%)	90~100	100	96~100
Concentration time	FAST	SLOW	FAST
Reproducibility R.S.D.(%)	3~15	2~10	1~3
Stability	BAD	GOOD	GOOD

a) Brooks *et al.*, 1967

c) Danielsson *et al.*, 1978

b) Kinrade and Van Loon, 1974

d) Riley and Taylor, 1968

brief summary of the comparison.

CONCLUSIONS

The combination of sample concentration by APDC chelate coprecipitation and analysis by flame atomic absorption spectrophotometry provides a valuable procedure for the determination of dissolved Cd, Co, Cu, Ni, Pb and Zn in the coastal sea water. Some of the advantages of the present technique over others are simple in sample concentration, rapid in measurements and the elimination of interferences. And this technique also has high recovery (above 96%) and high concentration factor (160 times).

Good results have been obtained on the analyses of Cd, Cu, Pb and Zn in the coastal sea water by the present method (Lee *et al.*, 1979). However, in order to use this technique successfully, care must be taken especially for cleanliness of laboratory and contamination from reagents and glasswares.

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