Determination of Trace Metals in Waters by FAAS

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Determination of Trace Metals in Waters by FAAS after Enrichment as Metal-HMDTC Complexes Using Solid Phase Extraction

Şerife Tokalıoğlu,[*] Şenol Kartal, and Latif Elçi[†]

Department of Chemistry, Erciyes University, Faculty of Art and Science, TR-38039, Kayseri, TURKEY
[†]Department of Chemistry, Pamukkale University, Faculty of Art and Science, TR-20020, Denizli, TURKEY

A method has been described for the determination of Cu(II), Pb(II), Ni(II), Cd(II), Mn(II) and Fe(III) by flame atomic absorption spectrometry (FAAS) after preconcentration on Amberlite XAD-16 resin, using hexamethyleneammonium-hexamethylenedithiocarbamate (HMA-HMDTC) as a chelating agent, and NH_3/NH_4Cl buffer solution (pH 9). Influences of various analytical parameters such as pH, concentration of nitric acid, amount of analytes, diverse ions and sample volume were investigated. The relative standard deviation (RSD) and the detection limit (LOD) were found in the range of 0.8-2.9% and 0.006-0.277 µg/mL, respectively. Recoveries obtained by the column method were quantitative (>95%) at optimum conditions. The method was applied to the determination of some metal ions in seawater and wastewater samples. A high preconcentration factor (about 150 for seawater and 75 for wastewater samples) and simplicity are the main advantages of this suggested method.

Keywords : Amberlite XAD 16 resin, Preconcentration, Seawater, Wastewater.

Introduction

Efforts to determine trace metals directly and reliably by flame atomic absorption spectrometry (FAAS) is limited owing to the low concentrations of analytes and matrix interferences. Therefore, separation and enrichment techniques are of great importance in trace metal analysis by modern instrumental methods. To enhance the sensitivity and the precision of the method, preconcentration and separation techniques,[1] such as coprecipitation,[2,3] liquid-liquid phase extraction,[4,5] ion exchange,[6,7] and recently, solid-phase extraction,[8-10] are most frequently used. In the case of the solid-phase extraction, the enrichment of the trace elements with various chelating agents using finely pulverized adsorbent resins of the macroreticular type, has been widely used for the determination of trace metals in different samples associated with various instrumental techniques. Among these techniques, FAAS is preferred because it is simple and inexpensive.[11]

In the solid-phase extraction, the synthetic adsorbent resins, especially Amberlite XAD series (XAD-2, -4, -7, -8, -16, and -1180 etc.), have been widely used to enrich trace elements from aqueous solutions.[12,13] Of the Amberlite XAD series adsorbents, Amberlite XAD-16 resin exhibits the highest surface area (825 $m^2 g^{-1}$) and is a nonionic polymeric adsorbent. Therefore, the Amberlite XAD-16 was selected for our experiments.

Dithiocarbamates, such as sodium diethyldithiocarbamate (DDC) and ammonium pyrrolidinedithiocarbamate (APDC), have been widely used as chelating agents for the separation, preconcentration and determination of trace metals because of their thermodynamically stable metal complexes.[14,15]

Dithiocarbamate compounds have sulfur atoms as electron-donor in their structures. Uncharged chelates form when metal ions react with bifunctional ligands, such as dithio-carbamates, dithizone, oxine etc. Metals that give sparingly-soluble sulphides can be extracted as complexes with ligands that bond through sulphur atoms, *e.g.* dithizone and dithiocarbamates.[16] Also, the high molar absorptivities of metal dithiocarbamate complexes make them useful spectro-photometric reagents for trace metal analyses. So far, HMA-HMDTC, a dithiocarbamate compound, has been mainly used for the preconcentration of trace metals with various methods.[4,17] However, HMA-HMDTC has not been used frequently in analytical chemistry compared with the other dithiocarbamates. In recent years a few papers concerning the determination of metal ions in different media or various samples by using HMA-HMDTC have been published, touting this compound in various methods, such as coprecipitation,[18] solvent extraction,[4,19,20] and more extensively as a precipitate collector in colloid flotation technique.[21-27] At the same time, HMA-HMDTC is a suitable chelating agent for high-performance liquid chromatography (HPLC) of metal complexes, because the metal-HMDTC complexes are more stable in the eluents of the reversed-phase HPLC.[17]

The present paper deals with a separation and enrichment of some heavy metals by means of metal-HMDTC complexes and solid-phase. In this study, a column packed with Amberlite XAD-16 resin was used to separate and pre-concentrate trace metals. The influences arising from pH, nitric acid concentration, amount of analytes, diverse ions, and sample volume on the recoveries were assessed. The procedure was successfully employed for the determination of the trace metals in the seawater and wastewater samples by FAAS.

[*]Corresponding author: e-mail: serifet@erciyes.edu.tr

Experimental Section

Instrument and chemicals. A Hitachi Z-8000 model atomic absorption spectrometer (Hitachi, Japan) with an air/acetylene flame and a Zeeman background corrector was used to determine of the metal ions in model solutions and in the water samples. The operating conditions suggested in the instrument data processor were followed.[28] All the pH measurements were made by means of a Nel digital pH-meter (Nel Co., Turkey) with a combined pH electrode.

Analytical reagent grade chemicals (Merck, Darmstadt, Germany) and doubly distilled water obtained by using a quartz apparatus were used. A stock solution of 1000 μg/mL in 1 M HNO_3 for each element interested was prepared from the corresponding nitrate salt. The standard working solutions were prepared by diluting the stock solutions when necessary. A stock solution of HMA-HMDTC (0.1%, w/v) was prepared daily by dissolving 0.1 g of HMA-HMDTC in ethyl alcohol (stored in a dark bottle to protect from light) and diluted to 1×10^{-5} M for the experiments. To avoid any contamination, all glassware were treated by soaking in concentrated nitric acid (1 : 1, v/v) for 24 hours and then rinsing with distilled water. The ammonia-ammonium chloride buffer solutions were used to adjust the pH of the solutions in the range of pH 8-10.

Sampling of seawater and wastewater. The seawater samples were taken from the Amasra Bay, in Zonguldak province of Turkey, on the South-West terrestrial basin of the Black Sea. The wastewater samples were collected from the Karasu stream in August 2000, which includes all municipal and industrial wastes of Kayseri province before reaching the wastewater treatment plant, in Kayseri province in Central Anatolian of Turkey. The samples were *in situ* acidified to pH 1 and then filtered through a Nuclepore cellulose membrane filter with a pore size of 0.45 µm, and stored in a refrigerator at 4 °C until the analysis.[29]

Column preparation. Amberlite XAD-16 resin (wet mesh size 20-50, Rohm and Haas Co.) was pulverized and sieved to 70-140 mesh. Pulverization increases the total surface area of the resin, which comes into contact with aqueous sample solution.[30] It was used after being washed with methanol, 1 M HNO_3 in acetone, water, 1 M NaOH, water, and acetone, respectively, and dried for an hour at 100 ºC.[31] A 400-mg of Amberlite XAD-16 resin suspended in water was packed into a glass column (10 mm i.d. × 100 mm height).

Procedure. Some preliminary studies were performed to determine the trace metals in water samples after preconcentration onto the column filled with Amberlite XAD-16 resin. For this purpose, to the model solutions of 25 mL including the trace metals (Cd(II) and Mn(II) 2.5 µg; Cu(II), Co(II) and Ni(II) 5 µg; Fe(III) and Cr(III) 10 µg; Pb(II) and Bi(III) 20 µg), 1 mL of NH_3/NH_4Cl buffer (pH 9.0) and the HMA-HMDTC reagent (1×10^{-5} M, in initial solution of 25 mL) to form metal-HMDTC complexes, formed in model solutions before entering the column, were added. The resin was preconditioned with 2-3 mL of a blank solution containing the HMA-HMDTC reagent, which was diluted ten fold according to the working solutions and NH_3/NH_4Cl buffer solution (pH 9.0). The model solutions (pH 9.0) containing metal-HMDTC complexes were introduced carefully to the column and then passed through the column at a flow rate of 2.0-2.5 mL/min by using a vacuum pump. The metal-HMDTC complexes retained on the column were eluted with 1 M HCl in acetone at a flow rate of 1 mL/min. Sample and eluent flow rates are important parameters to obtain quantitative retention and elution, respectively. After eluting, the concentrated solution obtained was evaporated near to dryness and then the residue was completed to 5 mL with 1 M HCl. The metal ions in this solution were determined by FAAS. After the elution procedure, the column was prepared by washing with acetone and water, respectively, for reusing.[12]

Preconcentration of trace metal ions from seawater and wastewater samples. An aliquot of 300 mL of seawater sample and of 150 mL of wastewater sample were used. The acidified samples were neutralized with 6 M NaOH and buffered to pH 9 with buffer NH_3/NH_4Cl, and then a sufficient aliquot of stock dithiocarbamate solution (0.1%, w/v) was added in which the reagent concentration was 1×10^{-5} M in the initial sample solution. The mentioned preconcentration procedure above was applied to the prepared sample solutions. The final volumes of the seawater and wastewater samples for measuring by FAAS were completed to 2 mL. The concentrations of the elements were determined by the injection method,[12] using an aliquot of 100 µL of these solutions.

Results and Discussion

Effect of reagent amount. A separation-preconcentration procedure was applied to 500 mL of model solution buffered with NH_3/NH_4Cl and not containing the reagent. Only Cr(III), Pb(II) and Fe(III) were quantitatively recovered. Probably, these metals are retained on the resin in hydroxide forms. On the other hand, in the model solutions of 500 mL, containing 1×10^{-6} M reagent, the recoveries for Cd(II), Mn(II), Co(II), Bi(III) and Ni(II) also increased to some extent, Cu(II) in addition to Cr(III), Pb(II) and Fe(III) was quantitatively recovered. In the light of these results, the concentration of the reagent added to the model solutions, including the NH_3/NH_4Cl buffer and the traces, was increased ten fold (up to 1×10^{-5} M), as the recovery for some metals (Cu, Cr and Bi) decrease when the reagent concentration was lower than 1×10^{-5} M. Therefore, the concentration of the reagent in the model solutions was used to be 1×10^{-5} M.

Effect of pH and concentration of nitric acid. One of the most crucial parameters affecting the preconcentration procedure is the pH of the solution, because the formation of soluble metal-complexes and their stabilities in aqueous solutions are strongly related to the pH of the medium. Therefore, an appropriate volume of the NH_3-NH_4Cl buffer solutions in which the pH values were between 8 and 10 changing with intervals of a 0.5 pH unit, was added to the
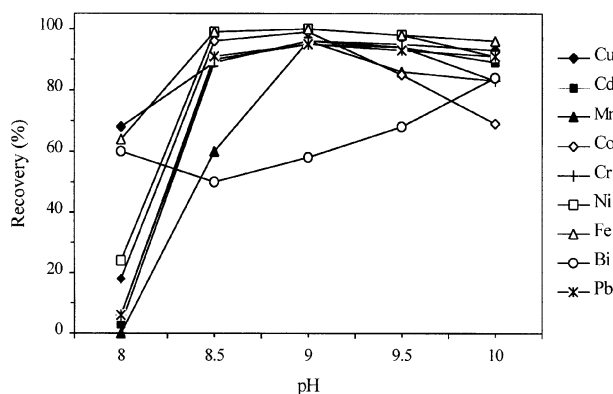
Figure 1. Effect of pH on the recoveries (%) of the elements.

model solutions containing the trace metal ions (Cd(II) and Mn(II), 2.5 μg; Cu(II), Co(II) and Ni(II), 5 μg; Cr(III) and Fe(III), 10 μg; Pb(II) and Bi(III), 20 μg) and the HMA-HMDTC, 1×10^{-5} M. Because of the recoveries (%) being measured quantitatively for all the elements, except for Bi, the pH was chosen as 9.0. The analytical results obtained after applying the separation-preconcentration procedure to the model solutions are illustrated in Figure 1.

The effect of nitric acid concentration (1×10^{-3}~1.0 M) on the enrichment procedure was examined in a medium containing the trace metal ions and the complexing agent. As can be seen from Figure 2, the recoveries were quantitative in the range of 1×10^{-3}~1.0 M HNO$_3$ for Cu(II), ≤ 0.01 M HNO$_3$ for Cd(II) and Pb(II), ≤ 0.1 M HNO$_3$ for Ni(II). With a concentration of HNO$_3$ higher than 1×10^{-2} M, the recovery for Bi(III) was quantitative. Because Bi(III) may undergo hydrolysis or form oxycation at pH values above 2. In addition, the recoveries were not quantitative for Mn(II) and Cr(III) (< 5%), Co(II) (≤ 42%), and Fe(III) (≤ 85%) for all the HNO$_3$ concentrations. At high concentrations of HNO$_3$, recoveries for Fe and Co may probably decrease due to the decomposition of Fe(HMDTC)$_3$ and Co(HMDTC)$_2$ complexes and/or their low stabilities. When the pH of the medium was adjusted with HNO$_3$, the number of recovered elements was lower than those of the NH$_3$/NH$_4$Cl buffer

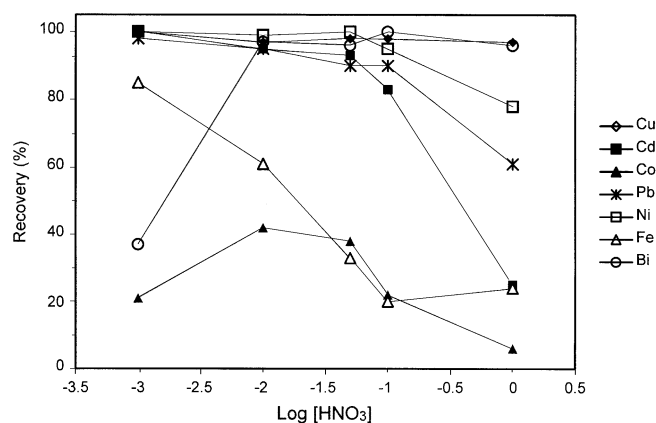medium. Because of this, the pH of the working medium was chosen to be 9.0 by means of NH$_3$/NH$_4$Cl buffer solution.

Effect of sample volume. In the analysis of a real sample using preconcentration, the sample volume is one of the important parameters for obtaining high concentration factors. Therefore, the effects of sample volume on the retention behavior of the analytes examined were studied by varying the volume from 100 to 1000 mL prepared using a medium containing the buffer solution (pH 9.0) and the reagent, 1×10^{-5} M. The effect of the sample volume between 100 and 1000 mL on the recoveries of the elements was examined and the results are shown in Figure 3. As can be seen, Cu(II) and Pb(II) up to 500 mL, Mn(II) up to 700 mL, and Fe(III), Ni(II) and Cd(II) up to 1000 mL were quantitatively recovered, except for Cr(III) and Bi(III). The recovery value of Co(II) was 28% for 100 mL of the model solution, and therefore, Co(II) was not determined in the seawater and wastewater samples.

Effect of analyte amount. To determine the influence of the analyte amounts on the recoveries, model solutions of 25 mL, including NH$_3$/NH$_4$Cl buffer, the reagent (1×10^{-5} M) and increasing amounts of the trace elements (1-40 μg, in a final solution of 5 mL) were prepared. The enrichment procedure was performed by using the column packed with 400 mg of Amberlite XAD-16 resin, and the results are given in Table 1. The recoveries were not quantitative for Mn(II) and Cd(II) when their amounts were higher than 10 and 20 μg, respectively. However, the recoveries for Cu(II), Cr(III), Pb(II), Ni(II) and Fe(III) were quantitative for amounts of 1-40 μg.

Effect of foreign ions. The model solutions, taking into consideration levels of the main concomitant ions, such as Ca(II), Mg(II), Na$^+$, K$^+$, Cl$^-$ and SO$_4^{2-}$, present in seawater and wastewater samples, were prepared to evaluate the matrix effects on analytical signals of the traces. For this purpose, the model solutions containing 2.5 μg for Cd(II) and Mn(II); 5 μg for Cu(II), Ni(II), and Co(II); 10 μg for Fe(III) and Cr(III), and 20 μg for Pb(II) and Bi(III), plus concomitant ions (100-5000 μg/mL K$^+$; 10-40000 μg/mL Na$^+$ and also up to about 61700 μg/mL Cl$^-$ ion; 10-5000 μg/

Figure 2. Variation of the recovery values (%) with the concentration of nitric acid.
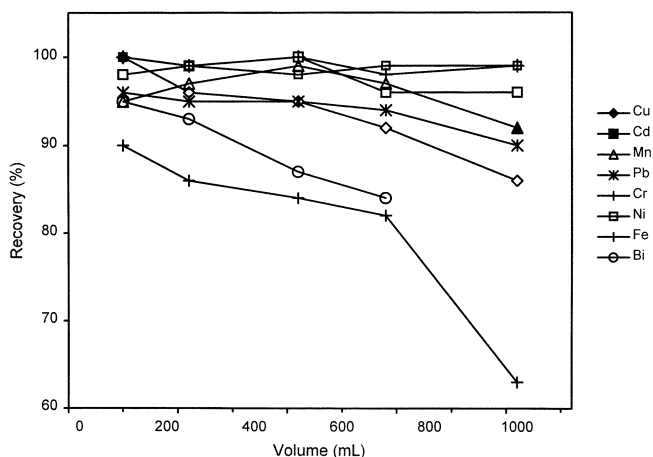

Figure 3. Variation of the recoveries (%) with the sample volume.

Table 1. Variation of the recoveries with increasing amounts of the elements in a medium containing NH_3/NH_4Cl buffer (pH 9) and HMA-HMDTC reagent (1×10^{-5} M)

Amount of element, μg	Recoveries (%)						
	Cu(II)	Cd(II)	Mn(II)	Cr(III)	Pb(II)	Ni(II)	Fe(III)
1	100	97	95	96	97	100	96
2	98	97	94	97	95	99	95
10	95	96	92	95	96	97	95
20	93	95	90	94	94	98	94
40	93	72	83	93	93	99	95

mL Ca(II) and Mg(II); 100-200 µg/mL SO_4^{2-}) were prepared. The results acquired by using the model solutions buffered with NH_3/NH_4Cl and including the reagent,

analytes, and concomitants, are shown in Table 2. Quantitative recovery values of the elements after the preconcentration procedure were barely affected by the concomitants (Ca(II), Mg(II) and Na^+). However, the recoveries were quantitative only for the concentrations of matrix ions are less or equal to 500 mg/mL K^+ for Ni(II), 1000 mg/mL K^+ for Fe(III), and 100 mg/mL SO_4^{2-} for Pb(II) and Ni(II). Stated in another way, a large portion of the matrix components passed through the column without retention. The low levels of matrix ions in the eluate solution are of great importance in the determination of the trace metals tested, because their interfering effects are small when they exist in low levels in the final solution. The results obtained from these experiments (Table 2) demonstrate that the presence of large amounts of alkali and alka-

Table 2. Interfering effects of various matrix components on the determination of the trace metals in the model solutions (n = 3)

Metal ions, µg/mL	In eluate, µg/mL	Recovery (%)						
		Cd(II)[a]	Cu(II)[b]	Mn(II)[a]	Pb(II)[c]	Cr(III)[d]	Ni(II)[b]	Fe(III)[d]
Na^+	–	–[e]	99	98	99	99	98	100	99
(NaCl)	10	1.03	100	99	99	99	98	99	98
	50	6.0	99	97	97	98	96	100	100
	100	7.6	97	98	96	97	96	99	99
	250	9.8	98	97	96	99	95	95	98
	500	28.5	95	96	97	96	96	96	99
	1000	47.5	97	96	96	95	97	96	100
	10000	56	99	100	98	95	98	100	98
	20000	65.5	98	97	96	96	97	100	99
	40000	140	100	97	98	98	99	97	100
Ca(II)	–	–	99	98	99	99	98	100	99
[Ca(NO$_3$)$_2$]	10	1.25	100	99	99	97	99	100	99
	50	3.23	98	98	98	96	98	99	98
	100	4.98	99	98	96	96	98	99	100
	250	21.4	97	96	97	95	97	98	99
	500	27.7	100	97	96	95	96	100	100
	1000	40.6	100	100	97	93	95	100	98
	5000	30.0	99	94	99	92	96	98	98
Mg(II)	–	–	99	98	99	99	98	100	99
(MgCl$_2$)	25	2.4	98	99	97	98	99	100	100
	50	4.7	97	98	95	96	96	99	97
	100	6.2	97	96	96	95	95	98	99
	250	21.7	98	97	95	95	95	99	96
	500	22.0	97	96	96	94	94	100	98
	1000	19.7	98	98	95	93	92	99	98
	5000	37.3	100	99	97	89	93	100	100
K^+	–	–	99	98	99	99	98	100	99
(KCl)	100	0.58	99	98	89	99	99	98	99
	250	1.53	101	95	98	98	98	100	97
	500	3.2	99	97	96	97	99	97	98
	1000	5.5	101	96	97	97	97	115	103
	5000	21.0	107	96	105	99	102	117	115
SO_4^{2-}	–	–	99	98	99	99	98	100	99
(Na$_2$SO$_4$)	100	–	102	98	101	97	103	100	105
	200	–	99	95	95	86	93	112	103

[a]0.1 µg/mL. [b]0.2 µg/mL. [c]0.8 µg/mL. [d]0.4 µg/mL. [e]Not determined

Table 3. Relevant regression results for the calibration graph, detection limit and precision

Element	$R \pm t \cdot s/\sqrt{n}$ (%)[a]	RSD % (n = 10)	LOD[b] µg/mL (n = 20)	Regression equation	Correlation coefficient
Cu(II)	98 ± 1.4	1.9	0.006	A = 0.0002 + 0.01362 · C	0.9999
Cd(II)	99 ± 0.5	1.4	0.009	A = 0.0004 + 0.07426 · C	0.9999
Mn(II)	99 ± 0.6	1.7	0.019	A = -0.0002 + 0.04676 · C	1.0000
Pb(II)	99 ± 2.2	2.9	0.034	A = 0.0003 + 0.00594 · C	0.9999
Cr(III)	98 ± 1.0	0.8	0.016	A = 0.0004 + 0.00971 · C	0.9995
Ni(II)	100 ± 0.9	1.3	0.101	A = 0.0013 + 0.01906 · C	0.9995
Fe(III)	99 ± 2.0	1.4	0.140	A = 0.0012 + 0.02456 · C	0.9998
Co(II)	–[c]	–	0.025	A = 0.0006 + 0.02150 · C	0.9999
Bi(III)	–	–	0.277	A = 0.0014 + 0.00422 · C	0.9984

[a]P = 0.95. [b](n = 20, 3s), A: Absorbance, C: Concentration (µg/mL). [c]Not determined

line earth metals in the sample have no significant effect on the recoveries of the studied metal ions.

The direct atomic absorption spectrometric determinations of some metals can be performed when they are present in high levels in water samples (*e.g.*, Fe and Mn in wastewater samples). For this reason, the effects of matrix components in seawater and wastewater samples on the determination of Cu(II), Pb(II), Cd(II), Cr(III), Ni(II), Fe(III), Mn(II), Co(II) and Bi(III) elements without using the enrichment procedure in the model solutions were also investigated by FAAS. No interference on the elements studied was observed when the concentrations of matrix ions were as follows; $K^+ \leq 5000$ mg/mL, Mg(II) ≤ 5000 mg/mL (up to 500 mg/mL for Bi(III) and 1000 µg/mL for Ni(II)), Ca(II) ≤ 1000 mg/mL, and Na^+ ≤ 20000 mg/mL. Therefore, the proposed column procedure can be successfully applied to the determination of trace elements in both salty and wastewaters.

Calibration graph, detection limit, precision and recovery. In the preparation of the calibration standards for Cu(II), Pb(II), Ni(II), Cd(II), Mn(II), Fe(III), Cr(III), Co(II) and Bi(III), the stock standard solutions of these elements were used by diluting in appropriate ratios with 1.0 M HCl. The standard solutions used for the calibration procedures were prepared before use by dilution of the stock solution with 1.0 M HCl. After determining the optimum preconcentration circumstances, the precision of the method was investigated by using the model solutions containing the spiked elements. The detection limits are commonly defined as analyte concentration giving a signal equal to three times of standard deviation of blank signals.[29] The results of the detection limits, the precision, the analytical equations, and the regression data are summarized in Table 3.

The trace metal ions, in concentrations similar to those usually present in the seawater and the wastewater samples, were added to the samples. Then matrix separation and preconcentration procedures were applied. The recoveries of metals for spiked seawater and wastewater samples are given in Table 4. The high recoveries (> 95%) show the accuracy and validity of the proposed method. Fe(III) and Mn(II) were not spiked to the wastewater samples due to their high levels allowing to their direct determinations. Therefore, the preconcentration procedure and the recovery

Table 4. Recoveries (%) for the spiked elements in seawater and wastewater samples (n = 3)

Element	Added, µg	Seawater		Wastewater	
		Found, µg	Recovery (%)	Found, µg	Recovery (%)
Cu(II)	2.0	1.92	96	1.98	99
	4.0	–[a]	–	4.36	109
Pb(II)	4.0	–	–	4.24	106
	8.0	8.00	100	–	–
	12.0	11.88	99	11.76	98
Ni(II)	1.0	0.96	96	–	–
	2.0	1.86	93	1.92	96
	4.0	–	–	4.32	108
Cd(II)	0.4	0.416	104	–	–
	0.8	0.80	100	–	–
	1.0	–	–	0.97	97
	1.6	1.63	102	1.65	103
Fe(III)	1.0	1.05	105	–	–
	2.0	2.04	102	–	–
Mn(II)	1.0	1.01	101	–	–

[a]Not determined.

studies were not applied to these elements.

Application of the method. We applied the suggested method, finding the concentrations of the trace metal ions investigated in both the seawater with high salinity and the wastewater samples, and the results are given in Table 5. Also, to determine the total metal content of the wastewater sample, the evaporation process was performed by using acid digestion (nitric acid and perchloric acid mixture).[32] As can be seen from Table 5, the Pb(II), Ni(II) and Cd(II) levels obtained by means of the suggested method were lower than those of the evaporation method; the Cu(II), Fe(III) and Mn(II) concentrations were in good agreement for both methods. Reasons for this may be the pH variations in sample in which the pH of the wastewater sample acidified (pH 1) was adjusted to pH 9 before the analysis. Meanwhile, the equilibrium of metal-humic complexes may be established again, and also the rate of equilibrium of metal-humic complexes may be different for each metal. This phenomenon may cause the change of the free metal ion levels in

Table 5. Element levels obtained by the proposed method for both seawater and wastewater samples (also total metal concentrations obtained by evaporation)

Element	Concentration, μg/L[a]; $\bar{x} \pm t \cdot s/\sqrt{n}$		
	Wastewater sample		Seawater sample
	By the proposed method	By evaporation	By the proposed method
Cu(II)	6.96 ± 1.64 (9)[b]	7.97 ± 0.51	5.29 ± 0.60 (5)
Pb(II)	10.8 ± 2.5 (9)	41.1 ± 7.0	1.71 ± 0.06 (4)
Ni(II)	21.1 ± 2.6 (8)	32.8 ± 2.7	2.05 ± 0.18 (6)
Fe(III)	1264 ± 70 (13)	1530 ± 115	9.37 ± 1.63 (3)
Mn(II)	217 ± 17 (13)	228 ± 7	1.34 ± 0.39 (4)
Cd(II)	0.99 ± 0.82 (8)	9.72 ± 0.75	0.36 ± 0.03 (7)

[a]Uncertainty at 95% confidence level. [b]Number of replicates.

sample solution to be analyzed. In this case, the rate of equilibrium of metal-humic complexes for the Pb(II), Ni(II) and Cd(II) elements may probably be higher than others investigated.

As can be seen in Tables 3 and 5, all the metal contents found after the preconcentration procedure in the seawater and the wastewater samples are higher than the corresponding limits.

Conclusions

Solid-phase extraction with Amberlite XAD-16 resin by using HMA-HMDTC reagent as metal chelating agent provides an effective preconcentration and separation procedure for the determination of Cu(II), Pb(II), Mn(II), Cd(II), Ni(II), and Fe(III) metals in seawater and wastewater samples. For the analytes of interest, the preconcentration factor was 150 and 75 for the seawater and the wastewater samples, respectively. The proposed procedure is precise, accurate, and a reliable technique for the preconcentration and separation of some trace heavy metal ions in water samples, such as seawater with high salinity and wastewater.

References

1. Mizuike, A. *Enrichment Techniques for Inorganic Trace Analysis;* Springer-Verlag: Berlin, Heidelberg, New York, 1983; p 2.
2. Elçi, L.; Ṣahin, U.; Öztaş, S. *Talanta* **1997**, *44*, 1017.
3. Hiraide, M.; Chen, Z. S.; Kawaguchi, H. *Anal. Sci.* **1991**, *7*, 65.
4. Dapaah, A. R. K.; Ayame, A. *Anal. Chim. Acta* **1998**, *360*, 43.
5. Rodríguez, M. A.; Zambrano, J. A. B.; Ordaz, A. A.; Mendoza, R. N.; Medina, T. I. S. *Talanta* **1998**, *45*, 875.
6. Kenawy, I. M. M.; Hafez, M. A. H.; Akl, M. A.; Lashein, R. R. *Anal. Sci.* **2000**, *16*, 493.
7. Zhu, W.; de Leer, E. W. B.; Kennedy, M.; Alaerts, G. J. F. R. *Fresenius J. Anal. Chem.* **1998**, *360*, 74.
8. Tunçeli, A.; Türker, A. R. *Anal. Sci.* **2000**, *16*, 81.
9. Tokalıoğlu, Ṣ.; Kartal, Ṣ.; Elçi, L. *Anal. Sci.* **2000**, *16*, 1169.
10. Takahashi, A.; Igarashi, S. *Anal. Sci.* **2000**, *16*, 433.
11. Tunçeli, A.; Türker, A. R. *Analyst* **1997**, *122*, 239.
12. Tokalıoğlu, Ṣ.; Kartal, Ṣ.; Elçi, L. *Mikrochim. Acta* **1997**, *127*, 281.
13. Soylak, M.; Elçi, L.; Doğan, M. *Anal. Lett.* **1997**, *30*(3), 623.
14. Marques, A. L. B.; Chierice, G. O. *J. Braz. Chem. Soc.* **1998**, *9*, 531.
15. Anezaki, K.; Chen, X.; Ogasawara, T.; Nukatsuka, I.; Ohzeki, K. *Anal. Sci.* **1998**, *14*, 523.
16. Marczenko, Z. *Separation and Spectrophotometric Determination of Elements*; Ellis Horwood Ltd.: Chichester, 1986; p 107.
17. Shijo, Y.; Yoshida, H.; Kitamura, T.; Yoshimoto, E.; Uehara, N. *Anal. Sci.* **1996**, *12*, 761.
18. Pavlovska, G.; Stafilov, T.; Cundeva, K. *Fresenius J. Anal. Chem.* **2001**, *369*(7/8), 670.
19. Zendelovska, D.; Cundeva, K.; Stafilov, T. *Mikrochim. Acta* **2000**, *135*(1/2), 55.
20. Pavlovska, G.; Stafilov, T.; Cundeva, K. *Fresenius J. Anal. Chem.* **1998**, *361*(2), 213.
21. Dapaah, A. R. K.; Takano, N.; Ayame, A. *Anal. Chim. Acta* **1998**, *386*(3), 281.
22. Pavlovska, G.; Cundeva, K.; Stafilov, T. *Separ. Sci. Technol.* **2000**, *35*(16), 2663.
23. Yamamoto, Y.; Sugita, M.; Ueda, K. *Bull. Chem. Soc. Jpn* **1982**, *55*(3), 742.
24. Ichinoki, S.; Yamazaki, M. *Anal. Chem.* **1985**, *57*(12), 2219.
25. Cundeva, K.; Stafilov, T.; Pavlovska, G. *Microchem. J.* **2000**, *65*(2), 165.
26. Cundeva, K.; Stafilov, T.; Pavlovska, G. *Spectrochim. Acta B* **2000**, *55*(7), 1079.
27. Zendelovska, D.; Pavlovska, G.; Stafilov, T. *Talanta* **2001**, *54*(1), 139.
28. *Instructions Manual;* Hitachi Z-8000 Model AAS, Tokyo, 1983.
29. Lajunen, L. H. J. *Spectrochemical Analysis by Atomic Absorption and Emission*; Royal Society of Chemistry: Cambridge, 1992; p 9.
30. Hiraide, M.; Uchitomi, K. *Anal. Sci.* **1999**, *15*, 1051.
31. Tokalıoğlu, Ṣ. *Ph.D. Thesis*; Erciyes University: Kayseri (Turkey), 1997.
32. Vandecasteele, C.; Block, C. B. *Modern Methods for Trace Element Determination*; John Wiley & Sons Ltd.: Chichester, 1997; p 68.