

Preconcentration of Iron(III), Lead(II), Cobalt(II) and Chromium(III) on Amberlite XAD-1180 Resin Loaded with 4-(2-Pyridylazo)-resorcinol (PAR) and Their Determination by FAAS

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Received May 15, 2006

In this study, a solid phase extraction method has been developed for the preconcentration and separation of the elements Cr(III), Fe(III), Co(II) and Pb(II) at trace levels by using a column packed with Amberlite XAD-1180 resin loaded with 4-(2-pyridylazo)-resorcinol (PAR) reagent. After preconcentrating, the metals retained on the column were eluted with 20 mL of 3 mol/L HNO₃ and then determined by flame atomic absorption spectrometry (FAAS). The factors affecting the recovery of the elements, such as pH, type and concentration of eluent, volume of sample and elution solution, and matrix components, were also ascertained. The recoveries of Cr(III), Fe(III), Co(II) and Pb(II) were found to be 99 ± 4, 97 ± 3, 95 ± 3 and 98 ± 4%, respectively, under the optimum conditions at 95% confidence level and the relative standard deviations found by analyzing of nine replicates were ≤ 4.4%. The preconcentration factors for Cr(III), Fe(III), Co(II) and Pb(II) were found as 75, 125, 50 and 75 respectively. The detection limits (DL, 3s/b) were 3.0 µg/L for Cr(III), 1.25 µg/L for Fe(III), 3.3 µg/L for Co(II), and 7.2 µg/L for Pb(II). The recoveries achieved by adding of metals at known concentrations to samples and the analysis results of Buffalo river sediment (RM 8704) show that the described method has a good accuracy. The proposed method was applied to tap water, stream water, salt and street dust samples.

Key Words : Amberlite XAD 1180, PAR, Solid phase extraction, Flame atomic absorption spectrometry

Introduction

Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the preconcentration of trace elements before their analysis due to their frequent low concentrations in numerous samples. Additionally, since high levels of non-toxic components usually accompany analytes, a clean-up step is often required.¹ In recent years, solid phase extraction (SPE) has been successfully used for the separation and sensitive determination of metal ions. The use of SPE enables the simultaneous preconcentration of trace elements and removal of interferences, and reduces the usage of organic solvents that are often toxic and may cause contamination. SPE furnishes high preconcentration factors for trace elements. It can be interfaced on-line with analytical techniques, such as liquid chromatography (LC) or atomic absorption spectrometry (AAS).¹⁻³

Various solid phase extractors containing Amberlite XAD resins,^{4,5} activated carbon,⁶ cellulose,⁷ microcrystalline benzophenone,⁸ and silica gel⁹ have been used to preconcentrate trace metal ions. Amberlite XAD resins are good supports for developing chelating matrices. The retention of trace elements on such sorbents either requires the addition of a ligand to the sample or ligands may be attached to the sorbent by physical adsorption (impregnation) or chemical bounding (immobilization). A number of reagents have been investigated for impregnation of the sorbents as a means of increasing retention capacity and selectivity of the sorbent for trace elements, namely Amberlite XAD-2 loaded with

pyrocatechol,¹⁰ calmagite,² 1-(2-pyridylazo)-2-naphthol,¹¹ and 2-(methylthio) aniline;¹² Amberlite XAD-4 loaded with dithiocarbamates;¹³ Amberlite XAD-16 loaded with *N,N*-dibutyl-*N*-benzoylthiourea;¹⁴ polyurethane foam loaded with sodium diethyldithiocarbamate;¹⁵ activated carbon loaded with pyrogallol red;¹⁶ and silica gel loaded with 1-(2-thiasolylazo)-2-naphthol.¹⁷

Amberlite XAD-1180 resin (Rohm and Haas Co., Philadelphia, USA) is a crosslinked polystyrene-divinylbenzene copolymer having a surface area of 650 m² g⁻¹. It has physical, chemical and thermal stability. This adsorbent has been used for the preconcentration and separation of trace metals in various samples in our previous works.^{18,19} 4-(2-Pyridylazo)-resorcinol (PAR), is a versatile organic chromogenic reagent and it forms complexes with a variety of transition metals at different pH ranges. Most metal-PAR chelates are red or red-violet in color.²⁰ Up to now, any information in literature could not be found on the usage of Amberlite XAD-1180 impregnated with PAR for preconcentrating of trace metal ions.

In this paper, a new separation/preconcentration method was described for the determination of Cr(III), Fe(III), Co(II) and Pb(II) in water, salt, street dust and certified sediment samples (RM 8704 Buffalo river sediment) by FAAS using Amberlite XAD-1180 resin loaded with PAR.

Experimental Section

Apparatus. A Perkin Elmer 3110 model flame atomic absorption spectrometer equipped with an air-acetylene

burner was used for the determination of Cr(III), Fe(III), Co(II) and Pb(II) elements. The most sensitive wavelengths proposed by manufacturer for the determination of analytes were as follows: 357.9 nm for Cr, 248.3 nm for Fe, 240.7 nm for Co and, 283.3 nm for Pb. The slit width was 0.2 nm for Fe, 0.7 nm for Cr, Co and Pb. All the pH measurements were made by using a Jenco 672 digital pH meter.

Chemicals. All reagents were of analytical reagent grade. Double distilled water was used for the preparation of solutions. The stock solutions (1000 µg/mL) of elements were prepared from their nitrate salts in 1% HNO₃ and diluted daily prior to use. The 0.2% (w/v) of PAR solution was prepared by dissolving 0.2 g of the reagent in 100 mL of ethyl alcohol. The buffer solutions having pH values between 8 and 10 were prepared by using NH₃/NH₄Cl reagent.

Preparation of Amberlite XAD-1180 resin loaded with PAR. Amberlite XAD-1180 resin was treated with nitric acid (1 mol/L) and sodium hydroxide (1 mol/L) solutions, respectively, and then washed with distilled water until pH of supernatant was neutral. Afterwards it was dried in an oven at 110 °C. 1.0 g of the resin was saturated overnight with 25 mL of 0.2% (w/v) PAR solution by stirring in a beaker. The XAD-1180/PAR resin obtained was filtered and washed with water, and then dried at 110 °C. 0.5 g of the resin was packed into a glass column (10 mm i.d. and 100 mm in length). After each use, the resin was rinsed with some distilled water.

Preconcentration procedure performed using XAD-1180/PAR resin. The column method was tested with model solutions prior to its application to natural samples. The pH of model solutions (50 mL) including 20 µg of Fe(III) and Co(II), 40 µg of Pb(II) and Cr(III) was adjusted to 9.5 using ammonia/ammonium chloride buffer solution and then the solutions were passed through the column filled with XAD-1180/PAR resin at a flow rate of 2 mL/min. The metals retained as metal-PAR complexes on the resin were eluted with 20 mL of 3 mol/L HNO₃ solution. The eluate was evaporated near to dryness and then completed to 10 mL with 1 mol/L HNO₃. Cr(III), Fe(III), Co(II) and Pb(II) metal ions were determined by FAAS.

The analysis of standard reference material and street dust. A 50 mg of the reference material (RM 8704 Buffalo river sediment, dried at 110 °C for 2 h) sample was dissolved in a beaker by adding 10 mL of aqua regia. The mixture was heated on a hot plate until to almost dryness. Then, 10 mL of aqua regia was added again to the residue and the mixture was evaporated to dryness. The insoluble part was filtered through a filter paper with blue band by using some hot 1 mol/L HNO₃, 4 mL of 1 mol/L NaF was added to the filtrate in order to prevent the precipitation of Fe(III) found in the sample in excess amounts in hydroxy forms. So, Fe(III) ions have been masked by F⁻ in the solution as FeF₆³⁻ anionic complex. The pH of this solution was adjusted to pH 9.5 by adding NH₃/NH₄Cl buffer. The total volume was made up to 50 mL with water. The column procedure described above was applied to separate and preconcentrate the metal ions from the sample solution. After the elution, the eluate was

evaporated near to dryness and completed to 5 mL with 1 mol/L HNO₃. The determination of Pb, Cr and Co metals in the final solution was performed by using FAAS.

The dissolving procedure described for the analysis of certified reference matter was also applied for street dust sample.

Analysis of the water samples. Tap water samples were taken from Erciyes University, Kayseri and analysed without pre-treatment. The stream water samples were collected in pre-washed polyethylene bottles. These samples were filtered through a Millipore cellulose membrane filter with 0.45 µm of pore size and then acidified with 5 mL of concentrated nitric acid per liter of the samples. The samples were analysed by the separation/preconcentration procedure the mentioned above. For the analysis, the aliquots of 100-150 mL of the tap water and the stream water samples were used.

The analysis of salt sample. For analyzing salt sample, a 5.00 g NH₄Cl salt of analytical grade was dissolved in distilled water and diluted to 50 mL with water. The pH of the solutions was adjusted to 9.5 using ammonia/ammonium chloride buffer solution and then the recommended separation and preconcentration procedure was applied to the solutions for determining of Cr, Fe, Co and Pb elements.

Results and Discussion

To determine the optimum conditions for quantitative recovery of iron, lead, cobalt and chromium by using Amberlite XAD-1180 resin loaded with PAR, various analytical parameters such as pH, type of eluent, concentration and volume of eluent, and volume of sample solution were investigated.

Effect of pH. The effect of pH on the sorption of metals on Amberlite XAD-1180 resin loaded with PAR was examined in the pH range of 8-10. The solutions prepared were passed through the column at a flow rate of about 2 mL/min. The metal ions retained were eluted by 20 mL of 2 mol/L HNO₃ and then determined by FAAS. The results are demonstrated in Figure 1. At the pH 9.5, the recoveries obtained for Cr(III), Fe(III), Pb(II), and Co(II) were 97, 94, 91, and 92%, respectively. Therefore, the optimum pH of the sample solution was selected as pH 9.5. Recovery of Pb(II) and Co(II) are not quantitative due to the use of the non-

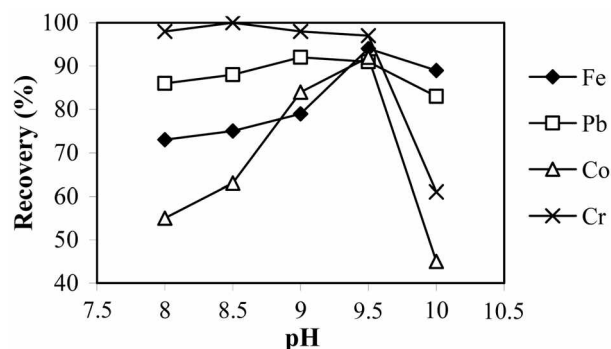


Figure 1. The effect of pH on the recovery of elements.

suitable concentration of eluent. In subsequent experiments, the effect of eluent was studied.

Effect of type, concentration and volume of eluent. In order to desorb the metals retained on the XAD-1180/PAR resin, HNO₃ and HCl acids were used as eluting reagents at different concentrations. As can be seen from Table 1, the quantitative recoveries for Cr(III), Fe(III), Co(II) and Pb(II) ions were obtained with 3 mol/L HNO₃. The effect of volume of 3 mol/L HNO₃ was also investigated. For the eluting volumes of 20 and 30 mL, the recoveries of the elements were found to be quantitative. So, 20 mL of 3 mol/L HNO₃ was used to elute the retained metal ions in the following experiments.

Effect of sample volume. One of the most important parameters for obtaining high preconcentration factors is the sample volume. The effect of sample volume on the recovery of Cr(III), Fe(III), Co(II) and Pb(II) was investigated in the range of 50-250 mL volume of the model solutions containing 20 µg of Fe(III) and Co(II), and 40 µg of Cr(III) and Pb(II) ions, at pH 9.5. The results in Table 2 show that Fe(III) for all the volumes studied, Pb(II) and Cr(III) up to volume of 200 mL, and Co(II) up to volume of 100 mL were recovered quantitatively. When the volume of final solution was 2 mL, the preconcentration factors for Cr(III), Fe(III), Co(II) and Pb(II) were found to be 75, 125, 50 and 75, respectively.

Effect of interfering ions. The effect of some major components present in natural samples such as Na(I), K(I), Ca(II), Mg(II), Cl⁻, and SO₄²⁻ ions on the recoveries of analyte ions was investigated by the proposed method. The interfering elements were added to the model sample

Table 1. The effect of type, concentration and volume of eluents on the recovery of metals (sample volume 50 mL, n = 3)

Type and concentration of the eluent	Volume of eluent (mL)	Recovery (%)			
		Cr	Fe	Co	Pb
1 mol/L HNO ₃	20	77	77	68	84
2 mol/L HNO ₃	20	97	94	92	91
3 mol/L HNO ₃	10	92	97	91	100
	20	98	97	98	101
3 mol/L HNO ₃	30	95	102	97	105
	20	94	108	85	97
1 mol/L HCl	20	79	90	82	93
2 mol/L HCl	20	74	82	77	87

Table 2. Effect of sample volume on the retention of metal ions (n = 3)

Volume of sample (mL)	Recovery (%)			
	Cr	Fe	Co	Pb
50	100	100	98	97
100	94	100	94	95
150	96	98	88	100
200	89	98	83	89
250	88	97	75	76

solutions as their nitrate or chloride salts. 50 mL of model solutions containing 20 µg Fe(III), 40 µg Pb(II), 20 µg Co(II), and 40 µg Cr(III) and the matrix ions were prepared and the proposed procedure was applied. Table 3 shows the effect of the interfering ions on the recoveries of the analytes. In the medium containing 1000 mg/L of alkaline and alkaline earth metals, while the signals of iron and lead ions are not affected from matrix components, the recoveries values for cobalt and chromium are not quantitative.

Repeatability of the method. The repeatability of the method was examined under the optimum experimental conditions described above by using the model solutions. For this purpose, the analyses were performed by applying the proposed method in nine replicates. The metal contents in eluate solution were determined by FAAS. The mean recovery for the metals and the relative standard deviations (RSD) were illustrated in Table 4. The RSDs were ≤ 4.4% for all the elements.

Limits of detection. Aliquots of 50 mL of the blank solutions were passed through the column filled with XAD-1180/PAR. The determination of metals was performed with FAAS. When it was taken into consideration the preconcentration factors for the elements, the detection limits (3s/b, n = 10) for Fe(III), Pb(II), Co(II) and Cr(III) were found to be 1.25, 7.2, 3.3, and 3.0 µg/L, respectively.

Reusability of the XAD-1180/PAR resin. The stability

Table 3. Effect of matrix ions on the recovery of iron, lead, cobalt and chromium (n = 3)

Ion	Concentration µg/mL	Recovery (%)			
		Fe	Pb	Co	Cr
Na ⁺	500	95	98	90	93
	2500	97	101	93	94
K ⁺	500	84	98	90	94
	1000	79	90	81	85
Ca ²⁺	2500	79	83	78	66
	500	91	103	92	86
Mg ²⁺	1000	92	96	94	83
	2500	88	91	85	86
SO ₄ ²⁻	500	90	91	60	87
	1000	87	80	67	83
Pb ²⁺	2500	84	71	57	85
	500	95	96	95	94
Mn ²⁺	10	92	-	44	99
Co ²⁺	50	102	97	47	82
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	10	96	77	-	89
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	1000	98	98	70	86

Table 4. Repeatability of the method (n = 9)

Element	$R \pm ts\sqrt{n}$ (%) ^a	RSD (%)
Fe	97.2 ± 3.3	4.1
Pb	98.4 ± 3.6	4.3
Co	94.8 ± 2.6	3.5
Cr	99.2 ± 3.5	4.4

^aAt 95% confidence level.

Table 5. The analysis results of the certified reference material (RM 8704 Buffalo river sediment)

Element	Concentration, $\mu\text{g/g}$ ($\bar{x} \pm ts/\sqrt{n}$)		
	Certified ^a	Found ^b	Relative error (%)
Pb	150 \pm 17	162 \pm 1	+8.0
Cr	121.9 \pm 3.8	115.8 \pm 0.6	-5.0
Co	13.57 \pm 0.43	12.60 \pm 0.09	-7.0

^aThe major components of the RM 8704 Buffalo river sediment Al (6.10%), Ca(2.64%), C (3.35%), Fe(3.97%), Mg(1.20%), K(2.00%), and Na (0.55%). ^bMean of five determinations at 95% confidence limit.

Table 6. The recoveries of the analytes in the spiked stream water, tap water and salt samples (n = 3, for each concentration spiked, sample volume 100 mL, final solution volume 5 mL, the salt amount 5.00 g)

Element	Added for final solution, $\mu\text{g/mL}$	Stream water	Tap water	Salt (NH ₄ Cl)
		Recovery of added amounts (%) \pm SD		
Cr	2	97.6 \pm 4.1	99.7 \pm 7.0	
	4	94.5 \pm 6.3		
	8			98.4 \pm 5.5
Fe	1		95.6 \pm 5.5	
	3			98.3 \pm 4.2
Co	1	93.0 \pm 6.1	94.1 \pm 1.0	
	2	94.5 \pm 4.7		
	3			94.0 \pm 3.9
Pb	2	104 \pm 7	101 \pm 6	
	4	100 \pm 2		
	8			101.3 \pm 3.3

and recyclability of the XAD-1180/PAR resin were assessed by using the changes in the recoveries of iron, lead, chromium and cobalt after 15 adsorption-elution cycles. It was found that the change in the recoveries for all the elements were \leq 2.5%. After 15 cycles, the mean recoveries (R% \pm SD) were found to be 96.2 \pm 2.5 for Cr, 97.8 \pm 2.3 for Fe, 94.1 \pm 2.4 for Co, and 97.6 \pm 1.9 for Pb.

Accuracy of the method. In order to evaluate the accuracy of the proposed preconcentration method, the analytes were determined in certified standard reference material (RM 8704 Buffalo river sediment), spiked water and salt samples. The results obtained from analysis of the certified reference material, the water and salt samples are depicted in Table 5 and 6, respectively. As can be seen from the tables, the achieved relative error values (%) were lower than 8% and recoveries (%) varied from 93 to 108, in which the method described has a good accuracy. The results obtained from the proposed method were in a good agreement with the certified values for Pb, Co and Cr.

Application of the method. The preconcentration method described was applied to 100-150 mL of stream water and tap water samples, and also NH₄Cl salt and street dust samples. As can be seen from Table 7, Cr(III), Co(II) and Pb(II) concentrations in the water and salt samples were below the detection limit of the method.

Table 7. The results of analysis of water, NH₄Cl and street dust samples (n = 5)

	Concentration, $\bar{x} \pm ts/\sqrt{n}$				
	Stream water ^a (1)	Stream water ^a (2)	Tap water ^a	Salt (NH ₄ Cl) ^b	Street dust ^b
Cr	< DL ^c	< DL	< DL	< DL	60.3 \pm 3.1
Fe	216 \pm 8	26.5 \pm 3.1	10.1 \pm 2.4	0.42 \pm 0.20	— ^d
Co	< DL	< DL	< DL	< DL	22.8 \pm 4.0
Pb	< DL	< DL	< DL	< DL	111 \pm 9

^a $\mu\text{g/L}$ at the 95% confidence level. ^b $\mu\text{g/g}$ at the 95% confidence level. ^cDetection limit. ^dNot determined.

Conclusion

The preconcentration method described by using Amberlite XAD-1180/PAR resin for the determination of Cr, Fe, Co and Pb elements in water samples has a good accuracy, repeatability, and sensitivity. The preparation of sorbent is easy and the preconcentration factors obtained are sufficiently large. Amberlite XAD-1180 resin loaded PAR seems to be stable up to at least 15 runs. The RSD of the method was \leq 4.4%. The results obtained from the proposed method were in a good agreement with the certified values for Pb, Co and Cr with a relative error lower than 8%.

Acknowledgement. The authors wish to thank Ms D. Etyemez for her helps.

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