Column Preconcentration/Separation and Atomic Absorption Spectrometric Determinations of Some Heavy Metals in Table Salt Samples Using Amberlite XAD-1180

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A simple and sensitive solid phase extraction procedure on Amberlite XAD-1180 resin is presented for the determination of chromium, cobalt, manganese and nickel at trace levels by atomic absorption spectrometry. The analyte ions were quantitatively taken at pH 9 by using ammonia/ammonium acetate buffer without any chelating agent. The influences of some analytical parameters such as sample volume, eluent type and flow rates on the retention of Cr, Co, Mn and Ni ions were examined. No influences were observed from the matrix ions of table salt samples. The detection limits for Cr, Co, Mn and Ni were 0.27 μg/g, 0.11 μg/g, 0.13 μg/g and 0.086 μg/g, respectively. The proposed separation-enrichment method was applied for the atomic absorption spectrometric determinations of analyte ions in table salt with satisfactory results (recoveries greater than 95%, relative standard deviations lower than 10%).

Key Words: Determination, Preconcentration, Table Salt Samples, AAS, Amberlite XAD-1180.

Introduction

Trace heavy metal ions in environmental samples including natural waters, biological samples, fertilizers and table salts[1−8] have been repeatedly determined. For this purpose various instrumental techniques including ICP-MS, ICP-AES, spectrophotometry, voltammetry, polarography, x-ray fluorescence spectrometry, and neutron activation analysis have been widely used[8−14]. Atomic absorption spectrometry (AAS) is an important instrumental technique for the determination of trace heavy metal ions because of its low cost and

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short analyzing time[15−17]. However, the main limitations in atomic absorption spectrometric determinations are the interference effects of matrix ions and relatively low levels of analyte ions[17−19]. Preconcentration procedures are applied to samples both to separate analytes from the sample matrix and to concentrate them in a small volume. Prior to AAS determinations, the separation/preconcentration methods including liquid-liquid extraction[20,21], ion-exchange procedures[22,23], membrane filtration[24,25], cloud point extraction[26,27], electro-analytical techniques[28], and solid phase extraction[29−32] are generally used.

The preconcentration and separation methods based on the solid phase extraction of trace heavy metal ions in aqueous solutions are considered to be superior to liquid-liquid extraction[33−35]. Solid phase extraction is a multi-element separation/preconcentration method because of its simplicity, rapidity and ability to attain a high preconcentration factor. In solid phase extraction, various sorbents including activated carbon, C-18, C-60, C-70, Diaion HP-20, Ambersorb 563, chelating resins, silica gel and others[36−41] have been used for the preconcentration/separation of trace heavy metal ions from various media such as seawater and mineral waters, urine and geological samples.

Amberlite XAD adsorption resins have good physical properties such as porosity, uniform pore size distribution, and high surface area as chemically homogeneous non-ionic structures for large amounts of uncharged compounds, and they have been used as solid sorbents for the enrichment/separation of metal complexes[19,42]. Amberlite XAD-1180 is a polystyrene-divinyl benzene copolymer. It has been used for the separation and preconcentration of traces of metal ions in various media including natural waters [43,44].

The aim of the present work is to investigate the optimal analytical conditions, including pH and sample volume, for the preconcentration/separation of Cr, Co, Mn and Ni on Amberlite XAD-1180 without any chelating agent using different buffer solutions.

Experimental

Apparatus

A PerkinElmer Model 3110 atomic absorption spectrometer was used. Studies were carried out in an air/acetylene flame without any background correction. The operating parameters for the working elements were set as recommended by the manufacturers. A Nel pH-900 Model glass-electrode pH meter was employed to measure pH values.

Reagents and solutions

Analytical reagent-grade chemicals were employed for the preparation of all solutions. All aqueous solutions were prepared from double-quartz-distilled water. Stock metal ion solutions, 1000 mg/l (E. Merck, Darmstadt) were diluted daily to obtain reference and working solutions. The calibration curve was established using the standard solutions prepared in 1 M HNO_3 by dilution from stock solutions. The calibration standards were not submitted to the separation/preconcentration procedure.

A phosphate buffer (0.1 M) was prepared by adding an appropriate amount of phosphoric acid (Merck, Darmstadt) to sodium dihydrogen phosphate solution to give a solution of pH 2. Acetate buffers (0.1 M) were prepared by adding an appropriate amount of acetic acid (Merck, Darmstadt) to ammonium acetate solutions to give solutions of pH 4-6 and ammonium ammonia buffer solutions (0.1 M) were prepared by

adding an appropriate amount of ammonia (Merck, Darmstadt) to ammonium chloride solutions to give solutions of pH 8-10.

Amberlite XAD-1180 is a polystyrene divinylbenzene copolymer (surface area: 600 m^2/g, pore diameter: 140 Å). In order to remove organic and inorganic contaminants, Amberlite XAD-1180 adsorption resin (20-50 mesh) (Sigma Chem., St. Louis) was washed successively with methanol, water, 1 M HNO$_3$ in acetone, water, 1 M NaOH and water.

Column preparation

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 Amberlite XAD-1180 resin in water. Prior to use, the resin was preconditioned with buffer solution. After each experiment, the column was rinsed with water and stored for the next experiment.

Separation/preconcentration procedure

The present method was first tested with model solutions. A 40-50 ml of solution containing 10-20 μg of chromium, cobalt, manganese and nickel was brought to the desired pH (between 2 and 10). The column was preconditioned with 10-15 ml of the water brought to the same pH as that of the working solution. The buffered metal solution was passed through the column at a flow rate of 2 ml/min. The sample solution was permitted to flow through the column under gravity. The column was then washed with the same buffer solution as that used for preconditioning. The retained metals on Amberlite XAD-1180 were eluted with 10 ml of 1 M HNO$_3$ in acetone. The eluent was evaporated over a hotplate to near dryness at 35 °C in a hood and was diluted to 5-10 ml with 1 M HNO$_3$. The metal concentrations in the solution were determined by flame AAS.

Recommended procedure for salt samples

For the determination of metal ions in salt samples, 1.0000 g of table salt was dissolved in distilled water and diluted to 25 ml with distilled water. The pH of the solution was adjusted to pH 9 with ammonia/ammonium chloride buffer solution, and the preconcentration procedure was then applied to this solution. The retained metals on Amberlite XAD-1180 were eluted with 10 ml of 1 M HNO$_3$ in acetone. The eluent was evaporated over a hotplate to near dryness at 35 °C in a hood and was diluted to 2.0 ml with 1 M HNO$_3$. The metal concentrations in the final solution were determined by flame AAS.

Results and Discussion

Effect of pH on the recoveries

The influence of pH of the aqueous solution on the retention of chromium, cobalt, manganese and nickel was investigated in the pH range 2-10 by using different buffer solutions. For this purpose, phosphate buffer, ammonium acetate buffers and ammonium chloride buffer solutions were used for pH 2, pH 4-6 and pH 8-10, respectively. The results are depicted in Figure 1. The recovery values of the analyte ions were generally found to be below 30% at the acidic and neutral pH values. The recovery values for chromium ions were quantitative at the pH range of 7.5-10.0. Quantitative recoveries for Mn, Ni and Co were obtained in the

pH range of 8.5-10. The virtually quantitative recoveries for the investigated analyte ions at pH > 8 could result from the formation of hydroxide and amine complexes of the analytes. All subsequent studies were performed at pH 9 with ammonia/ammonium chloride buffer.
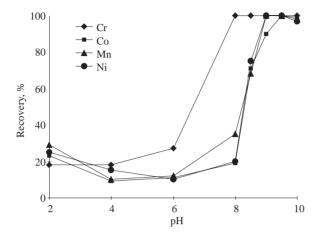

Figure 1. The effect of pH on the retention of analyte ions (N = 3).

Effect of sample volume

The effect of the sample solution volume on the sorption of analyte ions on XAD-1180 column at a 5 ml/min flow rate was studied in the sample volume range of 25-1000 ml. The results are depicted in Figure 2. The adsorptions of analyte metal ions with 500 mg of Amberlite XAD-1180 were not affected in the case of manganese and nickel in the working range of the sample volume. Cobalt and chromium were quantitatively recovered in the sample volume range of 25-200 ml. Above 200 ml, the percentage sorption of cobalt and manganese ions was under 95%.
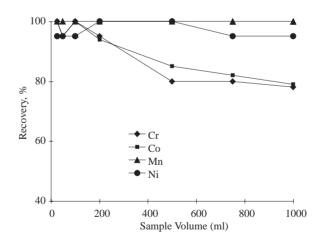

Figure 2. The effects of sample volume on the retentions of analyte ions (N = 3).

Influence of flow rate

The influence of flow rate on the adsorption of analyte ions was studied. Flow rate variations in the range of 1-12 ml/min had no significant effect on the recoveries. All subsequent experiments were performed at a 5 ml/min flow rate.

Effect of resin amount and eluent volume

As in our previous studies[19,42], it was found that 1 M HNO_3 in acetone was the most suitable eluent for the elution of analytes retained using inorganic and organic ligands on Ambertite XAD resins. The minimum volume of 1 M HNO_3 in acetone required for the quantitative elution of the retained analyte complexes was found to be 8.0-10 ml. The quantitative recoveries for all the examined analytes were obtained in the range of 300-600 mg resin. In the light of these results, 500 mg of Amberlite XAD-1180 was used in all experiments.

Influences of the matrix ions

The influences of the matrix ions on the retentions of the investigated analyte ions were examined in the model solutions including each analyte ion. Quantitative recoveries ($> 95\%$) for 20,000 mg/l of NaCl, for 2500 mg/l of K^+, for 2500 mg/l of Mg^+, for 1000 mg/l of Ca^{2+} and for 1000 mg/l of SO_4^{2-} were obtained. The recoveries of sodium, potassium, magnesium and calcium ions were determined using a flame photometer and/or FAAS and they were found to be less than 0.5%.

Analytical performance

The analytical performance of the system for the enrichment of analyte ions was examined. The enrichment factor was 100. The detection limit for chromium, cobalt, manganese and nickel based on three times the standard deviations of the blank was 0.27 μg/g, 0.11 μg/g, 0.13 μg/g and 0.086 μg/g, respectively (N = 20). The relative standard deviations of determinations were below 10%.

Recovery studies

For recovery studies, various amounts of analyte ions were spiked into a table salt sample. The results are given in Table 1. The results obtained in these experiments demonstrate that the presence of NaCl in the samples had no significant effect on the recovery of analyte ions.

Analyte ions in real samples

The preconcentration method proposed was applied to the flame atomic absorption spectrometric determination of analyte ions from some table salt samples purchased from a local market. The results are given in Table 2.

Conclusion

The proposed method is simple, fast and economical. For quantitative recoveries of analyte ions on Amberlite XAD-1180, it is sufficient to adjust the pH of the aqueous solutions to pH 9 with ammonia/ammonium buffer without any chelating agent. The Amberlite XAD-1180 resin column can be used at least 500 times for the quantitative recovery of analyte ions. The procedure was characterized by good reproducibility and accuracy. The presented preconcentration procedure shows high tolerance to interference from matrix ions. The potential use of the presented method may be in the preconcentration of analyte ions in other high salt content samples, including mineral waters and dialysis concentrates.

Table 1. Analysis of table salt spiked with analyte ions. (Sample amount: 1.0 g, Final volume: 10 ml, N = 4).

Element	Added, μg	Found, μg x ± sd*	Recovery, %
Cr	0	N.D.	-
	2.5	2.5 ± 0.1	100
	5	5.0 ± 0.1	100
	10	9.6 ± 0.1	96
Co	0	N.D.	-
	1	1.00 ± 0.04	100
	2.5	2.4 ± 0.1	96
	5	4.9 ± 0.2	98
Mn	0	N.D.	-
	1	0.91 ±0.03	91
	2.5	2.4 ± 0.1	96
	5	4.5 ± 0.2	90
Ni	0	N.D.	-
	1	1.0 ± 0.1	100
	2.5	2.3 ± 0.2	92
	5	4.7 ± 0.2	94

*sd: standard deviation

N.D.: not detected

Table 2. Chromium, cobalt, manganese and nickel concentrations in table salts.

Sample	Concentration (μg/g)*			
	Cr	Co	Mn	Ni
I	2.05 ± 0.03	1.10 ± 0.09	N.D.	0.87 ± 0.06
II	1.57 ± 0.06	0.89 ± 0.04	N.D.	N.D.
III	N.D.	1.05 ± 0.15	N.D.	0.91 ± 0.03
IV	2.80 ± 0.12	1.11 ± 0.13	N.D.	1.24 ± 0.04

*±ts/$\sqrt{N}$, n: 5, P: 0.05,

Sample Amount: 1.0 g, Final Volume: 2.0 ml

N.D.: not detected

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