Sorbent extraction of rubeanic acid–metal chelates on a new adsorbent: Sepabeads SP70

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Abstract

A sorbent extraction procedure for lead, iron, cadmium and manganese ions on Sepabeads SP70 adsorption resin has been presented prior to their flame atomic absorption spectrometric determinations. By the passage of aqueous samples including analyte ions-rubeanic acid chelates through Sepabeads SP70 column, metal chelates adsorb quantitatively and almost all matrix elements will pass through the column to drain. The influence of potential interfering ions was also studied. The validation of the method was made though the analysis of LGC 6010 Hard drinking water, SRM 1577b Bovine liver and GBW 07603 Bush branches and leaves standard reference materials (SRM). The method was applied to the determination of analyte ions from various water, wastewater, cow meat and milk, red wine, and tobacco samples with successfully results.
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1. Introduction

Accurate and precise analyses of traces heavy metal ions by instrumental analysis techniques including inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), flame atomic absorption spectrometry (FAAS), etc. are an important part of the analytical chemistry [1–4] because of ecological and health problems associated with environmental contamination continues to rise. Due to the relatively simple and inexpensive equipment required, flame atomic absorption spectrometry (FAAS) is preferred as main instrument for many environmental chemistry laboratories for heavy metal determinations [5–7]. However in flame atomic absorption determinations of the heavy metal ions, unfavorable influences of matrix components of real samples and particularly low concentrations of heavy metal ions are two big problems [8–11]. Preconcentration step improves the analytical detection limit, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results and facilitate the calibration. In order to solve these important prob-

lems, separation/preconcentration procedures including coprecipitation [12–14], membrane filtration [15,16], electroanalytical techniques [17,18], cloud point extraction [19,20], solvent extraction [21], and ion-exchange [22,23] are widely used by the researchers around the world.

Solid phase extraction for the preconcentration and selective separation of trace metal ions from the environmental samples is very important and need much more attention because of its some advantages including its simplicity, to obtain high preconcentration factor, environmental friendly, etc. [24–26]. Main different methodologies are generally possible for the solid phase extraction of the metals: batch and column methodology [27–29]. Various solid phases including Chelex 100 [25], naphthalene [26], Amberlite XAD resins [27,28], synthetic polymers [30,31], polyurethane foam [32,33], C18 [34], activated carbon [35–37] have been used for the solid phase extraction of traces heavy metals in environmental samples prior to their instrumental analysis.

Rubeanic acid (dithiooxamide) is a reagent for spectrophotometric determination of traces metal ions [38–40]. Rubeanic acid has been used for preconcentration and determination of heavy metal ion from various media [41–45].

The aim of this work was to develop a solid phase extraction method for the separation and preconcentration of lead,

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iron, cadmium and manganese ions prior to atomic absorption spectrometric determination. The analytical parameters for the quantitative recoveries of analytes 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. A 10 cm long slot-burner heads, hollow cathode lamps were used. The operating parameters for working elements were set as recommended by the manufacturer. Surface characterization studies were performed with a LEO 440 scanning electron microscope for 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 the food and other samples were taken from our previous papers [46,47].

2.2. Reagents

All solutions were prepared with deionized distilled water. Otherwise stated, analytical-grade acetone, acids and other chemicals used in this study obtained from Merck, Darmstadt, Germany. The calibration curve was established using the standard solutions of analyte elements prepared in $1 \, mol \, l^{-1}$ HNO_3 by dilution from $1000 \, mg \, l^{-1}$ stock solutions (Merck). The calibration standards were not submitted to the preconcentration procedure.

The chelating agent was rubeanic acid (Merck, Darmstadt, Germany). 0.2% (m/v) of rubeanic acid solution was daily prepared in a water/ethanol (80/20, v/v) mixture. Standard reference materials (LGC 6010 Hard drinking water, SRM 1577b Bovine liver and GBW 07603 Bush branches and leaves) were used in the experiment.

Sepabeads SP70 is a divinylbenzene copolymer that was purchased from Sigma Chem. Co., St. Louis, USA. The SEM image of Sepabeads SP70 resin is shown in Fig. 1. The SEM image shows dense microstructure and granular grain. Its surface area is $800 \, m^2 \, g^{-1}$ [48]. It (20–60 mesh) was washed successively with methanol, water, $1 \, mol \, l^{-1}$ HNO_3 in acetone, water, $1 \, mol \, l^{-1}$ NaOH, and water, sequentially. A glass column containing 700 mg of Sepabeads SP70 in water suspension was 10 cm long and 1.0 cm in diameter. The bed height in the column was approximately 3.0 cm. The resin on the column was preconditioned with pH 8.0 buffer solution prior to percolation of the sample.

Sodium phosphate buffer ($0.1 \, mol \, l^{-1}$) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers ($0.1 \, mol \, l^{-1}$) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6. For pH 7,
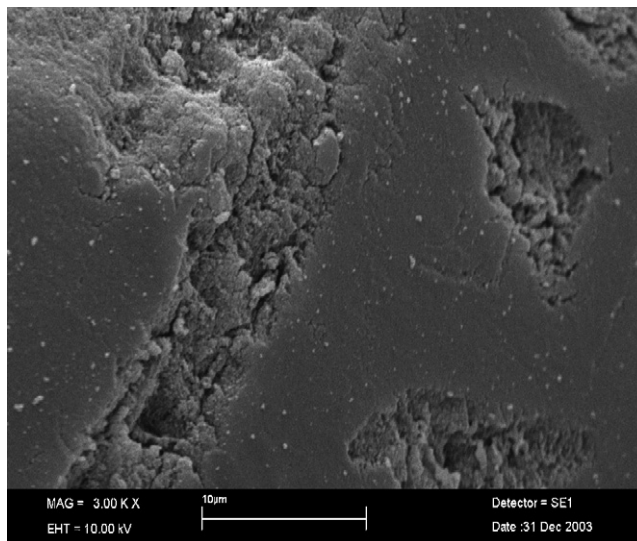

Fig. 1. SEM micrograph of Sepabeads SP70.

sodium borate ($0.1 \, mol \, l^{-1}$) buffer solution was used. Ammonium chloride buffer solutions ($0.1 \, mol \, l^{-1}$) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8–10.

2.3. Separation and preconcentration procedure

The Sepabeads SP70 column method was tested with model solutions. Model solutions (containing 10 μg of iron, 10 μg of manganese, 5 μg of cadmium and 20 μg of lead in 40 ml) were adjusted to desired pH. Then rubeanic acid was added to form the metal–rubeanic chelates. After 5–10 min, the solution was loaded to the column. The flow of sample solution through the column was gravitationally performed. After passage of the solution finished, the column was washed with a chelating agent solution adjusted to the working pH. The metals were recovered with the aid of 5–10 ml of $1 \, mol \, l^{-1}$ HNO_3 at $4.0 \, ml \, min^{-1}$ of flow rate. The lead, iron, cadmium and manganese concentrations in the final solution were determined by FAAS.

2.4. Analysis of real samples

The water samples analyzed were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pH of the samples was adjusted to 8. Then rubeanic acid solution was added. The sample was passed through the column. The rubeanic chelates adsorbed on column were eluted with $1 \, mol \, l^{-1}$ HNO_3. The levels of the investigated analyte ions in the samples were determined by FAAS.

SRM 1577b Bovine liver, GBW 07603 Bush branches and leaves standard reference materials (100 mg) were digested with 6 ml of HNO_3 (65%), 2 ml of H_2O_2 (30%) in microwave digestion system for 31 min and diluted to 50 ml with deionized water. A blank digest was carried out in the same way. Then the preconcentration procedure given above was applied to the final solutions.

For the microwave digestion of red wine and cow milk samples, 1.0 ml of wine or cow milk was mixed with 1.0 ml of concentrated HNO_3 and 0.5 ml of H_2O_2 in microwave system. For the microwave digestion of cow meat and tobacco samples, 1.0 g of tobacco or cow meat sample was digested with 4 ml of concentrated HNO_3 and 2 ml of concentrated H_2O_2 in microwave system. After digestion completed, the volume of the digested sample was made up to 25.0 ml with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration-separation procedure given above was applied to the samples.

3. Results and discussion

3.1. Effect of pH

One of the most important factors in a solid phase extraction procedure is the pH of the aqueous phase for the quantitative recoveries [49,50]. The reaction between analyte ions and the complexing agent can be influenced by changes of pH value. The influences of the pH on lead, iron, cadmium and manganese-rubeanic acid sorption onto Sepabeads SP70 adsorption resin was investigated over the range from 2.0 to 10.0 keeping other parameters constant. Fig. 2 shows that lead, iron, cadmium and manganese were effectively adsorbed in pH range 8–10. It was possible to carry out the determination of both ions at pH 8.0. In order to control the pH during the analytical procedure, it was adjusted to 8.0 with a buffer solution of ammonium chloride/ammonia.

3.2. Influences of the amounts of rubeanic acid

The influences of the amounts of rubeanic acid on the quantitative recoveries of the analyte ions were also examined. A 0–8.0 ml portion of a 0.2% (m/v) rubeanic acid solution was added to model solution containing 5–20 μg of each analyte ions. The amounts of investigated ions adsorbed on the Sepabeads SP70 resin were examined. The studies were
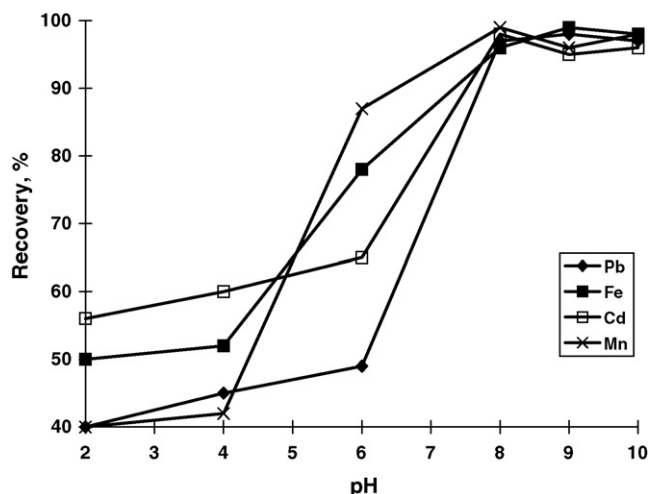

Fig. 2. The influence of the pH on the recovery of analyte ions on Sepabeads SP70 (chelating agent: rubeanic acid, eluent: $1 \, mol \, l^{-1} \, HNO_3$, $N = 3$).

also performed without rubeanic acid. The recoveries of lead, iron, cadmium and manganese were below 20%. Over 1.0 ml of 0.2% (m/v) rubeanic acid solution, lead, iron, cadmium and manganese were quantitatively adsorbed. This situation concluded that rubeanic acid as complexing agent is necessary for preconcentration studies on Sepabeads SP70 resin column. All further studies were performed by using 2.0 ml of 0.2% rubeanic acid.

3.3. Effects of sample volume

The effect of the sample solution volume on the metal sorption was also studied at pH 8 by passing 25–250 ml volumes through the column at a $4 \, ml \, min^{-1}$ flow rate. In these studies 2.0 ml of 0.2% (m/v) rubeanic acid was used. The adsorption of the metal ions with 700 mg of Sepabeads SP70 was not affected by sample volume below 100 ml. Above 100 ml the percent sorption decreased for the analytes.

3.4. Effects of the amount of resin

The effect of the amount of Sepabeads SP70 on the sorption of metal ions at pH 8.0 was examined in the range of 300–900 mg. Quantitative recoveries (>95%) of lead, iron, cadmium and manganese ions were observed in the range of 600–800 mg. The recoveries of analytes above 800 mg of resin were below 95% with 10 ml of the eluent. In the proposed procedure, 700 mg of Sepabeads SP70 is recommended.

3.5. Effect of eluent

A $1 \, mol \, l^{-1} \, HNO_3$ was the most suitable eluent for the elution of the analytes retained using organic ligands on the polymeric adsorbents as in previous studies [28,46,47,51–54]. The minimum volume of $1 \, mol \, l^{-1} \, HNO_3$ required for the quantitative elution of the retained analyte complexes was found to be 5.0 ml. Under optimal constant conditions, the flow rates of sample volume and eluent solution were studied in the range of $1–10 \, ml \, min^{-1}$. The best results were obtained at $4.0 \, ml \, min^{-1}$ for retention and elution.

3.6. Effect of matrix

Various concentrations of matrix ions were added to 40 ml of model solution containing 5–20 μg of each metal ion to investigate possible effects of these ions on Sepabeads SP70. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±5% related to the preconcentration and determination of analytes. Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and Cl^- did not interfere with the determination at 2000, 1000, 500, 500, 250 and $2000 \, mg \, l^{-1}$, respectively. The small amounts retained of the matrix ions were removed by washing with 10 ml of blank solution. It can be seen that the major matrix ions in the natural water samples show no noticeable interference in the preconcentration of some trace metal ions by the developed method.

Table 1
The results for reference standard materials ($N = 4$)

Element	LGC 6010 hard drinking water ($\mu g\,l^{-1}$)		SRM 1577b bovine liver ($\mu g\,g^{-1}$)		GBW 07603 bush branches and leaves ($\mu g\,g^{-1}$)	
	Certified value	Our value	Certified value	Our value	Certified value	Our value
Pb	97	92.8 ± 2.1	0.129	0.132 ± 0.01	47	45.2 ± 1.8
Fe	226	220.5 ± 5.8	184	175.6 ± 6.1	1070	1020 ± 45
Cd	–	BDL	0.5	0.48 ± 0.04	(0.38)	0.36 ± 0.03
Mn	50	48.3 ± 1.4	10.5	9.98 ± 0.10	61	58.7 ± 3.9

BDL: below the detection limit. The values in the parentheses are not certified.

3.7. Capacity of the resin

Batch method was used to investigate the adsorptive capacity of Sepabeads SP70 resin. A 0.1 g resin was added 50 ml of solution containing 1.0 mg of metal ion at pH 8.0 and rubeanic acid. 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 resin was found 2.3 mg for lead, 4.9 mg for iron, 5.1 mg for cadmium and 4.2 mg for manganese.

3.8. Detection limits

The limits of detection (LOD) of the proposed method for the determination of investigated elements were studied under the optimal experimental conditions. The detection limits based on three times the standard deviations of the blank ($N = 20$, $X_L = X_b + 3s$, where X_L is the limit of detection and X_b is the blank value) for lead, iron, cadmium and manganese were found to be 0.95, 0.89, 1.58 and 1.23 $\mu g\,l^{-1}$, respectively.

3.9. Recovery of spikes from water samples

Different amounts of the investigated metal ions were spiked in a bottled drinking water and a tap water to estimate the accuracy of the procedure. The resulting solutions were submitted to the presented 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%. The standard deviation values for the spiked samples were in the range of 1–5%. These values were quantitative and it shows that the presented method can be applied for the separation/preconcentration of analyte ions in the real samples like natural waters.

3.10. Application to real samples

The method presented was checked to analyzing different reference materials (LGC 6010 Hard drinking water, SRM 1577b Bovine liver and GBW 07603 Bush branches and leaves) for the determination of lead, iron, cadmium and manganese ions. The certified and observed values for SRMs were given in Table 1. The results found were in good agreement with the certified values of SRMs.

Table 2
The application of the presented method in natural water samples for contents of analyte ions ($N = 4$)

Element	Tap water ($\mu g\,l^{-1}$)	Wastewater ($\mu g\,l^{-1}$)	Rain water ($\mu g\,l^{-1}$)
Pb	4.50 ± 0.30	8.19 ± 0.67	2.86 ± 0.24
Fe	24.1 ± 1.3	32.8 ± 2.7	10.7 ± 0.8
Cd	BDL	7.86 ± 4.16	BDL
Mn	7.26 ± 0.58	10.9 ± 0.8	4.87 ± 0.35

BDL: below the detection limit.

Table 3
Levels of analyte ions in microwave digested various samples ($N = 4$)

Element	Cow meat ($\mu g\,g^{-1}$)	Red wine ($\mu g\,l^{-1}$)	Cow milk ($\mu g\,l^{-1}$)	Turkish tobacco ($\mu g\,g^{-1}$)
Pb	0.25 ± 0.02	BDL	BDL	1.52 ± 0.11
Fe	50.3 ± 3.6	3250 ± 160	1175 ± 85	48.1 ± 3.2
Cd	0.46 ± 0.04	BDL	BDL	1.18 ± 0.10
Mn	4.83 ± 0.28	58.7 ± 4.9	23.5 ± 1.2	77.3 ± 5.5

BDL: below the detection limit.

The solid phase extraction procedure presented for lead(II), iron(III), cadmium(II) and manganese(II) ions was applied to three different samples from Tokat city, Turkey. The results were given in Table 2. The proposed method has been combined with the microwave assisted digested samples including cow meat, red wine, cow milk and tobacco samples. These samples were digested by closed microwave system, and then preconcentration/separation procedure given in Experimental was applied. The results are given in Table 3.

4. Conclusion

The proposed preconcentration/separation procedure provides a fast and simple method for the enrichment of lead, iron, cadmium and manganese on Sepabeads SP70. The matrix effects with the present method were reasonably tolerable. The recoveries were quantitative (94–103%). The method can be successfully applied to the separation and determination of analyte ions in various real samples. The resin on the column could be used at least 200 times.

Acknowledgements

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