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Sorbent extraction of 4-(2-thiazolylazo) resorcinol (TAR)–metal chelates on Diaion SP-850 adsorption resin in order to preconcentration/separation

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ABSTRACT

A sensitive and simple separation-enrichment technique for the determination of trace amounts of some metal ions was described. By the passage of aqueous samples including Fe(III), Cu(II), Ni(II) and Co(II) ions–4-(2-thiazolylazo) resorcinol (TAR) chelates through Diaion SP-850 column, metal chelates adsorb quantitatively and almost all matrix elements were passed through the column to drain. Quantitative recoveries for analyte ions were obtained at pH 6 at 3 ml/min flow rate of sample solution in 0.5 g Diaion SP-850 filled glass column. The investigations were also carried out on the interferences from other concomitant ions in the sorption process. After optimization, a preconcentration factor of 60 and a recovery values as % higher than 95 were achieved. The detection limit ($N = 10$, 3 sigma) for Fe(III), Cu(II), Ni(II) and Co(II) were found as 3.6, 1.1, 2.8 and 2.3 $\mu g\, l^{-1}$, respectively. The applications to the determination of iron, copper, nickel and cobalt in real samples and the validation of the analytical methodology employing NIST SRM 1549 milk powder, NIST RM 8433 Corn Bran and BCR 144R Sewage sludge of domestic origin as certified reference materials were performed.

1. Introduction

The accumulation of heavy metals like Cd, Pb, Cu, Zn, Cr, Fe and Ni in environmental and food samples is an important problem for human beings [1–6]. Instrumental techniques such as atomic absorption spectrometry, atomic emission spectrometry, inductively coupled plasma-mass spectrometry, electroanalytical techniques [7–13] are used for the determination of heavy metals in real samples. However, there is two main problems in these determinations are lower elements concentrations than the qualification limits of the instrument and the negative or positive effects of concomitant ions [14–19]. Generally in order to solve these problems, separation–preconcentration methods including solvent extraction, cloud point extraction, membrane filtration, flotation, electro-deposition and other methods are used by the researchers [20–27].

Solid phase extraction is a popular technique for separation and preconcentration of heavy metal ions [28–31]. It very important and need much more attention for the preconcentration and selective separation of trace heavy metal ions from the environmental samples because of some its some advantages including its simplicity, to obtain high preconcentration factor, environmental friendly, etc. [32–35]. Some adsorbents including zeolites [36], activated carbon [37,38], amberlite resins [39–41], chromosorb [42], clinoptilolite [43], etc. have been used for the solid phase extraction of traces heavy metals in environmental samples prior to their instrumental analysis.

4-(2-Thiazolylazo) resorcinol (TAR) is a spectrophotometric reagent for the determination of metal ions [44,45]. Its metal chelates have been also used for the preconcentration of metal ions by solid phase extraction [46–48]. According to our literature survey, 4-(2-thiazolylazo) resorcinol (TAR)–metal chelates–Diaion SP-850 combination is not used for the preconcentration–separation of traces metal ions in the food and environmental samples.

The aim of presented work was to develop a solid phase extraction method for the separation and preconcentration of Fe(III), Cu(II), Ni(II) and Co(II) ions as 4-(2-thiazolylazo) resorcinol chelates prior to atomic absorption spectrometric determination. The chemical variables affecting the sensitivity of the presented preconcentration procedure were studied in detail.

2. Experimental

2.1. Apparatus

The instrumental detection system used in this work was a PerkinElmer Model 3110 flame atomic absorption spectrometer (Norwalk, CT, USA). All measurements were carried out in an air/acetylene flame. 10 cm long slot-burner heads, hollow cathode lamps were used. The operating parameters for working elements

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were set as recommended by the manufacturer. All measurements were carried out without background correction. A pH meter, Nel pH-900 (Ankara, Turkey) Model glass-electrode was employed for measuring pH values in the aqueous phase. The pure water used all experiments was purified in a Human model RO 180 (HUMAN Corp., Seoul, Korea), resulting water with a conductivity of 1 μS cm^{-1}.

2.2. Reagents

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 of investigated analyte elements prepared in 1 mol l^{-1} HNO_3 by dilution from 1000 mg l^{-1} stock solutions (Merck). The calibration standards for analytes were not submitted to the separation–preconcentration procedure.

The chelating agent was 4-(2-thiazolylazo) resorcinol (Merck, Darmstadt, Germany). 0.1% (m/v) of TAR solution was daily prepared in a water/ethanol (25/75, v/v) mixture. The certified reference materials from various origins (NIST SRM 1549 milk powder, NIST RM 8433 Corn Bran and BCR 144R Sewage sludge of domestic origin) were used in the experiments.

Diaion SP-850 is an aromatic type adsorbent. It is based on crosslinked polystyrenic matrix. Its surface area is 1000 m^2 g^{-1}. Diaion SP-850 is widely used in different industrial fields; extraction of antibiotic intermediates from fermentation broth, separation-enrichment of peptides, or food additives, debittering of citrus juice [49,50]. Diaion SP-850 was purchased from Sigma Chem. Co. St. Louis, MO, USA. 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 500 mg of Diaion SP-850 in water suspension was 10 cm long and 1.0 cm in diameter. The bed height in the column was approximately 2.0 cm. The resin on the column was preconditioned with pH 6.0 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. 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.

2.3. Model works

Model solutions containing analyte ions were adjusted to desired pH. Then 4-(2-thiazolylazo) resorcinol was added to form the metal-4-(2-thiazolylazo) resorcinol chelates. After 5–10 min, the solution was loaded to the Diaion SP-850 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. Subsequently, metal-4-(2-thiazolylazo) resorcinol chelates retained on Diaion SP-850, were eluted at 4 ml min^{-1} of flow rate with 10 ml of 1 M HNO_3 in acetone. The effluent was evaporated to near dryness and made up to 5.0 ml with 1 M HNO_3. The levels of the investigated analyte ions in the samples were determined by AAS.

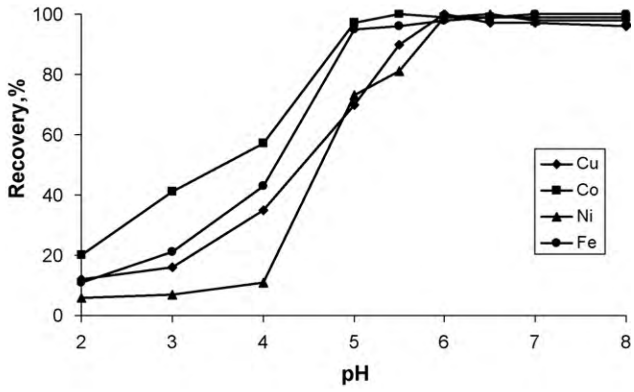

Fig. 1. The influence of the pH on the recovery of analyte ions (chelating agent: TAR, eluent: 1 mol l^{-1} HNO_3 in acetone, $N = 3$).

2.4. Analysis of real samples

0.5 g of certified reference material (NIST SRM 1549 milk powder, NIST RM 8433 Corn Bran and BCR 144R Sewage sludge of domestic origin), black tea and rice samples was digested with 10 ml concentrated HNO_3 at 95 °C. The mixture was evaporated almost to dryness and mixed with 3 ml of H_2O_2. Then it was again evaporated to dryness. After evaporation 8–9 ml of distilled water was added and the sample was mixed. The resulting mixture was filtered through a blue band filter paper. The filtrate was diluted to 25 ml with distilled water. Then the procedure given in Section 2.3 was applied. The analytes in final solution were determined with flame AAS.

The water sample analyzed was filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pH of the samples was adjusted to 6. Then TAR solution was added. The sample was passed through the column. The TAR chelates adsorbed on column were eluted with 1 M HNO_3 in acetone. The effluent was evaporated to near dryness and made up to 5.0 ml with 1 M HNO_3. The levels of the investigated analyte ions in the samples were determined by AAS.

3. Results and discussion

3.1. Effect of pH

The pH of the aqueous phase is one of the most important factors in a solid phase extraction procedure for the quantitative recoveries [51–53]. The influences of the pH on Fe(III), Cu(II), Ni(II) and Co(II)–TAR chelates on the sorption onto Diaion SP-850 resin was investigated over the range from 2.0 to 8.0 keeping other parameters constant. The results are depicted in Fig. 1. The analyte ions were effectively adsorbed in pH range 6.0–8.0. It was possible to carry out the determination of both ions at pH 6.0. In order to control the pH during the analytical procedure, it was adjusted to 6.0 with a buffer solution of acetate/acetic acid.

3.2. Influences of the amounts of ligand

The effects of the amounts of TAR on the quantitative recoveries of the analyte ions on Diaion SP-850 were also examined in the range of 0.0–1.0 mg of TAR. The results are depicted in Fig. 2. The recoveries of nickel and cobalt were below 40% without TAR. Over 0.25 and 0.50 mg of TAR, cobalt and nickel were quantitatively adsorbed, respectively. Copper and iron ions were quantitatively recovered without ligand and with ligand. In order to recover all analyte ions quantitatively with together, all further studies were performed by using 0.50 mg of TAR.