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Solid Phase Extraction and Graphite Furnace Atomic Absorption Spectrometry for the Determination of Heavy Metal Ions

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A solid phase extraction method was developed for the preconcentration and separation of trace amounts of chromium, nickel, silver, cobalt, copper, cadmium and lead from environmental samples by complexation with 2-(2-quinolinylazo)-resorcin (QAR) followed by adsorption onto Diaion SP-850 solid phase extraction column. 1.0 mol L^{-1} HNO_3 was used as eluent. The recoveries of analytes at pH 8.0 with 800 mg of resin were more than 95 % without interference from alkaline, earth alkaline and some metal ions. The detection limits by three sigma for analyte ions were 0.32 µg L^{-1} for Cr(III), 0.21 µg L^{-1} for Ni(II), 0.14 µg L^{-1} for Ag(I), 0.36 µg L^{-1} for Co(II), 0.18 µg L^{-1} for Cu(II), 0.25 µg L^{-1} for Cd(II) and 0.30 µg L^{-1} for Pb(II). The validation of the procedure was performed by the analysis of the certified standard reference materials and the presented procedure was applied to the determination of analytes in biological, water and soil samples with good results (recoveries more than 95 % and RSD % lower than 3.5 %).

Key Words: Solid phase extraction, Heavy metal ions, 2-(2-Quinolinylazo)resorcin, Atomic absorption spectrometry.

INTRODUCTION

In spite of great improvements in sensitivity and selectivity of modern instrumental analysis, difficulties still lie in the analysis of environmental samples for trace heavy metals because of both their low abundance levels in the samples and the high complexity of the sample matrices[1,2]. Hence, preliminary concentration and matrix-removal steps are frequently required for the accuracy and precision of the analytical results.

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Various preconcentration techniques including solvent extraction, coprecipitation, cloud point extraction, ion-exchange and electroanalytical techniques[3-7] have been used for the enrichment and separation of heavy metals at trace levels in various environmental samples around the world.

Solid phase extraction is an attractive separation-preconcentration technique for heavy metal ions with more advantages (simplicity, flexibility, economic, rapid, higher enrichment factors, absence of emulsion, low cost because of lower consumption of reagents, more importantly environment friendly). Various solid phase extraction materials have been successfully used for the preconcentration and separation of heavy metal ions at trace levels[8-12].

2-(2-Quinolinylazo)-resorcin (QAR) is chosen as a spectrophotometric reagent for the heavy metal ions in this present work. It can reacts with chromium, nickel, silver, cobalt, copper, cadmium and lead at room temperature rapidly[13,14]. The aim of the presented work to show the possibility of the usage of Diaion SP-850 polymeric resin as an adsorbent for the separation and preconcentration of heavy metal-QAR chelates. The optimum analytical conditions for the quantitative recoveries of chromium, nickel, silver, cobalt, copper, cadmium and lead ions on Diaion SP-850 adsorption resin were investigated.

EXPERIMENTAL

A Perkin-Elmer Model A Analyst 600 graphite-furnace atomic absorption spectrometer equipped with a Model AS-800 autosampler (Norwalk, CT) was used with monoatomic hollow cathode lamps. A Beckman F-200 pH meter was used for the pH measurements. All analytical procedures were carried out in a Hitachi Model ECV-843 BY clean bench (Hitachi, Japan). A Fei Yue DS-200 closed vessel microwave system (maximum pressure 2000 psi, maximum temperature 300 ºC) was used for samples digestion.

All solutions were prepared with deionized double distilled water. Otherwise stated, analytical-grade acids and other chemicals were used in this study obtained from Tianjin Chemical Factory, P.R. China. The calibration curve was established using the standard solutions prepared in 1.0 % (m/v) of HNO_3 by dilution from 1000 mg L^{-1} stock solutions (Chinese Standards Center, P.R. China). The calibration standards were also submitted to the preconcentration procedure. QAR was synthesized as reported earlier[13,14] and a 0.1 % (m/v) solution of QAR was prepared daily in ethanol. Standard reference materials (rice GBW08458 and human hair GBW08126) were used in the experiment. Buffer solutions of ammonia-ammonium chloride (0.5 mol L^{-1}, pH 8.0) were prepared by dissolving 0.5 mol (26.8 g) of ammonium chloride in water, adjusted the pH to 8.0 with ammonia and diluted to the volume of 1000 mL.

Diaion SP-850 was purchased from Sigma Chem. Co. (St. Louis, USA). Diaion SP-850 is an aromatic type adsorbent is the standard grade and is based on crosslinked polystyrenic matrix. Its surface area is 1000 m^2 g^{-1}. It is widely used in different industrial fields; extraction of antibiotic intermediates from fermentation broth, separation of peptides or food additives *etc*[15]. It (20-60 mesh) was washed successively with methanol, water, 1.0 mol L^{-1} HNO_3 in acetone, water, 1.0 mol L^{-1} NaOH and water, sequentially.

Preconcentration procedure: Teflon column was 2.0 cm long and 1.0 cm in diameter (Fig. 1). The 2.0 mm of sieve plate was placed to prevent loss of the resin beads during sample loading. Then, 800 mg of Diaion SP-850 resin was poured into the column. 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.

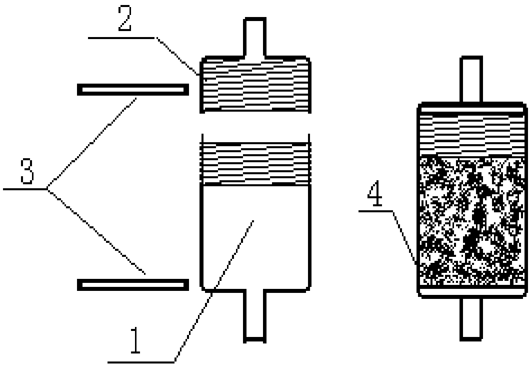

Fig. 1. SPE cartridge (1) Tube for fill in samples, (2) Screw cap for sealing the tube),(3) Sieve plate, (4) Diaion SP-850 adsorbent

The method was tested with model solutions before its application to real samples. 10 mL of buffer solution (pH 10) and 5.0 mL of 0.1 % QAR solution were added to 30-235 mL of solution containing 5-20 mg of analyte ions. The column was preconditioned with the buffer solution. Metal-QAR solution was passed through the column at a flow rate of 10 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 2.0 mL of 1.0 mol L^{-1} HNO_3 in the reverse direction. The eluent was analyzed by the atomic absorption spectrometry.

Sample preparation: For biological samples, 0.25 g of sample was weighed accurately into the 25 mL Teflon high-pressure microwave acid-digestion bomb. To which, 3.0 mL of concentrated nitric acid and 3.0 mL of 30 % hydrogen peroxide was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated at full power for 6 min. The digested material was evaporated to near dryness. The residue was dissolved with 10 mL of 1 % of nitric acid and the preconcentration procedure given above was applied to the samples.

For water samples, the samples were immediately acidified by adding several drops of nitric acid and filtrated with 0.45 µm filter, then the preconcentration procedure given above was applied to the samples.

For soil samples, 0.1 g of sample was weighed into a 25 mL of teflon high-pressure microwave acid-digestion bomb. To which, 2 mL of concentrated nitric acid and 1 mL of hydrofluoric acid were added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated at full power for 20 min. The digested material was evaporated to incipient dryness. Then, 10 mL of 1 % nitric acid was added and heated close to boiling to leach the residue. After cooled, the preconcentration procedure given above was applied to the samples.

AAS Analysis: The graphite furnance atomic spectrometric (GFAAS) analysis condition is listed in Table-1. For samples analysis, a 10 µL aliquot of the samples or standard solution was injected into the graphite cuvette for the GFAAS determination. No matrix modifier was used. The atomic absorption signals were measured with the Zeeman background corrector in operation. The measurement was repeated three times and the obtained signals were averaged.

TABLE-1
OPERATING CONDITIONS FOR GFAAS

	Cr	Co	Ni	Cu	Ag	Cd	Pb
Lamp settings wavelength (nm)	357.9	242.5	232.0	324.8	328.1	228.8	283.3
Spectral band width (nm)	0.7	0.2	0.2	0.7	0.7	0.7	0.7
Lamp current (mA)	10	30	25	15	10	6	10
Furnace temperature (ºC)							
Drying 1 (ramp 1 s, hold 5 s)	110	110	110	110	110	110	110
Drying 2 (ramp 5 s, hold 15 s)	130	130	130	130	130	130	130
Ashing (ramp 10 s, hold 30 s)	1000	700	600	700	500	350	600
Atomizing (ramp 0 s, hold 5 s)	2400	2400	2300	2000	1700	1500	1600
Clean-up (ramp 1 s, hold 3 s)	2500	2450	2450	2450	2450	2450	2450

RESULTS AND DISCUSSION

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 is one of the main factor for quantitative recoveries of the analytes[9,13].

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), Ni(II), Ag(I), Co(II), Cu(II), Cd(II) and Pb(II) as QAR chelates on Diaion SP-850 resin is 6.8-10.0. 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.

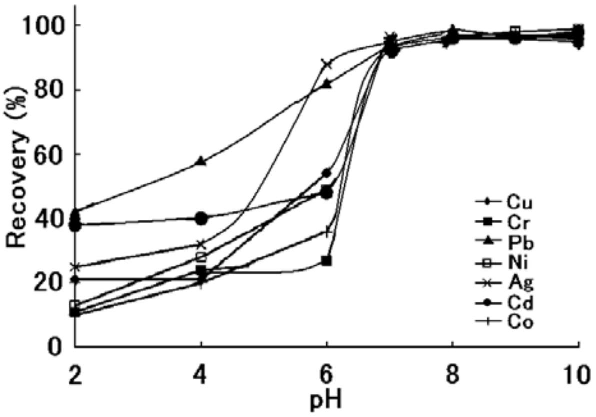

Fig. 2. Influences of pH on the recoveries (ligand: QAR; amounts of analytes: 10 µg Cu, 20 µg Cr, 20 µg Pb, 10 µg Ni, 10 µg Ag, 5 µg Cd, 10 µg Co; eluent: 1.0 mol L^{-1} HNO_3)

Influences of amount of ligand on the recoveries: In order to determine the amounts of QAR required for quantitative recoveries for chromium, nickel, silver, cobalt, copper, cadmium and lead ions, the proposed method was applied, changing QAR amounts at the range of 0-10 mL of 0.1 % solution. The recoveries were not quantitative without QAR. The recovery values of the analyte metal ions increased with increasing amounts of QAR added and reached a constant value with at least 2.5 mL of 0.1 % solution of QAR. On this basis, studies were carried out at QAR amounts of 5.0 mL. This amount of QAR is enough for the separation preconcentration procedure because of the very low level of the investigated metal ion concentrations in real samples.

Effects of the amount of resin: The amounts of solid phase extraction material is another important factor on the column studies for the quantitative recoveries of metal chelates[16,17]. 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 when the resin used above 600 mg. Therefore, in the proposed procedure, 800 mg of Diaion SP-850 resin is recommended.

Solid phase extraction: In order to study the adsorptive capacity of SP-850 resin, batch method was used. To 0.1 g resin was added to 50 mL of solution containing 1 mg of metal ion at pH 8 and QAR existed. After shaking for 1 h, the mixture was filtered. 10 mL of the supernatant solution was diluted to 100 mL and the analyte ions were determined by atomic absorption spectrometry. This procedure was repeated for each analyte ions, separately. The capacity of 1 g of Diaion SP-850 was found 15 mg for chromium, 12 mg for nickel, 20 mg for silver, 18 mg for cobalt, 22 mg for copper, 8 mg for cadmium and 15 mg for lead.

The influence of flow rate on the adsorption of analyte ions was also studied. Flow rate in the range of 2-20 mL min^{-1} had no significant effect on the recoveries of the investigated elements. All subsequent experiments for this study were performed at 10 mL min^{-1} flow rate.

The desorption of the retained analyte metal ions from column was examined using various elution solutions. The quantitative recoveries (> 95 %) were obtained for the investigated elements with 2 mL of 0.5-3.0 mol L^{-1} HNO_3, 3.5 mL of 0.4-3.5 mol L^{-1} HCl, 4 mL of 1.0-3.5 mol L^{-1} H_2SO_4 and 4 mL of 1.0-2.5 mol L^{-1} $HClO_4$. The maximum enrichment factor was achieved when 0.5-3.0 mol L^{-1} HNO_3 was selected as eluent. Therefore, 1 mol L^{-1} HNO_3 was selected as eluent in this experiment.

The studies suggested that it is easier to elute the retained metal ions in the reverse direction in comparison to the forward direction (only 2 mL of eluent was needed when eluted in reverse direction. However, 10 mL of eluent was needed when eluted in forward direction). Thus, it is also recommended to invert the column before elution (Fig. 3).

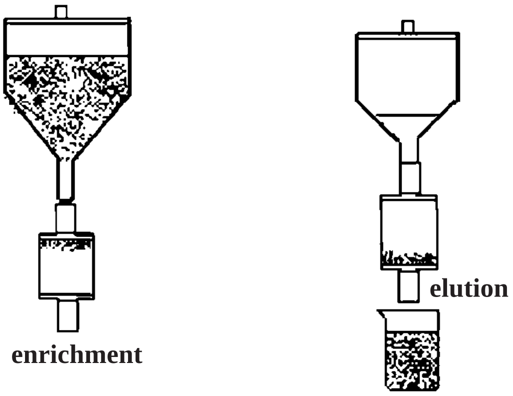

Fig.3. Elution the metal ions in the reverse direction

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 10 mL min^{-1} flow rate. The results are given in Fig. 4. The adsorption of the metal ions was not affected by sample volume below 300 mL. The percent sorption decreased for the analytes above 300 mL. The recoveries of analytes decrease probably due to the excess analytes loaded over the column capacity with increasing sample volume above 300 mL. The adsorbed metals can be eluted with 2 mL of 1 mol L^{-1} HNO_3 and a preconcentration factor of 125 is achieved by this technique.

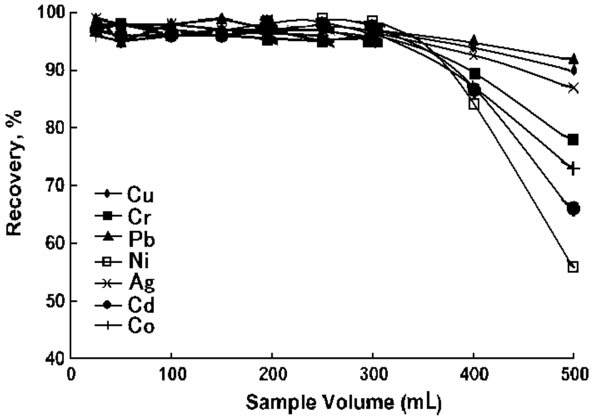

Fig. 4. Effect of the sample volume on the recoveries of analyte ions from the Diaion SP-850 column (N: 4; pH: 8; ligand: QAR; amounts of analytes: 10 µg Cu, 20 µg Cr, 20 µg Pb, 10 µg Ni, 10 µg Ag, 5 µg Cd, 10 µg Co; eluent: 1 mol L^{-1} HNO_3)

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 5000 mg L^{-1} of NaCl, for 2000 mg L^{-1} of Mg^{2+}, for 1000 mg L^{-1} of K^+, Ca^{2+}, SO_4^{2-}, 100 mg L^{-1} for Zn^{2+}, 50 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.

Recovery of spikes from the samples: In order to estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked in water, soil and biological samples. 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 were in the range of 91-106 %. These values were quantitative and it shows that the present method can be applied for the separation/preconcentration of analyte ions. The relative standard deviation for the analyte ions (7 repeat determinations) were below 3.5 %.

Application to real samples: The solid phase extraction procedure presented for chromium, nickel, silver, cobalt, copper, cadmium and lead ions were applied to water, biological and soil samples. The results for biological samples were given in Table-2, for water and soil samples were given in Table-3. For water and soil samples, a standard method using ICP-MS had also been used as reference method and the result are shown in Table-4.

TABLE-2
DETERMINATION RESULTS OF CERTIFIED STANDARD BIOLOGICAL SAMPLES

Samples	Standard value (µg/g)	By this method (µg/g)	RSD % (n = 5)
Rice (GBW08458)	Ag (0.127), As (0.285), B (64.5), Bi (0.342), Ca (2900), Cd (0.218), Ce (1.25), Co (4.71), Cr (3.76), Cu (10.2), Fe (54), Hg (0.086), Mg (360), Mn (22.5), Mo (0.735), Ni (3.83), Pb (0.852), V (2.86), Zn (13.2)	Ag (0.134), Cd (0.201), Co (4.68), Cr (3.86), Cu (10.8), Ni (3.96), Pb (0.846)	≤ 3.5
Human hair (GBW08126)	As (0.121), B (38.4), Bi (0.825), Ce (0.643), Cd (0.528), Co (6.25), Cr (0.816), Cu (11.2), Fe (123), Hg (0.142), Mg (136), Mn (68.2), Ni (5.61), Pb (1.06), Sn (1.24), Se (0.0412), V (3.86), Zn (18.7)	Cd (0.508), Co (6.29), Cr (0.828), Cu (10.5), Ni (5.43), Pb (1.12)	≤ 3.2

TABLE-3
DETERMINATION RESULTS (µg/L) OF THE SAMPLE WITH PRESENT METHOD

Components	Water samples (µg/L)				Soil sample (µg/g)	RSD % (n=7)	Recovery (%)
	Pure water	Well water	Tap water	Lake water			
Ag	8.36	10.2	18.5	35.8	2.01	3.4	93-98
Ni	18.6	25.4	41.2	12.8	8.14	3.0	94-101
Co	22.6	38.2	26.4	53.7	11.8	3.5	92-103
Cu	21.8	32.4	28.5	82.1	27.2	2.8	93-104
Cr	18.6	21.3	31.4	45.2	10.8	3.2	94-102
Cd	2.58	5.42	12.9	28.2	4.52	3.1	93-101
Pb	5.87	18.7	14.3	38.6	8.43	2.9	92-97

TABLE-4
DETERMINATION RESULTS (μg/L) OF THE SAMPLE WITH ICP-MS METHOD

Components	Water samples (μg/L)				Soil sample (μg/g)	RSD % (n=7)	Recovery (%) (n = 5)
	Pure water	Well water	Tap water	Lake water			
Ag	8.11	11.6	21.1	32.8	1.86	3.8	93-96
Ni	21.4	26.8	39.7	12.4	8.25	3.5	89-98
Co	21.8	38.8	27.4	54.6	2.08	3.4	90-102
Cu	22.5	33.4	26.8	81.2	28.2	3.6	91-106
Cr	17.4	19.8	32.8	43.9	11.5	4.1	94-105
Cd	2.64	5.61	13.2	28.4	4.68	3.6	93-101
Pb	5.64	17.8	15.6	3.74	8.56	3.5	92-104

Conclusion

The developed method is successfully employed for analysis of water, soil and geological materials after successful validation. The present method is economic and less time consuming. 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 behaviour. The elution was easily performed with 1.0 mol L^{-1} HNO_3 and the metal ions in 250 mL solution can be concentrated to 2.0 mL, representing an enrichment factor of 125 was achieved. 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[3,4,18-22]. The matrix effects with the method were reasonably tolerable.

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