

Preconcentration and separation with Amberlite XAD-4 resin; determination of Cu, Fe, Pb, Ni, Cd and Bi at trace levels in waste water samples by flame atomic absorption spectrometry

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Abstract

A method for the preconcentration of Cu, Fe, Pb, Ni, Cd and Bi as their diethyldithiocarbamate chelates was proposed using a column filled with Amberlite XAD-4 resin. The retained analytes on the resin were recovered with a small volume of acetone. The metal ions in the effluent were determined by a flame atomic absorption spectrometer. Different factors including pH of sample solution, sample volume, amount of XAD-4 resin, amount of ligand, eluent volume and matrix effects for preconcentration were examined. The recoveries for the analytes under the optimum working conditions were higher than 95%. The relative standard deviations of the determinations were below 9%. The limits of detection (3 s, $n = 20$) for analytes were found to be between 4 and 23 $\mu\text{g l}^{-1}$. The proposed method was applied to the analysis of some waste waters from the organized industrial region of Kayseri. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Trace metal ions have important roles in our life functioning in a wide spectrum. Thus the determination of trace metal ions is becoming increasingly important because of the increased interest in environmental samples including water,

soil and plant, etc. Flame atomic absorption spectrometry is widely used because of its low cost, but its sensitivity is usually insufficient for the low concentrations in environmental samples. Also, the matrix interferences are another problem in the atomic absorption spectrometric determinations. To solve these problems, a preconcentration and matrix elimination step are required. The most widely used preconcentration methods are coprecipitation [1–3], ion exchange [4,5], solvent ex-

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traction [6,7] and solid phase extraction [8–10]. Solid phase extraction is an attractive technique based on use of a sorbent that retains the analytes. The analytes are eluted from the sorbent using a suitable solvent.

In solid phase extraction, various sorbents such as activated carbon, C-18, silicagel, microcrystalline naphthalene etc. [11–15] have been used. Amberlite XAD resins have been also used for the preconcentration of trace metal ions from various media such as natural water samples, urine, geological samples etc. [16–20]. Amberlite XAD-4 resin is a well-known member of Amberlite XAD resins and has found widespread application for the separation/enrichment of trace metals ions [21–23].

In the present work, a simple and sensitive separation/preconcentration method using an Amberlite XAD-4 resin column has been established prior to flame atomic absorption spectrometric (FAAS) determination of some trace metal ions in waste water samples from the industrial region of Kayseri.

2. Experimental

2.1. Reagents and solutions

Analytical reagent-grade chemicals were employed for the preparation of all solutions. All aqueous solutions were prepared from double-quartz-distilled water. Stock metal ion solutions, 1000 mg l⁻¹ (E. Merck, Darmstadt) were diluted daily for obtaining reference and working solutions. The calibration curve was established using the standard solutions prepared in 1 M HNO₃ by dilution from stock solutions. The calibration standards were not subjected to the preconcentration procedure.

A sodium diethyldithiocarbamate (Na-DDTC) solution, 1.0 × 10⁻² M, was prepared by dissolving the required amount of Na-DDTC in water immediately before use. Acetate buffer solutions were prepared by mixing of appropriate volumes of 1 M acetic acid (Merck, Darmstadt) and 1 M sodium acetate solutions (Merck,

Darmstadt) for pH 2–6. For pH 7, a 250 ml of borate buffer was prepared by use of 2.5 ml of 1 M HCl and 0.445 g NaBO₂ (Merck, Darmstadt). Ammonium chloride buffer solutions were prepared by mixing of appropriate amounts of 0.1 M ammonia (Merck, Darmstadt) and 0.1 M ammonium chloride solutions for pH 8–10. pH of the buffer and the buffered solutions were controlled with the pH meter. Amberlite XAD-4 Resin (Sigma Chem. Co., St. Louis, Catalog No. 20276, particle size 20–60 mesh) grounded to 0.1–0.2 mm was prepared with the washing steps reported previously [24].

The glass column, having a stopcock and a porous disk, was 10 cm long and 1.0 cm in diameter. A small amount of glass wool was placed on the disc to prevent loss of the resin beads during sample loading. Then, 500 mg of Amberlite XAD-4 resin was slurried in water, then poured into the column. The bed height of resin in the column was approx. 20 mm. It was washed successively with water, acetone, water, respectively. It was conditioned with 10–15 ml of pH 6 buffer. After each use, the resin in the column was washed with large volumes of water and stored in water for the next experiment.

2.2. Instrument

Metal determinations were performed using a Perkin–Elmer Model 3110 flame atomic absorption spectrometer. All measurements were carried out in air/acetylene flame. The operating parameters for elements were set as recommended by the manufacturer.

A pH meter with a glass and calomel electrode pair, Delta 320 Mettler, was employed for measuring pH values.

2.3. Preconcentration procedure

The performance of column method was tested with model solution prior to its application to waste water samples. For this, 50 ml of the model solution containing 5 µg each of Cu(II), Fe(III),

Ni(II) and Cd(II), and 10 μg each of Bi(III) and Pb(III) was buffered to desired pH. Three milliliters of 0.05% m/v Na-DDTC solution was added to form the metal-DDTC chelates. After 5–10 min, the solution was loaded to the column. The flow of sample solution through the column was gravitationally performed at range of 1.0–7.0 ml min^{-1} . The flow rate of solution was controlled by use a stopcock of column. After passage of the solution finished, the column was washed with an aqueous solution adjusted to the working pH. Then, the retained metals were recovered from the column by the aid of 10 ml of acetone at 1.0 ml min^{-1} of flow rate. The effluent was evaporated to near dryness. The residue was diluted to 5 or 10 ml with 1 M HNO_3 . The metal concentrations in the final solution were determined by a flame atomic absorption spectrometer (FAAS).

2.4. Determination of metal ions in waste waters

Waste water samples were collected from four different stations in the industrial region of Kayseri. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm . For the preconcentration procedure, pH of the sample, 500 ml, was adjusted to 6. Then, the ligand solution was added. After 10 min, the sample was passed through the column at a 5 ml min^{-1} flow rate. The metal chelates retained on XAD-4 were eluted with 10 ml of acetone. The effluent was evaporated to near dryness and made up to 5 or 10 ml with 1M HNO_3 . The determination of metal ions in the final solution was performed by FAAS.

3. Results and discussion

To obtain quantitative recoveries of Cu, Fe, Pb, Ni, Cd and Bi on Amberlite XAD-4 column, separation/preconcentration procedure was optimized for various parameters such as pH, sample volume and concentration of Na-DDTC. The percentage of metal retained was calculated from the amounts of metal in the starting sample and the amounts of metal eluted from the column.

3.1. Effect of pH

The effect of the pH on the retention of metal-DDTC complexes on the Amberlite XAD-4 resin column was studied by applying of the proposed procedure to the model solution prepared at different pH values (Fig. 1). The results indicate that Cu, Fe, Pb, Ni, Cd and Bi ions are recovered quantitatively, $\geq 95\%$, over range of pH 5–7. Therefore, the working pH was chosen as 6.0 for the following measurements.

3.2. Effect of Na-DDTC concentration

The concentration of Na-DDTC plays an important role to obtain the quantitative recoveries of metal ions, because in its absence the resin does not retain the metal ions. However, the excess amounts of Na-DDTC prevent the retentions of metal ions due to sorption competitions between metal-DDTC chelate and diethyldithiocarbamate (DDTC) on the resin. Therefore, the influences of Na-DDTC concentration on the recovery of the examined metal ions were investigated in the range of 1.0×10^{-5} – 1.0×10^{-2} M DDTC using the model solution given above. The recoveries of Cu, Fe, Pb, Ni, Cd and Bi increased with increasing concentrations of Na-DDTC added and reached a constant value over 95% with at least 5.0×10^{-4} M. After 5×10^{-3} M NaDDTC, the recovery values are lower than 95%, due to the reason of explained above. On this basis, studies

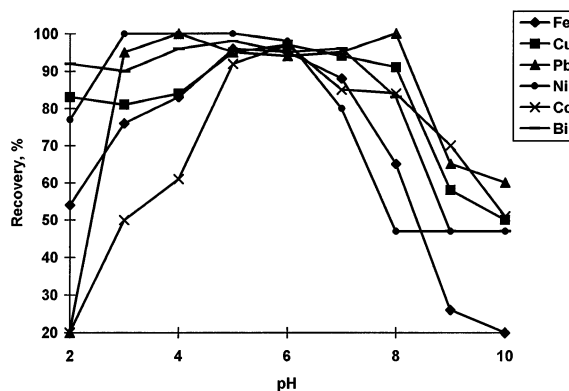


Fig. 1. Effect of pH on the recovery of Cu, Fe, Pb, Ni, Cd and Bi from the Amberlite XAD-4 column ($n = 3$, eluent: acetone).

Table 1

Effect of the sample volume on recoveries of the investigated metal ions ($n = 4$, eluent: acetone)

Sample volume (ml)	Recovery (%)					
	Cu	Fe	Pb	Ni	Cd	Bi
25	95	97	93	95	97	98
100	94	95	97	100	96	100
250	95	96	100	95	97	93
500	104	108	95	100	95	96
750	108	93	104	95	97	100

were carried out at a Na-DDTC concentration of 7.5×10^{-4} M.

3.3. Effect of resin amount and eluent volume

The resin amount and the eluent volume are other important parameters to obtain the quantitative recovery. The quantitative retention is not obtained by the smaller amount of resin than the optimum amount. On the other hand, the excess amount of resin also prevents the elution of the quantitative retained chelates by a small volume of eluent. For this reason, the resin amount and eluent volume were optimized. To test the resin amount for quantitative retention of analytes, different amounts of Amberlite XAD-4 from 200 to 800 mg, were filled into the column. The procedure was applied to the model solutions given above by use of these columns. The quantitative recoveries for all the examined analytes were obtained in range of 250–750 mg resin. In the light of these results, in the all experiments, 500 mg of XAD-4 grounded to 0.1–0.2 mm was used. On the other hand, the effect of resin particle size, over range of 0.08–0.5 mm, on the recovery was investigated using 500 mg resin amount. It was found that the resin particle size higher than 0.2 mm is insufficient to obtain the quantitative recovery values. The sample flow is prevented by the smaller particles than 0.1 mm.

It is known from the previous studies that acetone is the most suitable eluent for the elution of the analytes retained using organic ligands on XAD-4 resin [25–27]. In this work, acetone was chosen as an eluent. To recover the metal chelates retained on 500 mg resin in the column, the

minimum volume of acetone required was found to be 8.0 ml.

3.4. Effects of sample volume

Studies were performed also with solutions of large volume to explore the possibility of enriching solutions at low concentration with a high enrichment factor. The influences of the sample volume on the recoveries of the investigated metal ions were also examined. The results were given in Table 1. The recovery values were quantitative (>95%) until 750 ml of sample volume. The highest preconcentration factor was found to be 150, according to 5 ml of the final solution after the preconcentration and 750 ml of sample solution. The volume of the final solution can be reduced down to 1 or 2 ml; thus the higher preconcentration factor can be obtained.

3.5. Effects of matrix ions

Preconcentration procedures for trace metals can be strongly affected by the matrix constituents of the samples. For this reason, the reliability of the proposed method was examined in the presence of possible matrix ions of the waste water samples. Table 2 shows the effect of the matrix ions on the recoveries of the examined analytes from a model solution including the examined elements and the matrix ions. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the preconcentration and determination of analytes. It can be concluded from the results in Table 2 that alkaline and alkaline earth metal ions were almost not retained through the column due

to the low stability constant of their chelates. The small amounts retained of the matrix ions were removed by washing with 10–15 ml of the accompanying buffer solution. The large amounts of Cl^- and SO_4^{2-} have not affected the recoveries of the analyte ions. It was found that the waste waters analyzed in this work contain SO_4^{2-} in the range of 500–800 mg l^{-1} and Cl^- in the range of 150–1200 mg l^{-1} .

3.6. Analytical performance of the method

The analytical performance of the method can be shown for the results from FAAS measurements. The correctness of the procedure was confirmed by the recoveries of spiked analytes from the 50 ml of waste water sample. The results were as shown in Table 3. The recovery values given for the waste water in Table 3 and shown for the model solution prepared with doubly distilled water in Fig. 1 were higher than 95%, thus confirming the accuracy of the procedure.

The relative standard deviations ($n = 4$) with related to the determinations in the waste water samples were found to be lower than 9%. The detection limits (3 s, $n = 20$) for Cu, Fe, Pb, Ni, Cd and Bi were found to be 4, 15, 19, 23, 2 and 19 $\mu\text{g/l}$, respectively.

3.7. Cu, Fe, Pb, Ni, Cd and Bi levels of the waste water samples

Proposed method has been applied to the pre-concentration/separation of Cu, Fe, Pb, Ni, Cd and Bi ions in the waste water samples collected

Table 2

Effects of the matrix ions for the recoveries of the examined metal ions ($n = 4$)

Ion	Concentration in effluent (mg/l)	Tolerance limits (mg/l)
Na^+	8.0	50 000
K^+	2.1	2500
Mg^{2+}	5.1	5000
Ca^{2+}	8.7	2500
Cl^-	–	75 000
SO_4^{2-}	–	2500

Table 3

Analysis of the waste water samples, taken from various plants collection pool in the industrial region of Kayseri, spiked with Cu, Fe, Pb, Ni, Cd and Bi ($n = 4$, sample volume: 50 ml)

Element	μg added	μg found	Recovery (%)
Cu	0	24.5	–
	10	35.0	105
	20	44.9	102
	30	54.4	100
Fe	0	6.5	–
	10	16.6	101
	20	27.9	107
	30	36.2	99
Pb	0	–	–
	10	10.1	101
	20	19.4	98
	30	28.2	94
Ni	0	2.3	–
	10	11.8	95
	20	21.9	98
	30	31.1	96
Cd	0	–	–
	5	4.9	98
	10	9.6	96
	20	19.0	95
Bi	0	2.0	–
	10	12.1	101
	20	21.1	96
	30	32.1	100

from the various plants in the organized industrial region of Kayseri, Turkey. The levels of the investigated ions are given in Table 4. The results have been calculated on the assumption of 100% recovery of metal ions.

4. Conclusion

This work presents an alternative procedure to techniques as GFAAS and ICP-AES for the determinations of Cu, Fe, Pb, Ni, Cd and Bi at $\mu\text{g l}^{-1}$ levels in the waste waters. The procedure shows high tolerance to interferences from the matrix ions. The application of the proposed procedure can be extended to the determination of the investigated metal ions in the various samples having high salt contents as sea waters, urine and dialysis solutions.

Table 4

Concentration of Cu, Fe, Pb, Ni, Cd and Bi in the waste water samples taken from various plants in the organized industrial region of Kayseri ($n = 4$)

Analyte	Collection pool	Concentration ($\mu\text{g l}^{-1}$) ^a			
		Plant-1	Plant-2	Plant-3	Plant-4
Cu	490 ± 20	34 ± 3	173 ± 9	4.0 ± 0.1	n.d.
Fe	130 ± 6	86 ± 10	304 ± 8	43 ± 2	13 ± 1
Pb	n.d.	15 ± 1	103 ± 5	n.d.	100 ± 1
Ni	43 ± 3	51 ± 1	19 ± 1	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	n.d.	n.d.
Bi	42 ± 1	15 ± 2	60 ± 3	46 ± 2	43 ± 3

^a $\bar{x} \pm s$: mean ± standard deviation; n.d.: not detected.

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