

Solid-phase extraction of Fe(III), Pb(II) and Cr(III) in environmental samples on amberlite XAD-7 and their determinations by flame atomic absorption spectrometry

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Abstract

This paper describes a simple and accurate procedure for preconcentration of trace amounts of Fe(III), Pb(II) and Cr(III) ions. The preconcentration procedure is based on retention of *p*-xylenol blue chelates on Amberlite XAD-7. The analytes retained were eluted from Amberlite XAD-7 by using 1 mol L⁻¹ HCl. The influences of the analytical parameters including amounts of reagents, pH and type of eluent were also investigated. The detection limits of Fe, Pb and Cr were found to be 3.07, 18.6 and 3.27 μg L⁻¹, respectively. The accuracy of the procedure was checked by the analysis of an electrolytic copper wire sample. The relative error was less than 5%. The presented method was applied to the determination of Fe(III), Pb(II) and Cr(III) in water samples from Denizli, Turkey with good results such as recoveries more than 95%, relative standard deviations below 10%.

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1. Introduction

Heavy metals at trace levels have some roles in body functions. The effects of heavy metal ions on human life change from elements to elements [1,2]. For example, copper is necessary on the enzyme activation. Chromium (III) plays an important role in the working of insulin hormone. Because of these importances of trace heavy metals, the accurate determinations of them are an important subject of the analytical chemistry. Flame atomic absorption spectrometry (FAAS) is suitable instrumental technique as it rapid, simple and inexpensive. However, the concentrations of traces heavy metal ions in matrices as natural water, soil and environmental samples are below the detection limit of FAAS. In addition, high concentrations of matrix components may cause inaccuracies in a procedure which is based on external calibration with dilute aqueous standards. Therefore, a preconcentration–separation procedure is needed to improve the detection limits and selectivity of FAAS [3,4].

Solvent extraction [5,6], coprecipitation [7,8], cloud point extraction [9,10], ion exchange [11], membrane filtration [12,13] as preconcentration–separation techniques are widely used for the preconcentration of traces heavy metals from water sample. Among the preconcentration–separation techniques, solid-phase extraction (SPE) is one of the efficient preconcentration techniques for the trace heavy metal ions. It has a relatively high preconcentration factor and the ability of treating large volume samples free from contamination [14–16]. Various solid-phase materials including Ambersorb resins, Chromosorb resins, Diaion resins, naphthalene, silica gel, activated carbon, chelating resins and fibers [17–24] have been used up to now.

Amberlite XAD-resins have found widespread application for preconcentration of trace metal ions by aid of chelating and inorganic ligands [25,26]. The most successful and popular applications of SPE have been carried out using Amberlite XAD-7 resin having a hydrophilic surface and intermediate polarity, as a polyacrylic acid ester polymer [27–32]. In these studies, it has been used as solid-phase material impregnated, coated or immobilized with various chelating ligands. Also, there are many successful applications of SPE based on column technique that a column filled Amberlite XAD-7 resin is used for

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the retention of trace heavy metal-inorganic or chelating ligand complexes formed in sample solution [33–35].

In the present study, the column chromatographic separation and preconcentration of Fe(III), Pb(II) and Cr(III) as a *p*-xylenol blue complex was proposed. XAD-7 was used as retaining material in the column. The analytical parameter for the quantitative recoveries of analyte ions such as pH, amounts of reagents, sample volume, etc., were optimized.

2. Experimental

2.1. Apparatus

A Perkin-Elmer Model 700 atomic absorption spectrophotometer equipped with Perkin-Elmer single-element hollow cathode lamp and a 10 cm air-acetylene burner were used for the determination of iron, lead and chromium. All instrumental settings were those recommended in the manufacturer's manual book.

A pH meter (Hanna pH 211 Model with a glass-electrode) was employed for measuring the pH values in the aqueous phase.

2.2. Reagents and solutions

Deionized-triple distilled water and high purity reagents were used for all preparations of the standard and sample solution. The calibration standard solutions of Fe(III), Pb(II) and Cr(III), were prepared daily, through the appropriate dilutions of a 1000 mg L⁻¹ stock solution of the respective analyte (atomic absorption grade, Carlo Erba). The calibration standards were not submitted to the preconcentration procedure. The correlation coefficient of the calibration curves were generally 0.999. Stock solutions of diverse elements were prepared from the high purity compounds (Merck, Darmstadt, Germany).

A 1.2 × 10⁻³ mol L⁻¹ solution of *p*-xylenol blue (BDH Chemicals, No. 0583600) was prepared by dissolving the required amount of *p*-xylenol blue in a water/ethanol (75/25, v/v) mixture. The *p*-xylenol blue solution was prepared daily.

Amberlite XAD-7 was selected for preconcentration studies because it allows easy elution of the retained Fe(III), Pb(II) and Cr(III) on column. Amberlite XAD-7 resin (Sigma, St. Louis, MO) was purchased as 0.3–0.9 mm and dried for 3–4 h at 100 °C. To remove organic and inorganic contaminants, the resin was washed successively with methanol, water, 1 mol L⁻¹ HNO₃, water, 1 mol L⁻¹ NaOH and water, sequentially.

Phosphate buffer solution was prepared by mixing of appropriate volumes of 1 mol L⁻¹ phosphoric acid (Merck, Darmstadt, Germany) and 1 mol L⁻¹ sodium dihydrogen-phosphate solutions (Merck, Darmstadt, Germany) for pH 2. Acetate buffer solutions were prepared by mixing of appropriate volumes of 1 mol L⁻¹ acetic acid (Merck, Darmstadt, Germany) and 1 mol L⁻¹ sodium acetate solutions (Merck, Darmstadt, Germany) for pH 4 and 6. Ammonium chloride buffer solutions were prepared by mixing of appropriate amounts of 0.1 mol L⁻¹ ammonia (Merck, Darmstadt, Germany) and 0.1 mol L⁻¹ ammonium chloride (Merck, Darmstadt, Germany) solutions for pH 8–10.

2.3. Preparation of XAD-7 column

A short glass column with an inner diameter of 10 mm and a length of 100 mm, equipped with porous frits, was filled up to a height of about 25 mm with a suspension of 500 mg of Amberlite XAD-7 resin in water. The bed height in the column was approximately 2.0 cm prior to use; the resin was preconditioned with 10 mL of related buffer solution. After each experiment, the column was rinsed with a very large volume of the water and stored for the next use.

2.4. Preconcentration procedure

The proposed method was tested with model solutions before its application to the natural waters. Two millilitre of buffer solution (to result in the desired pH between 4 and 10) were added to 30–50 mL of solution containing 10–20 µg of the metal ions. The column was preconditioned with the related buffer solution. A 2 mL of 1.2 × 10⁻³ mol L⁻¹ *p*-xylenol blue was added. Metal chelates solution was passed through the column at a flow rate of 5 mL min⁻¹. The sample solution was permitted to flow through the column under gravity. The adsorbed *p*-xylenol blue chelates on the column were eluted by using 5 or 10 mL of 1 mol L⁻¹ HCl at a flow rate 5 mL min⁻¹. The eluent was analyzed for the determination of analytes by atomic absorption spectrometry.

2.5. Analysis of real samples

The procedure was applied directly to drinking water samples taken from a tap in our laboratory. For the analysis, 2 mL of 1.2 × 10⁻³ mol L⁻¹ *p*-xylenol blue solution was added to 300 mL of the sample buffered to pH 9. Subsequent treatments were the same those described in Section 2.4. The volume of the final solution for analysis was 5 mL.

Surface sea water sample was collected from Kusadasi Bay in the Aegean Sea in October 2004 were immediately filtered through a Sartorius cellulose nitrate membrane of pore size 0.45 µm. The samples were stored in 1 L polyethylene bottles and acidified to 1% with nitric acid and were subsequently stored at 4 °C in a refrigerator. For the separation/preconcentration, the pH of 300 mL of the sample was adjusted to 9. The concentration and determination steps were carried out as described above. The volume of the final solution was 5 mL.

The drinking water samples were also analyzed using a reference method based on membrane filter system. A 300 mL of the sample buffered to pH 9. The solution together with analyte ions was collected on a cellulose nitrate membrane filter, 0.45 µm pore size and 47 mm diameter. The collection of metal ions together with soluble cellulose membrane filter was dissolved in 0.5 mL of concentrated nitric acid, and the solution was diluted to 5 mL with water. The metal concentrations in the final solution were determined by flame AAS [36].

A 100 mg of copper wire (diameter 8 mm rod, produced by Erbakir-Denizli/Turkey) was accurately weighed into a 50 mL beaker and 0.5 mL of concentrated nitric acid was added to the sample. The beaker was covered with a watch-glass and the mixture was evaporated on a hot plate about 95 °C almost to

dryness. Then the solution was cooled and diluted to 10 mL with distilled water. Finally, the preconcentration procedure given above was applied to the final solutions. The same procedure was applied to the blank solution. The final solution was diluted to 2 mL.

3. Results and discussion

3.1. Effects of pH

One of the most important 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. The influences of pH on the retentions of analyte ions were examined using of appropriate buffer solutions. The results are given in Fig. 1. The quantitative recovery values were obtained for Fe(III) and Pb(II) as *p*-xylenol blue complex at the pH range of 8–10, almost 90% for Cr(III) at pH 9, respectively. pH 9.0 (almost 90% for Cr(III)) using ammonium/ammonia buffer having a good buffer capacity. The volume of the buffer solution had no effect on the retentions of analyte ions.

3.2. Effect of amount of *p*-xylenol blue

The influences of the amount of *p*-xylenol blue on the recoveries of analyte ions on XAD-7 resin were investigated. Quantitative recoveries of Fe(III), Pb(II) and Cr(III) in the model solutions containing 10–20 µg of analyte ions were obtained with the range of *p*-xylenol blue amounts of 0–5 mL of 1.2×10^{-3} mol L⁻¹ for iron, lead and chromium. The recoveries were not quantitative in the studies without *p*-xylenol blue. Due to insufficient ligand concentrations, the recoveries below 95% below 0.5 mL of *p*-xylenol blue. Above 5 mL of *p*-xylenol blue, the recovery values were not quantitative because of the competition between analyte *p*-xylenol blue chelate and *p*-xylenol blue for adsorption on Amberlite XAD-7. Therefore, 2 mL of 1.2×10^{-3} mol L⁻¹ of *p*-xylenol blue solution was used in all further works.

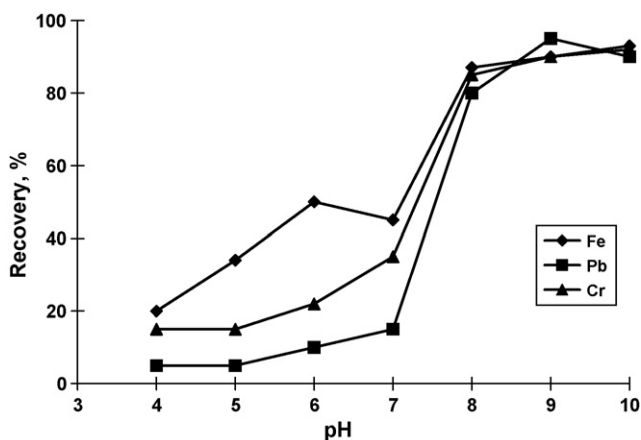


Fig. 1. Effects of pH on the recoveries of metal ions on Amberlite XAD-7 ($N=4$, eluent: 1 mol L⁻¹ HCl, amount of resin: 500 mg).

Table 1

The effect of various eluent solutions on the recoveries of analytes from Amberlite XAD-7 ($N=4$)

Eluent	Recovery (%)		
	Fe	Cr	Pb
0.5 mol L ⁻¹ HCl	84 ± 3	89 ± 2	78 ± 1
1 mol L ⁻¹ HCl	98 ± 2	89 ± 3	100 ± 3
2 mol L ⁻¹ HCl	94 ± 2	90 ± 2	92 ± 3
1 mol L ⁻¹ HNO ₃	98 ± 2	82 ± 2	89 ± 3
2 mol L ⁻¹ HNO ₃	93 ± 3	88 ± 2	87 ± 3
Ethanol	<5	<5	<5
1 mol L ⁻¹ NH ₃	<5	<5	<5
1 mol L ⁻¹ H ₃ PO ₄	78 ± 3	84 ± 2	98 ± 2
1 mol L ⁻¹ EDTA	56 ± 2	34 ± 3	95 ± 4

3.3. Eluent of type and volume of elution solution

The effects of 10 mL of various eluents on the recoveries of Fe(III), Pb(II) and Cr(III) retained on Amberlite XAD-7 column were investigated. The results are summarized in Table 1. Fe(III), Pb(II) and Cr(III) retained on Amberlite XAD-7 column after chelating *p*-xylenol blue could be completely eluted with 1 mol L⁻¹ HCl. Also, Fe(III) can be eluted using 2 mol L⁻¹ HCl, 1 mol L⁻¹ HNO₃ or 2 mol L⁻¹ HNO₃. However, in order to elute the three analytes from the column at the same time, 1 mol L⁻¹ HCl solution was selected as an eluent.

The effects of volume of 1 mol L⁻¹ HCl as eluent were also investigated with the range of 2–10 mL. Quantitative recovery values for analytes were obtained with 5 mL of 1 mol L⁻¹ HCl.

3.4. Effect of the sample and eluent flow rates

The effect of flow rates of sample and eluting solutions from the column on the retention and recovery of Fe(III), Pb(II) and Cr(III) ions was studied. It was found that the quantitative retention of Fe(III), Pb(II) and Cr(III) by the column is not very affected by the sample solution flow rate, in the range of 2–15 mL min⁻¹.

The influences of eluent flow rates on the recovery of analyte ions were examined in the flow rates range of 1–5 mL min⁻¹. The quantitative desorption values for analytes were obtained at 5 mL min⁻¹. For all further experiments for flow rates of sample 5 mL min⁻¹ and for flow rates of sample eluent solution is 2 mL min⁻¹ was selected as flow rate.

3.5. Effect of sample volume

In order to explore the possibility of enriching low concentrations of from the large sample volume, the influences sample volume on the recovery of Fe(III), Pb(II) and Cr(III) were also investigated. The effect of sample volume on the retention of metal ions was also investigated by passing 30–750 mL volumes through the Amberlite XAD-7 column. The results are depicted in Fig. 2. The adsorption of Fe(III), Pb(II) and Cr(III) with 0.5 g resin was not affected by sample volume till 300 mL. The high-

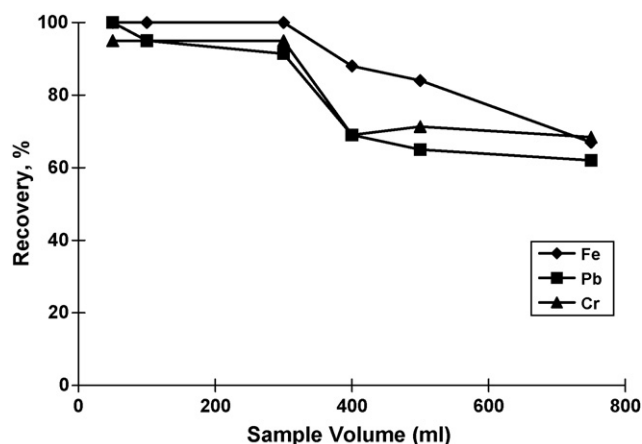


Fig. 2. Effects of sample volume on the recoveries of analytes ($N=3$, pH 9, eluent: 1 mol L^{-1} HCl, amount of resin: 500 mg).

est preconcentration factor was 60 for analyte ions when final volume was 5 mL.

3.6. Effect of matrix ions

The one of the main problem in the atomic absorption spectrometric determination of the heavy metal ions is interference from matrix components. In order to study the effect of poten-

Table 2

Tolerable limits of some ions on the recoveries of analytes ($N=4$)

Ion	Added as	Tolerable concentration (mg L^{-1})
Na^+	NaCl	30.000
K^+	KCl	500
Ca^{2+}	CaCl_2	300
Mg^{2+}	MgCl_2	600
Cl^-	NaCl	30.000
SO_4^{2-}	Na_2SO_4	5.000
HCO_3^-	NaHCO ₃	500
CO_3^{2-}	Na_2CO_3	500

tial interfering foreign ions on the preconcentration of Fe(III), Pb(II) and Cr(III) with the proposed procedure, fixed amounts of the analytes, $10 \mu\text{g}$ of Fe, $20 \mu\text{g}$ of Pb and Cr per 30 mL, were taken with increasing amounts of matrix ions and the procedure was followed. The results are given in Table 2. Commonly, encountered matrix components, such as alkali and alkaline earth elements do not form stable complexes and are not retained on the column under the working conditions used for the system. The tolerance limit defined as the ion concentration causing relative error $\leq \pm 5\%$ was found. The tolerable levels indicate that the procedure are suitable for the separation and preconcentration of the analyte ions in drinking water and sea water samples examined present study.

Table 3

Recovery of analyte spikes from drinking water and sea water ($N=3$, sample volume: 30 mL)

Analytes	Drinking water			Sea water		
	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$); $x \pm \text{S.D.}^a$	Recovery (%)	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$); $x \pm \text{S.D.}^a$	Recovery (%)
Fe	0.0	BDL	–	0.0	11.8 ± 0.7	–
	5.0	5.6 ± 0.2	112 ± 3	5.0	16.9 ± 0.3	102 ± 5
	10.0	10.0 ± 0.5	100 ± 5	10.0	21.9 ± 0.3	102 ± 3
	15.0	15.1 ± 0.8	101 ± 5	15.0	27.1 ± 0.3	102 ± 2
Pb	0.0	BDL	–	0.0	34.6 ± 3.0	–
	10.0	10.3 ± 0.4	103 ± 5	10.0	43.9 ± 0.6	93 ± 6
	20.0	18.7 ± 0.3	97 ± 4	20.0	53.2 ± 0.5	93 ± 3
	30.0	29.5 ± 0.8	98 ± 3	30.0	62.4 ± 0.3	93 ± 1
Cr	0.0	BDL	–	0.0	2.8 ± 0.7	–
	10.0	9.1 ± 1.0	91 ± 6	1.0	3.7 ± 0.01	90 ± 1
	20.0	18.3 ± 1.0	92 ± 2	2.0	4.6 ± 0.1	87 ± 5
	30.0	27.1 ± 0.6	90 ± 2	4.0	6.4 ± 0.1	88 ± 3

BDL: Below the detection limit.

^a S.D.: standard deviation.

Table 4

Determination of Fe, Pb and Cr in drinking and sea water samples (sample volume: 300 mL, final volume: 5 mL)

Analytes	Concentration of metals, $x \pm ts/\sqrt{N}$ ($\mu\text{g L}^{-1}$)				
	Tap water from laboratory		Tap water from stuff accommodation		Sea water
	Present method	Reference method [36]	Present method	Reference method [36]	
Fe	10.49 ± 0.66 (10)	N.D.	11.29 ± 0.75 (6)	N.D.	11.81 ± 0.32 (6)
Cr	3.17 ± 0.35 (10)	2.89 ± 0.29 (8)	2.22 ± 0.59 (10)	2.71 ± 0.52 (8)	2.84 ± 0.30 (3)
Pb	3.21 ± 0.07 (9)	3.56 ± 1.00 (10)	2.65 ± 0.51 (9)	3.23 ± 0.65 (10)	34.62 ± 3.01 (6)

The values in parenthesis are number of replicate analysis. BDL: Below the detection limit. N.D.: Not determined.

3.7. Analytical performance

In order to estimate the accuracy of the procedure, increasing quantities of analyte ions were spiked to a drinking water and sea water samples. The resulting solutions were submitted to the preconcentration procedure. The results are given in Table 3. A good agreement was obtained between the added and measured analyte amounts. The recovery values calculated for the added standards were always higher than 93% (almost 90% for Cr). It shows that the present method can be applied for the separation/preconcentration of Fe, Pb and Cr in the real samples which have high salt content. The relative standard deviation (R.S.D.) values for the determination of analytes in the spiked sample were in range of 1.1–6.6%.

The detection limits were calculated after presented preconcentration procedure applied to the blank solutions. The detection limits of the analytes based on three times the standard deviations of the blank ($k = 3, N = 20$) on a sample volume 30 mL for Fe(III), Pb(II) and Cr(III) were 3.07, 18.6 and 3.27 $\mu\text{g L}^{-1}$, respectively [37]. The detection limits could be decreased by increasing the sample volume.

3.8. Analysis of the real samples by the presented method

The method was applied to drinking water and sea water samples taken from a tap in our laboratory and stuff accommodation for the preconcentration and separation of analyte ions. The results are given in Table 4. The accuracy of the method was also checked by analysis of drinking water samples by the reference method based on membrane filtration [36] (Table 4). There is no significant difference at the 95% confidence level between the results obtained with two methods.

The method was applied to an electrolytic copper wire for the determination of iron, lead and chromium. The results in Table 5 are based on the average of five replicates. The results are in good agreement with the certified values. It can be concluded that the proposed method is free from interferences of the various constituents. A comparison using *t*-test demonstrates that there is not significant difference among the achieved results using the proposed method and the certified values.

3.9. Comparison with other solid-phase extraction methods

The comparative data from some recent papers on solid-phase extraction of traces metal ions on the various adsorbent for the figure of the merits are summarized in Table 6. The method

Table 5
Determination of Fe, Pb and Cr in an electrolytic copper wire sample

Element	Concentration (mg kg^{-1})		%R.S.D.
	Certified value	Observed value	
Fe	4.43 ± 0.59	4.18 ± 0.13 (7)	11
Pb	<0.1	0.074 ± 0.004 (6)	5.4
Cr	–	BDL	–

Mean expressed as 95% tolerance limit. The values in parenthesis are number of replicate analysis. BDL: Below the detection limit.

Table 6
Comparative data from some recent papers on solid-phase extraction

Analytes	Complexing media	Adsorbent	Eluent	PF	Detection limit ($\mu\text{g L}^{-1}$)	Relative standard deviation (%)	Reference
Cr, Mn, Fe, Co, Cu, Cd, Pb Pb, Ni, Cu, Mn	Alpha-benzoin oxime	Diaion SP-850	1 mol L ⁻¹ HNO ₃	50	0.28–0.73	<8	[38]
	Sodium bisphiperidine-1-yl-carbotetrathioate	Amberlite XAD-7	1 mol L ⁻¹ HNO ₃	50	2.8–3.2	<10	[39]
Cu, Fe, Pb	Methylthymol blue	Naphthalene methyltriocetyl ammonium chloride	3 mol L ⁻¹ HNO ₃	100	0.5–4.5	0.62–3.4	[40]
	2-Propylpiperidine-1-carbodithioate	Syringe filled with sorbent	3 mol L ⁻¹ HCl	100	0.2–0.34	0.11	[41]
Mn Fe, Cr, Pb	1-(2-Pyridylazo)-2-naphthol	Microcrystalline naphthalene	Dimethylformamide	20	5.0	3.8	[42]
	<i>p</i> -Xylenol blue	Amberlite XAD-7	1 mol L ⁻¹ HCl	60	3.07–18.6	<10	Present work

PF: Preconcentration factor.

presented in this study is most promising for the analyte ions as the preconcentration factor is 60. The preconcentration factor achieved with presented procedure is superior to some solid-phase extraction methods given in literature [38–45]. The elution was easily performed with 1 mol L⁻¹ HCl.

4. Conclusion

The presented method is characterized by quantitative recovery, satisfactory accuracy and precision for the determination of trace metals with multi-element preconcentration. 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 as geological and biological samples and similar media. Future works will be focused for testing *p*-xylenol blue as chelating agent and its performance with other adsorbent for on-line preconcentration of other metals in various samples.

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