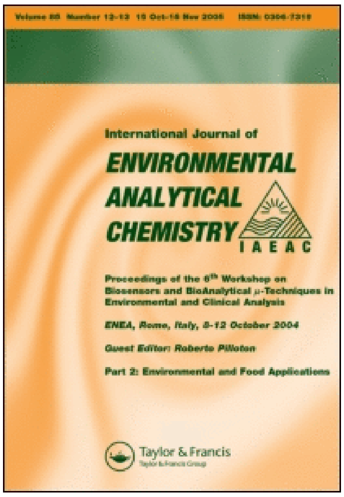

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PRECONCENTRATION AND SEPARATION OF TRACE METAL IONS FROM SEA WATER SAMPLES BY SORPTION ON AMBERLITE XAD-16 AFTER COMPLEXATION WITH SODIUM DIETHYL DITHIOCARBAMATE

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Sorption of some trace metal ions (Fe, Ni, Cu, Zn, Cd, Co) after complexation with sodium diethyl dithiocarbamate (Na-DDTC) on Amberlite XAD-16 was investigated in the pH range 2–10. All these metals were retained from pH 3 to 6. The retained metals can be eluted with various eluting agent such as 1 M nitric acid in acetone, 3 M nitric acid in ethanol. The method was applied to trace metal ions in surface sea water samples from Mersin Bay (Mediterranean Sea), Turkey. The relative standard deviations of the determination were less than 8%.

Keywords: Preconcentration; trace metals; Amberlite XAD-16; sodium diethyl dithiocarbamate (Na-DDTC); sea water; flame atomic absorption spectrometry

INTRODUCTION

Confident analytical results for the trace metal contents of sea waters collected from various locations of the world have been obtained[1–4]. To determine trace metals in sea water by instrumental analysis, a separation and preconcentration technique is frequently required, because of low concentration of the trace metal ions and high salt contents. Many preconcentration techniques for determination metal ions have been proposed, including extraction[5,6], ion exchange[7,8], coprecipitation[9–10], sorption[11–12]. These techniques have been used with instrumental methods of analysis, UV-vis spectrophotometry[6,11], ICP-AES[12], AAS[10,13],

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NAA[9,14], etc.. Recently preconcentration methods based on adsorption of complexed metals on Amberlite XAD copolymers have been widely applied to various matrices like anodic mud and natural waters[15–17].

Dithiocarbamates are widely used organic chelating agents and various dithiocarbamates complex strongly with many metal ions[18]. In most instances sodium diethyl dithiocarbamate (Na-DDTC) that has a larger formation constant for most complexes, is used in chemical enrichment of trace metal ions by various preconcentration techniques prior to their determination[19,20].

The purpose of this study was to use the chelating agent Na-DDTC and a mini column packed with Amberlite XAD-16 for the preconcentration of trace metal ions from sea water before their determination by flame atomic absorption spectrometry (FAAS).

EXPERIMENTAL

Apparatus

A Hitachi Z-8000 model Zeeman atomic absorption spectrometer was used in conjuction with monatomic hollow cathode lamps and a data-processing module which compensates for background absorbance. Atomic absorbance measurements were carried out in air/acetylene flame. 100 µl of samples were introduced into the nebulizer using the micro injection technique[21,22].

Reagents and Solutions

Redistilled deionized water from a quartz apparatus was used. Otherwise stated analytical-grade acetone, acids and other chemicals used in this study obtained from Merck, Darmstadt, Germany.

Standard solutions (1000 mg/l) of the elements were prepared by dissolution of pure metals or their salts (E. Merck, Darmstatd) and further diluted prior to use.

A Na-DDTC solution (1.0×10^{-2} M) was prepared by dissolving the requisite amounts of Na-DDTC in water immediately before use. The solution was discarded after one day.

Amberlite XAD-16 (Sigma, St. Louis, MO.) resin was ground and sieved (80–100 mesh fraction) and was purified by washing with methanol, water, 1 M nitric acid in acetone, water, 1 M NaOH, water and acetone, sequentially, in order to eliminate trace metal ions and other inorganic and organic contaminants in the resin[23].

Column

The Amberlite XAD-16 column was 10 cm long, and 0.5 cm in diameter. A small plug of glass wool was placed at the bottom of the column. The column contained about 300 mg resin (ca 30 mm bed). The resin column was prepared by aspirating a water slurry of Amberlite XAD-16 into the glass column. It was conditioned with 10–15 ml of pH 6 buffer. Then it was used for the preconcentration study.

Preconcentration Procedure

The column method was tested with model solutions before its application to sea water samples. For the metal determinations, to 50–100 ml of solution containing 5–10 μg of the metal ions was added 10 ml of buffer solution (to give the desired pH between 1–10) and 10 ml of 1.0×10^{-2} M Na-DDTC solution. The column was preconditioned by passing buffer solution. The metal/DDTC solution was passed through the column at a flow rate of 25 ml/min by the aid of a vacuum aspirator. After the passage of this solution, the column was rinsed twice with 10 ml of water. The adsorbed metal chelates on the column were eluted with 8–10 ml of 1M nitric acid in acetone. The eluate was evaporated over a hot plate to near dryness. The residue was dissolved 2 or 5ml of 1.0M HNO_3. The eluate was analyzed for the determination of metal concentrations by atomic absorption spectrometry. Blanks were determined by applying the same procedure to 50 ml of distilled water.

Sampling

The surface sea water samples were collected in prewashed (with detergent, doubly deionized distilled water, dilute HNO_3 and doubly deionized distilled water respectively) polyethylene bottles from four stations in Mersin Bay (Mediterranean Sea), Turkey in May 1994. The samples were filtered through a Millipore cellulose membrane of pore size 45μm. The samples were stored in 1 liter polyethylene bottles and acidified to 1 % with nitric acid and were subsequently stored at 4 °C in a refrigerator.

Preconcentration of Trace Metals from Sea Water

Prior to trace metal analysis, the acidified sea water sample was neutralized and adjusted to pH 6. To 500 ml of sample, 10 ml of 1.0×10^{-2} M Na-DDTC was added. The solution was passed through the XAD-16 column which was washed twice with 10 ml of water and adsorbed metals were eluted 8–10 ml of 1M nitric acid in acetone. The eluate was evaporated to near dryness. The residue was dissolved and transferred to a 2 ml volumetric flask with 1 M HNO_3. The concentrations of the eluted metal ions were determined by FAAS.

RESULTS AND DISCUSSION

Optimization of the Extraction Method

To obtain quantitative recovery of metal ions on XAD-16 column, the procedure was optimized for various analytical parameters such as pH, sample volume and amounts of Na-DDTC. The percentage of metal adsorbed on the column was calculated from the amounts of metal in the starting sample and the amounts of metal eluted from the column.

Effect of pH on Sorption

The sorption of metal ions on the Amberlite XAD-16 resin was studied at different pH values, with the other parameters kept constant. The pH of the model solution was adjusted to pH 2–6 with CH_3COO^-/CH_3COOH buffers, pH 7 with 0.01M borate buffer, and pH 8–10 with NH_3/NH_4^+ buffers. The maximum recoveries for Cu, Fe, Ni, Cd, Co and Zn were found at the pH ranges 3–6 (Figure 1). Quantitative recoveries for Pb and Cr were not observed at any pH.

Effect of the Sample Volume

The effect of the sample solution volume on the metal sorption was studied by passing 100–2000 ml volumes through the XAD-16 column at a 25 ml/min flow rate.

The adsorption of the metal ions with 0.3 g resin was not affected by sample volume below 1000 ml. At or above 1000 ml the percentage sorption was decreased for Fe, Ni, Cd and Co (Table I).

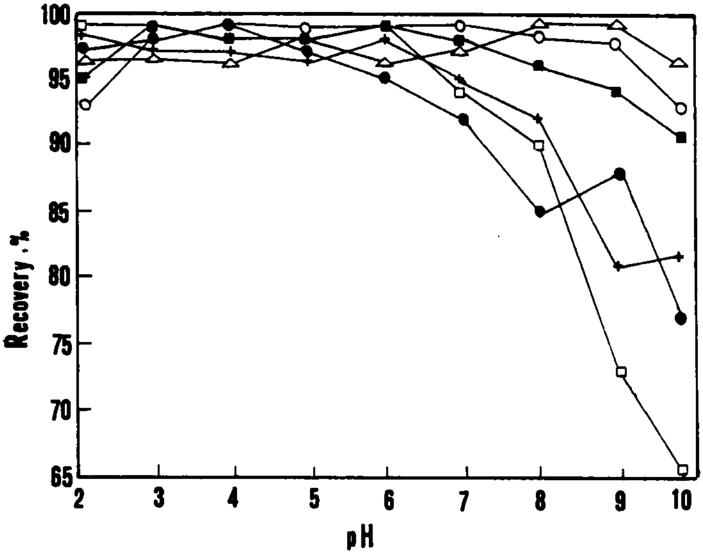

FIGURE 1 pH dependence of the recoveries of the metal ions on Amberlite XAD-16 column (Cu (□), Fe (●), Ni (△), Cd (+), Co (■) and Zn (○)).

The influence of flow rate on the adsorption of trace metals was studied. Flow rate variations in the range of 5–50 ml/min had no significant effect on the recoveries. All subsequent experiments were performed at 25 ml/min flow rate.

The effects of Na-DDTC concentration on the sorption of metal ions were investigated. The recovery of the metal ions increased with increasing concentrations of Na-DDTC added and reached a constant value with at least 0.3×10^{-3} M (Figure 2). On this basis, studies were carried out at a Na-DDTC concentration of 1.0×10^{-3} M.

TABLE I Effect of the sample volume on the sorption of Cu, Fe, Ni, Cd, Co, Zn (N = 4) using 0.3 g Amberlite XAD-16 resin

Sample Volume (ml)	*Recovery, %*					
	Cu	*Fe*	*Ni*	*Cd*	*Co*	*Zn*
100	99	99	98	95	99	96
250	99	98	97	96	97	99
500	100	96	95	94	102	99
750	97	98	96	95	96	102
1000	96	92	88	90	94	100
2000	99	73	64	81	90	103

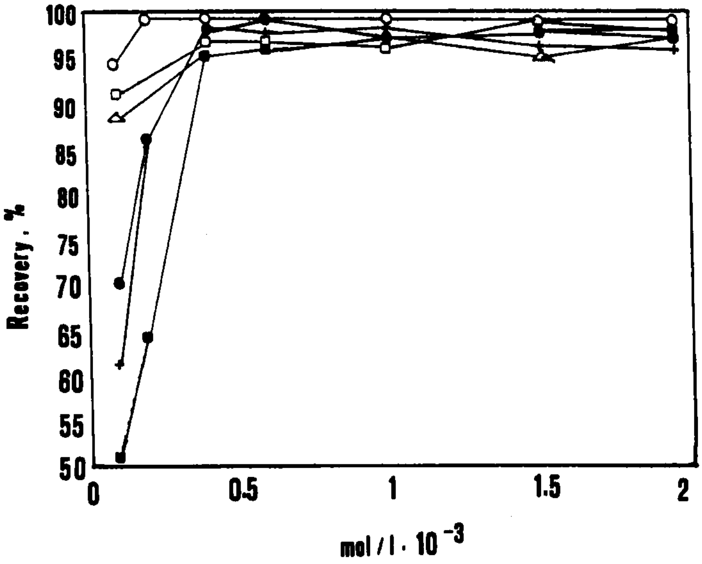

FIGURE 2 Effect of Na-DDTC concentration on the recoveries of metal ions (Cu (□), Fe (●), Ni (△), Cd (+), Co (■) and Zn (○)).

Desorption of the Metal Ions from XAD-16 Resin

The desorption of the retained metals from the XAD-16 column was tested using various eluting agents. The volume of the eluent was 10 ml; the same results were obtained with higher volumes of the eluent. Quantitative recoveries were obtained for Cu, Fe, Ni, Cd, Co and Zn with 1 M HNO_3 in acetone, 3 M HNO_3 in acetone and 3 M HCl in acetone. For Fe, Cd and Zn elution with 1 M HCl in acetone was quantitative. Recoveries with 1 M HNO_3 in ethanol and 3 M HNO_3 in ethanol were quantitative for Cd, Co and Zn. Quantitative recoveries were not observed with 1 M HNO_3, 1 M HCl, 1 M HCl in ethanol and 3 M HCl in ethanol.

Effect of Matrix Ions

In order to evaluate the feasibility of the method for sea water analysis, the effects of the major components of sea water were studied. Table II shows the effect of the matrix ions on the recoveries of Cu, Fe, Ni, Cd, Co and Zn. The high concentrations of Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^- and SO_4^{2-} did not affect the recovery of the trace metal ions. This reflects the lack of complexation with Na-DDTC for these ions[18]. To remove these ions from the XAD-16 column, the column was washed with two portion of 10 ml of distilled water prior to elution.

TABLE II Influence of matrix ions on the recoveries of Cu, Fe, Ni, Cd, Co and Zn (Sample volume: 100 ml, N=4)

Ions	*(mg/l)*	*Added As*	*Concentration of matrix ions in the eluent (mg/l)*	*Recovery, %*					
				Cu	*Fe*	*Ni*	*Cd*	*Co*	*Zn*
—			—	97	95	97	98	96	99
Na^+	5000	NaCl	3.2 ± 0.3	96	97	98	96	96	99
	10000		8.3 ± 0.6	98	98	96	95	98	98
	20000		19.8 ± 1.1	96	96	97	94	96	99
	50000		73.3 ± 2.1	95	95	96	96	90	99
Mg^{2+}	250	$MgCl_2$	0.4 ± 0.1	95	94	96	96	95	96
	500		1.1 ± 0.3	97	96	97	93	96	99
	1000		2.1 ± 0.2	102	103	99	98	93	99
	2500		3.3 ± 0.3	101	96	100	96	95	98
	5000		3.9 ± 0.4	100	93	100	96	95	99
K^+	100	KCl	0.2 ± 0.1	96	98	96	94	96	97
	250		0.9 ± 0.1	97	98	95	98	98	97
	500		1.1 ± 0.2	95	97	94	97	97	99
	1000		4.9 ± 0.5	98	96	96	95	99	99
	2500		9.5 ± 2.3	98	95	95	93	94	99
Ca^{2+}	100	$CaCl_2$	1.0 ± 0.1	100	97	95	97	101	98
	250		2.9 ± 0.3	95	99	96	95	97	99
	500		5.1 ± 0.7	103	104	96	98	95	98
	1000		5.8 ± 0.5	97	96	97	97	96	99
	2500		9.2 ± 2.4	95	97	98	99	95	98
Cl^-	5000	NaCl	13.2 ± 1.4	97	98	100	96	96	99
	10000		48.3 ± 4.6	98	98	99	95	97	98
	20000		59.8 ± 5.1	99	97	97	94	96	97
	50000		78.3 ± 4.1	95	96	98	96	99	97
$(SO_4)^{2-}$	100	Na_2SO_4	10.2 ± 1.1	97	98	98	94	96	98
	250		18.9 ± 2.4	97	96	95	97	98	97
	500		25.1 ± 3.2	95	97	93	97	97	99
	1000		34.9 ± 4.5	98	98	96	96	95	97
	2500		39.5 ± 5.3	97	95	95	94	94	99

Detection Limits

The detection limits of the investigated elements based on three times the standard deviations of the blank[24] (k = 3, N = 21) varied from 14 ng/l for Cd to 51 ng/l for Ni on a sample volume of 100 ml (Table III).

Recovery of Spikes from Artificial Sea Water

The recovery of the trace metal ions from an artificial sea water[25] was also studied. Satisfactory results (Table IV) were obtained for the elements exam-

TABLE III Detection limits[24a]

Element	*Detection Limits, ng/l*
Cu	20
Fe	44
Ni	51
Cd	14
Co	23
Zn	36

[a] Defined as the concentration of the analyte that gives to 3 times the standard deviation of the blank for 100 ml (k = 3, N = 21)

ined. The preconcentration factor in this study was 100. Higher preconcentration factors could be obtained using sample volumes larger than 500 ml.

Application to Surface Sea Water

The proposed method was applied to the analysis of surface coastal water samples from Mersin Bay (Mediterranean Sea) Turkey. The results are summarized Table V. The results have been calculated on the assumption of 100 %

TABLE IV Recovery data for the preconcentration of six trace metals from artificial sea water[25] (sample Volume: 500 ml)

Element	*μg added*	*μg found**	*Recovery; %*
Cu	2	2.0 ± 0.1	100
	5	4.9 ± 0.2	98
	10	10.2 ± 0.2	102
Fe	5	4.8 ± 0.2	96
	10	10.1 ± 0.1	101
	20	20.0 ± 0.3	100
Ni	2	1.9 ± 0.1	98
	5	5.1 ± 0.3	102
	10	9.7 ± 0.1	97
Cd	1	1.0 ± 0.1	100
	2	2.1 ± 0.3	105
	5	4.9 ± 0.2	98
Co	2	2.1 ± 0.2	102
	5	5.0 ± 0.3	100
	10	10.3 ± 0.4	103
Zn	0.2	0.20 ± 0.01	100
	0.5	0.53 ± 0.03	106
	0.8	0.80 ± 0.04	100

*Average of 4 experiments with 95 % confidence interval.

TABLE V Determination of Cu, Fe, Ni, Cd and Zn in surface sea water samples from Mersin Bay (Mediterranean), Turkey. (sample volume: 500 ml, eluent volume: 2 ml, N = 5)

Sample Location	*Concentration of Metals, μg/l**				
	Cu	*Fe*	*Ni*	*Cd*	*Zn*
Mersin Limani	8.4 ± 0.7	81.4 ± 5.1	10.3 ± 0.8	0.56 ± 0.08	0.48 ± 0.02
Mersin Sahil Yolu	6.7 ± 0.4	44.9 ± 1.1	6.0 ± 0.7	<0.20	0.29 ± 0.05
Erdemli Aykent	3.6 ± 0.2	16.4 ± 3.5	3.2 ± 0.1	<0.20	<0.20
Erdemli Özen	4.6 ± 0.4	14.9 ± 0.4	3.1 ± 0.2	<0.20	<0.20

*Mean expressed as 95% tolerance limit

recovery of the trace metal ions. Cobalt concentrations in all samples were found to be less than 0.20 μg/l. The relative standard deviations of the determination were less than 8%.

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