

Diaion SP-850 resin as a new solid phase extractor for preconcentration-separation of trace metal ions in environmental samples

Mustafa Soylak^{a,*}, Mustafa Tuzen^b

^a Erciyes University, Faculty of Art and Science, Department of Chemistry, 38039 Kayseri, Turkey

^b Gaziosmanpasa University, Faculty of Science and Arts, Chemistry Department, 60250 Tokat, Turkey

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Abstract

A solid phase extraction method was developed for the preconcentration and separation of trace amounts of chromium, manganese, iron, cobalt, copper, cadmium and lead from environmental samples by complexation with alpha-benzoin oxime followed by adsorption onto Diaion SP-850-solid phase extraction column. One molar per liter HNO₃ was used as eluent. The recoveries of analytes at pH 8.0 with 700 mg of resin were greater than 95% without interference from alkaline, earth alkaline and some metal ions. The detection limits by three sigma for analyte ions were 0.65 µg l⁻¹ for Cr(III), 0.42 µg l⁻¹ for Mn(II), 0.28 µg l⁻¹ for Fe(III), 0.73 µg l⁻¹ for Co(II), 0.30 µg l⁻¹ for Cu(II), 0.47 µg l⁻¹ for Cd(II) and 0.50 µg l⁻¹ for Pb(II). The validation of the procedure was performed by the analysis of the certified standard reference materials. The presented procedure was applied to the determination of analytes in tap, river and sea waters, rice, wheat, canned tomato and coal samples with successfully results (recoveries greater than 95%, R.S.D.'s lower than 8%).

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1. Introduction

The determination of heavy metals at trace levels in environmental is one of the targets of analytical chemists [1–3], due to their important roles in our life. There are many difficulties in determining trace amounts of heavy metals in environmental samples by flame atomic absorption spectrometry due to insufficient sensitivity of instrument and/or matrix interferences [4–7]. In order to achieve detection limits within the range of flame atomic absorption spectrometry. An initial preconcentration step allows lower limits of detection for analytes, as well as the separation of the analytes from its matrix, which may interfere in atomic absorption spectrometric determinations [8,9].

Various preconcentration techniques including solvent extraction [10,11], coprecipitation [12–14], cloud point extraction [15,16], ion-exchange [17,18] and electroanalytical tech-

niques [19,20] have been used for the enrichment and separation of heavy metals at trace levels in various environmental samples including foods and natural waters by the researchers around the world. Solid phase extraction is an attractive separation-preconcentration technique for heavy metal ions with some important advantages: simplicity, flexibility, economic, rapid, higher enrichment factors, absence of emulsion, low cost because of lower consumption of reagents, more importantly environment friendly [21,22]. Various solid phase extraction materials including styrofoam [23], cellulose [24], activated carbon [25], Lewatit S 100 [26], titanium dioxide [27], polyurethane foam [28,29], Chelex 100 [30], microcrystalline naphthalene [31], modified silica [32–34] and chelating resins [35,36] has been successfully used for the preconcentration-separation of heavy metal ions at trace levels.

Alpha-benzoin oxime is a spectrophotometric reagent for the heavy metal ions in various media including natural waters and other samples [37–39]. It has been also used on some preconcentration studies including solid phase extraction, solvent extraction and cloud point extraction as chelating agent [40–42].

* Corresponding author. Tel.: +90 352 4374933; fax: +90 352 4374933.
E-mail address: soylak@erciyes.edu.tr (M. Soylak).

The aim of the presented work to show the possibility of the usage of Diaion SP-850 polymeric resin as adsorbent for the separation/preconcentration of heavy metal-alpha-benzoin oxime. The optimum analytical conditions for the quantitative recoveries of chromium, manganese, iron, cobalt, copper, cadmium and lead ions on Diaion SP-850 adsorption resin were investigated.

2. Experimental

2.1. Apparatus

Perkin-Elmer Model 3110 and Perkin-Elmer Analyst 700 atomic absorption spectrometer were used in the studies. All measurements were carried out in an air/acetylene flame. Ten centimeter long slot-burner heads, hollow cathode lamps were used. The operating parameters for working elements, which were given in Table 1 were set as recommended by the manufacturer.

SEM images were obtained on a LEO 440 scanning electron microscope (SEM). A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used. Digestion conditions for microwave system for SRM 1633b Coal fly ash and SRM 1573a Tomato leaves, rice, wheat, canned tomato and coal samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min.

2.2. Reagents

All solutions were prepared with deionized double distilled water. Otherwise stated, analytical-grade acids and other chemicals were used in this study obtained from Merck, Darmstadt, Germany. The calibration curve was established using the standard solutions prepared in 1 mol l⁻¹ HNO₃ by dilution from 1000 mg l⁻¹ stock solutions (Merck). The calibration standards were not submitted to the preconcentration procedure.

Alpha-benzoin oxime was purchased from E. Merck, Darmstadt, Germany. A 0.1% (m/V) solution of alpha-benzoin oxime was prepared daily in a water/ethanol (75/25, v/v) mixture. Standard reference materials (NRCC-SLRS 4 Riverine Water, SRM 1573a Tomato leaves and SRM 1633b Coal fly ash) were used in the experiment. Buffer solutions were prepared as previously reported [43].

Table 1
Instrumental conditions for the measurements of the analytes by FAAS

Analyte	Wavelength (nm)	Slit width (nm)	Lamb current (mA)
Cr	357.9	0.7	12
Mn	279.5	0.2	20
Fe	248.3	0.2	30
Co	240.7	0.2	30
Cu	324.8	0.7	15
Cd	228.8	0.7	8
Pb	283.3	0.7	15

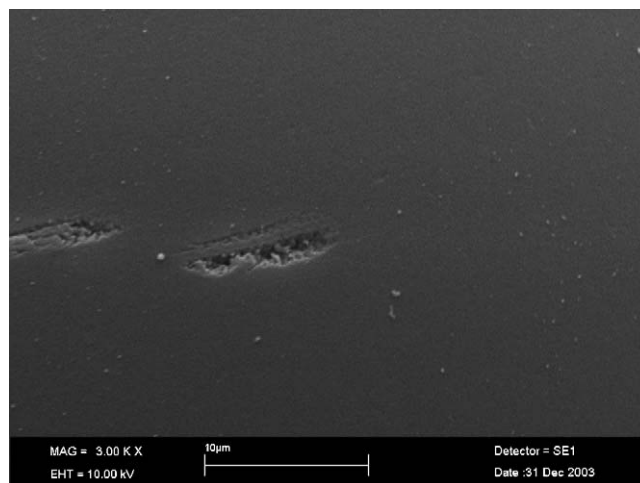


Fig. 1. SEM micrographs of Diaion SP-850.

Diaion SP-850 was purchased from Sigma Chem. Co. St. Louis, USA. The SEM image of Diaion SP-850 resin is shown in Fig. 1. The SEM image shows dense microstructure and granular grain. Diaion SP-850 is an aromatic type adsorbent is the standard grade and is based on crosslinked polystyrenic matrix. Its surface area is 1000 m² g⁻¹. It is widely used in different industrial fields; extraction of antibiotic intermediates from fermentation broth, separation of peptides or food additives, debittering of citrus juice, etc. [44]. It (20–60 mesh) was washed successively with methanol, water, 1 mol l⁻¹ HNO₃ in acetone, water, 1 mol l⁻¹ NaOH and water, sequentially.

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, 700 mg of Diaion SP-850 resin was slurried in water, and then poured into the column. The resin was preconditioned under optimum pH. The bed height of resin in the column was approximately, 20 mm. It was washed with water, acetone and water, sequentially. It was conditioned with 10–15 ml of pH 8.0 with ammonia/ammonium chloride buffer. The resin bed was washed with plenty of distilled water until neutral pH and subsequently reused.

2.3. Preconcentration procedure

The method was tested with model solutions before its application to real samples. Ten milliliter of buffer solution (to give the desired pH between 2 and 10) and alpha-benzoin oxime solution were added to 30–40 ml of solution containing 5–20 µg of analyte ions. The column was preconditioned with the buffer solution. Metal-alpha-benzoin oxime solution was passed through the column at a flow rate of 5 ml min⁻¹ using a vacuum aspirator. After passing of this solution, the column was rinsed twice with 10 ml of water. The adsorbed metal chelate on the column was eluted with 10 ml portion of 1 mol l⁻¹ HNO₃. The eluent was analyzed for the determination of metal concentrations by atomic absorption spectrometry.

2.4. Analysis of the real samples

SRM 1633b Coal fly ash and SRM 1573a Tomato leaves (250 mg) and coal sample (1.0 g) were digested with 6 ml of HNO_3 (65%), 2 ml of H_2O_2 (30%) in microwave digestion system and diluted to 50 ml with deionized water [43,45]. A blank digest was carried out in the same way. Then the preconcentration procedure given above was applied to the final solutions.

In order to the microwave digestion of canned tomato, rice and wheat, 1.0 g of sample from Tokat was digested with 6 ml of concentrated HNO_3 and 2 ml of concentrated H_2O_2 in microwave system. After digestion the samples, the volume of the digested sample was made up to 25.0 ml with distilled water [43,45]. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the samples.

NRCC-SLRS 4 Riverine Water, tap from Tokat city, river water from Tokat and seawater from Black Sea analyzed were filtered through Millipore cellulose membrane filter (0.45 μm pore size). The pH of the samples was adjusted to 8.0 with buffer solution. The sample was passed through the column. The metal-chelates adsorbed on Diaion SP-850 column were eluted with $1 \text{ mol l}^{-1} \text{ HNO}_3$. The levels of analyte ions in the samples were determined by flame atomic absorption spectrometry.

3. Results and discussion

In order to obtain quantitative recoveries of chromium, manganese, iron, cobalt, copper, cadmium and lead ions on the Diaion SP-850 column, the preconcentration procedure was optimized for various analytical parameters, such as pH, sample volume and amount of Diaion SP-850, matrix effects, etc. The percent of metal ions adsorbed on the column was calculated from the amounts of metal ions in the starting sample and the amounts of metal ions eluted from the column.

3.1. Influences of pH on sorption

In the solid phase extraction studies for heavy metal ions based on chelation, the influence of pH of the aqueous solution one of the main factor for quantitative recoveries of the analytes [14,24,36,45–47]. Due to this important point, the influences of pH were investigated at the pH ranges 2–10 with model solutions, keeping the other parameters constant. The recovery values for the analyte metals were shown in Fig. 2. The optimum pH range for quantitative recoveries of Cr(III), Mn(II), Fe(III), Co(II), Cu(II), Cd(II) and Pb(II) as oxime chelates on Diaion SP-850 resin is 8.0–10.0. All subsequent studies were carried out at pH 8 with ammonia/ammonium chloride buffer. The volume of buffer added (10 ml) had no effect on the recoveries.

3.2. Influences of amount of ligand on the recoveries

In order to determine the amounts of alpha-benzoin oxime required for quantitative recoveries for chromium, manganese, iron, cobalt, copper, cadmium and lead ions, the proposed method was applied, changing alpha-benzoin oxime amounts

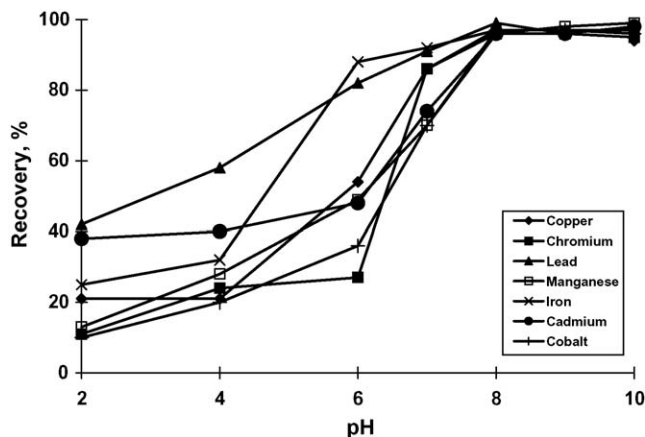


Fig. 2. Influences of pH on the recoveries ($N: 4$; ligand: alpha-benzoin oxime; amounts of analytes: $10 \mu\text{g Cu}$, $20 \mu\text{g Cr}$, $20 \mu\text{g Pb}$, $10 \mu\text{g Mn}$, $10 \mu\text{g Fe}$, $5 \mu\text{g Cd}$, $10 \mu\text{g Co}$; eluent: $1 \text{ mol l}^{-1} \text{ HNO}_3$).

at the range of 0–5 ml of 0.1% solution. The recoveries were not quantitative without alpha-benzoin oxime. The recovery values of the analyte metal ions increased with increasing amounts of alpha-benzoin oxime added and reached a constant value with at least 1.5 ml of 0.1% solution of alpha-benzoin oxime. On this basis, studies were carried out at alpha-benzoin oxime amounts of 2.0 ml. This amount of alpha-benzoin oxime is enough for the separation/preconcentration procedure because of the very low level of the investigated metal ion concentrations in real samples.

3.3. Effects of the amount of resin

Also the amounts of solid phase extraction material are another important factor on the column studies for the quantitative recoveries of metal chelates [48,49]. The effect of the amount of Diaion SP-850 on the sorption of metal ions at pH 8.0 was examined in the range of 300–900 mg. The results demonstrated that, quantitative recoveries (>95%) of the working elements were observed in the range of 600–800 mg. Above 800 mg, the recoveries were below 95% with 10 ml of the eluent. When 25 ml of eluent was used, the recoveries were quantitative with 800 mg of Diaion SP-850. In the proposed procedure, 700 mg of Diaion SP-850 is recommended.

3.4. Effect of flow rate and desorption studies

The influence of flow rate on the adsorption of analyte ions was also studied. Flow rate in the range of 1–10 ml min^{-1} had no significant effect on the recoveries of the investigated elements. All subsequent experiments for this study were performed at 5 ml min^{-1} flow rate.

The desorption of the retained analyte metal ions from column was examined using various elution solutions. The selected volumes of the eluents were 5.0 and 10.0 ml, but the same results were obtained with higher volumes. Quantitative recoveries (>95%) were obtained for the investigated elements with $1 \text{ mol l}^{-1} \text{ HNO}_3$, $2 \text{ mol l}^{-1} \text{ HNO}_3$, $1 \text{ mol l}^{-1} \text{ HCl}$ and $2 \text{ mol l}^{-1} \text{ HCl}$. These results agree with the data given in literature [50–52].

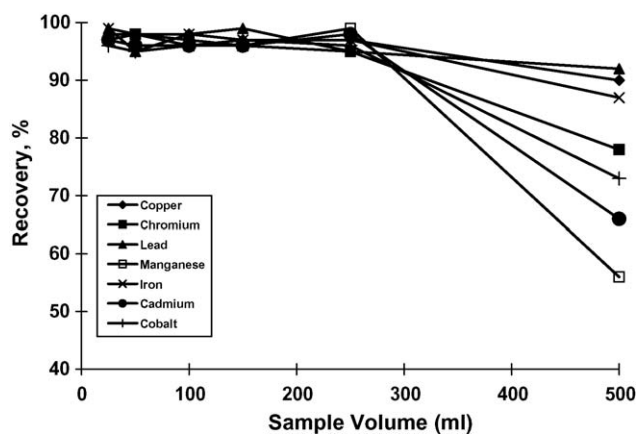


Fig. 3. Effect of the sample volume on the recoveries of analyte ions from the Diaion SP-850 column ($N=4$; pH: 8; ligand: alpha-benzoin oxime; amounts of analytes: $10 \mu\text{g Cu}$, $20 \mu\text{g Cr}$, $20 \mu\text{g Pb}$, $10 \mu\text{g Mn}$, $10 \mu\text{g Fe}$, $5 \mu\text{g Cd}$, $10 \mu\text{g Co}$; eluent: $1 \text{ mol l}^{-1} \text{ HNO}_3$).

For all other works 10 ml of $1 \text{ mol l}^{-1} \text{ HNO}_3$ was selected as eluent.

3.5. Effect of the sample volume on the recoveries

The effect of the sample solution volume on the metal sorption on Diaion SP-850 was studied by passing 20–500 ml volumes through Diaion SP-850 column at a 5 ml min^{-1} flow rate. The results were given in Fig. 3. The adsorption of the metal ions was not affected by sample volume below 250 ml. The percent sorption decreased for the analytes above 250 ml. The recoveries of analytes decrease probably due to the excess analytes loaded over the column capacity with increasing sample volume above 250 ml. The adsorbed metals can be eluted with 5.0 ml of $1 \text{ mol l}^{-1} \text{ HNO}_3$ and a preconcentration factor of 50 is achieved by this technique.

3.6. Effect of foreign ions

In order to evaluate the possibility of selective recovery of analyte ions in the presence of alkaline, earth alkaline metals and major anions of the real samples, the procedure has been performed with 50 ml solutions containing such ions. Quantitative recoveries ($>95\%$) for 2500 mg l^{-1} of NaCl , for 1000 mg l^{-1} of Mg^{2+} , for 1000 mg l^{-1} of K^+ , for 1000 mg l^{-1} of Ca^{2+} , for 1000 mg l^{-1} of SO_4^{2-} , 20 mg l^{-1} for Zn^{2+} , 20 mg l^{-1} for

Al^{3+} were obtained. These tolerable levels of foreign ions were enough for the quantitative separation of analyte ions from the matrix of the real samples.

3.7. Capacity of the resin

In order to study the adsorptive capacity of SP-850 resin, batch method was used. To 0.1 g resin was added 50 ml of solution containing 1.0 mg of metal ion at pH 8.0 and alpha-benzoin oxime. After shaking for 1 h, the mixture was filtered. Ten milliliter of the supernatant solution was diluted to 100 ml and the analyte ions were determined by flame atomic absorption spectrometry. This procedure was repeated for each analyte ions, separately. The capacity of one gram of Diaion SP-850 was found 0.08 mmol for chromium, 0.11 mmol for manganese, 0.10 mmol for iron, 0.07 mmol for cobalt, 0.09 mmol for copper, 0.06 mmol for cadmium and 0.02 mmol for lead.

3.8. Detection limits

The detection limits based on three times the standard deviations of the blank were $0.65 \mu\text{g l}^{-1}$ for Cr(III), $0.42 \mu\text{g l}^{-1}$ for Mn(II), $0.28 \mu\text{g l}^{-1}$ for Fe(III), $0.73 \mu\text{g l}^{-1}$ for Co(II), $0.30 \mu\text{g l}^{-1}$ for Cu(II), $0.47 \mu\text{g l}^{-1}$ for Cd(II) and $0.50 \mu\text{g l}^{-1}$ for Pb(II) ($k=3$, $N=21$) after applying the preconcentration procedure.

3.9. Recovery of spikes from water samples

In order to estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked in a bottled drinking water and a tap water. The resulting solutions were submitted to the preconcentration procedure. Good agreement was obtained between the added and found analyte content using the recommended procedure. The recovery values for the analyte ions in the range of 94–103%. These values were quantitative and it shows that the presented method can be applied for the separation/preconcentration of analyte ions in the natural waters.

3.10. Analyte contents of SRM samples

The method presented was checked to analyzing different reference materials (NRCC-SLRS 4 Riverine Water, SRM 1573a

Table 2
The results for reference standard materials ($N=4$)

Element	NRCC-SLRS 4 Riverine water ($\mu\text{g l}^{-1}$)		SRM 1633b Coal fly ash ($\mu\text{g g}^{-1}$)		SRM 1573a Tomato leaves ($\mu\text{g g}^{-1}$)	
	Certified value	Our value	Certified value	Our value	Certified value	Our value
Cr	0.33	BDL	198.2	188.6 ± 10.3	1.99	1.90 ± 0.12
Mn	3.37	3.25 ± 0.30	131.8	128.6 ± 8.7	246	240.5 ± 8.9
Cu	1.81	1.77 ± 0.14	112.8	107.4 ± 7.8	4.7	4.5 ± 0.2
Co	0.033	BDL	(50)	48.5 ± 1.6	0.57	0.55 ± 0.05
Cd	0.012	BDL	0.784	0.770 ± 0.05	1.52	1.55 ± 0.10
Pb	0.086	BDL	68.2	65.8 ± 3.2	–	BDL

BDL: Below the detection limit. The values in the parenthesis is not certified.

Table 3

The application of the presented method in natural water samples for contents of analyte ions ($N=4$)

Element	Tap water ($\mu\text{g l}^{-1}$)	River water ($\mu\text{g l}^{-1}$)	Sea water ($\mu\text{g l}^{-1}$)
Cr	BDL	2.78 ± 0.12	6.37 ± 0.45
Mn	6.92 ± 0.44	8.52 ± 0.50	7.10 ± 0.48
Fe	15.6 ± 1.1	10.2 ± 0.7	35.8 ± 2.8
Co	BDL	BDL	3.60 ± 0.21
Cu	3.60 ± 0.20	7.10 ± 0.55	4.96 ± 0.32
Cd	2.69 ± 0.10	3.58 ± 0.24	6.25 ± 0.37
Pb	5.12 ± 0.35	4.27 ± 0.17	3.66 ± 0.21

BDL: Below the detection limit. Mean expressed as 95% tolerance limit.

Table 4

Levels of analyte ions in microwave digested various samples ($N=4$)

Element	Rice ($\mu\text{g g}^{-1}$)	Wheat ($\mu\text{g g}^{-1}$)	Canned tomato ($\mu\text{g g}^{-1}$)	Coal ($\mu\text{g g}^{-1}$)
Cr	0.58 ± 0.05	0.36 ± 0.03	0.62 ± 0.05	45.7 ± 3.4
Mn	7.4 ± 0.5	12.5 ± 0.9	5.8 ± 0.3	69.7 ± 4.6
Fe	9.4 ± 0.8	17.8 ± 1.3	43.8 ± 2.2	563 ± 45
Co	0.29 ± 0.22	0.45 ± 0.26	0.75 ± 0.06	12.4 ± 1.1
Cu	2.2 ± 0.2	4.6 ± 0.2	4.0 ± 0.2	27.1 ± 1.9
Cd	0.36 ± 0.02	0.29 ± 0.02	BDL	0.93 ± 0.06
Pb	BDL	0.27 ± 0.02	BDL	16.3 ± 1.2

BDL: Below the detection limit. Mean expressed as 95% tolerance limit.

Tomato leaves and SRM 1633b Coal fly ash) for the determination of investigated analyte ions. The certified and observed values for SRMs were given in Table 2. The results found were in good agreement with the certified values of SRM's. If the concentration levels of the most common matrix constituents of reference standard materials analyzed and the accuracy of the presented method are considered together, it can be concluded that the proposed method is free from interferences of the various constituents.

3.11. Application to real samples

The solid phase extraction procedure presented for chromium, manganese, iron, cobalt, copper, cadmium and lead ions was applied to three different samples. The results were given in Table 3. The proposed method has been combined with the microwave assisted digested samples including rice, wheat, canned tomato and coal samples. These samples were digested by closed microwave system, and then preconcentration/separation procedure given in Section 2 was applied. The results are given in Table 4.

4. Conclusion

The developed method is successfully employed for analysis of agricultural and geological materials after successful validation. Some advantages of the proposed method are: The use of Diaion SP-850 as solid phase extraction materials is new. The method is also economic. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of

Diaion SP-850 was as high as greater than 200 cycles without any loss in its sorption behavior. The elution was easily performed with $1 \text{ mol l}^{-1} \text{ HNO}_3$. The analytical performance of the method is comparable with other separation-preconcentration methods. The limits of detection of analyte ions are superior to those of some preconcentration/ separation techniques for analyses [9–12,34–36]. The matrix effects with the method were reasonably tolerable. Also the method is relatively rapid as compared with previously reported procedures for the enrichment of traces metal ions.

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