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Analytical Methods

Synthesis and application of a new functionalized resin for use in an on-line, solid phase extraction system for the determination of trace elements in waters and reference cereal materials by flame atomic absorption spectrometry

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ABSTRACT

The synthesis and characterization of the resin Amberlite XAD-4 functionalized with 2,6-pyridinedicarboxaldehyde and its application in an on-line system for the preconcentration of cadmium, cobalt, copper, lead and manganese prior to determination using flame atomic absorption spectrometry (FAAS) is proposed. Metal ions retained on the modified resin were eluted using 1.0 mol L^{-1} HNO_3 solution and aspirated directly to the nebulizer–burner system of a FAAS instrument using a flow injection system. Detection limits (3σ) were determined to be 0.13 μg L^{-1} for Cd, 0.29 μg L^{-1} for Cu, 0.23 μg L^{-1} for Mn, 0.58 μg L^{-1} for Co and 2.19 μg L^{-1} for Pb using a 10 mL of water sample loading volume. The limits of detection would be 100 times higher with units of μg kg^{-1} for the solid samples in which their dilution ratios as (volume/weight) were 100. Enrichment factors ranged from 23.6 to 28.9 (for Co and Mn, respectively). The proposed method was successfully applied to determination of the analytes in natural water samples and certified reference materials.

1. Introduction

Heavy metals are ingested by humans mainly through their diet. The determination of the concentrations of these heavy metals in food and waters is very important because of their role in our body. Some of the heavy metals are essential to life whereas others are toxic even at very low concentrations. In this regard, the determination of trace metals in environmental samples including natural waters has been undertaken routinely to determine the level of pollution which could create health problems (Arain et al., 2009; Baig et al., 2009; Kazi et al., 2009; Kazi et al., 2010; Khoder, Hassan, & El-Abssawy, 2010; Soylak & Dogan, 1996).

Since the worldwide consumption of cereal products is so high, their potential role as vehicles of major, minor and trace elements, as well as heavy metals, in the human diet have received considerable attention in the last few decades. Wheat is a valuable commodity on the global market because it is one of the most consumed cereals. Analyses for metals in wheat flours are therefore important from both a nutritional and a toxicological point of view (Kirchmann, Mattson, & Eriksson, 2009; Vrcek & Vrcek, 2012). In this sense, lead and cadmium levels in food products are controlled by Regulation 1881/2006 of the 2006 European Union Council, which set maximum levels in cereals of 0.2 and 0.1 mg kg^{-1} for lead and cadmium, respectively (EC, 2006). The World Health Organization (WHO) has given the permissible limit of Cd and Cu in foods of 0.3 and 40 mg kg^{-1}, respectively (WHO, 1999).

Atomic spectrometric methods are employed extensively for the quantification of metal species (Pereira & Arruda, 2003). In particular, FAAS has been one of the most commonly applied methods for the determination of inorganic elements in a variety of samples. However, the main problem with this technique is its relatively poor sensitivity for some elements meaning that it cannot determine metals at the μg L^{-1} level. To improve FAAS sensitivity, preconcentration procedures are required (Goswami & Singh, 2002). Preconcentration techniques such as liquid–liquid extraction, precipitation and solid phase extraction (SPE) are frequently used prior to detection. Solid phase extraction has found increasing application for the preconcentration of trace metals and the elimination of matrix interferences prior to AAS determination. This is because it offers advantages such as improved accuracy, high enrichment factor and low consumption of organic solvents. Despite all of these advantages, the batch-mode of SPE can be time-consuming, it can require large sample or reagent volumes and has the potential for

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contamination and analyte loss (Liu, Su, Wu, & Pu, 2002). These batch-mode drawbacks can be overcome, to a great extent, by applying on-line methods. Flow injection (FI) matrix separation and analyte preconcentration coupled to FAAS has become a popular method for the determination of trace metals because of its low cost and high sample throughput (Zhang, Pu, Liu, Sun, & Su, 2002). Up to now, various SPE sorbents have been employed for the preconcentration and determination of trace elements in batch and FI modes. Multi-walled carbon nanotubes (Tuzen & Soylak, 2007), microcrystalline naphthalene (Dadfarnia, Shabani, & Dehghani, 2006), polyurethane foam (Dos Santos, Santos, & Ferreira, 2003), silica-gel (Fan, Wu, Wei, Peng, & Peng, 2007), styrene–divinylbenzene (Amberlite XAD) (Divrikli, Akdogan, Soylak, & Elci, 2007; Dogru, Gul-Guven, & Erdogan, 2007), chitosan (Sabarudin, Noguchi, Oshima, Higuchi, & Motomizu, 2007), chelating resins (Martins, Da Silva, Laranjeira, & De Favere, 2005; Yebra, Carro, Enriquez, Moreno-Cid, & Garcia, 2001) and various polymers have been used as solid-phase materials. Amberlite XAD resins have been widely used to develop several chelating materials for preconcentration procedures because of their good chemical and physical properties such as porosity, high surface area, durability and purity (Baytak & Turker, 2005; Dos Santos, Herrmann, Ribeiro, & Curtius, 2005; Kara, Fisher, & Hill, 2005; Lemos & Baliza, 2005). Selective chelating resins with high metal ion uptake capacity may be designed by immobilizing a small sized polydentate ligand moiety onto Amberlite XAD resins either through surface sorption or through chemical modification. Chemical modification involves the insertion of an appropriate functional group (linkage/spacer group) such as –N=N–, –CH_2– or –N=C– on the surface of the polymeric support and then immobilization of a particular ligand by a condensation reaction or coupling reaction. Resins of moderate to high porosity have an increased surface area and hence more of the ligand may be attached. Subsequently, the amount of metal ion that may be retained on the chelating sites is also increased.

In this work, 2,6-pyridinedicarboxaldehyde has been covalently bonded with the commercially available polystyrene-divinyl benzene co-polymer, Amberlite XAD-4 through a –C=N– group resulting in a chelating resin. This resin was packed in a mini-column and used in flow injection system for the on-line FAAS determination of cadmium(II), cobalt(II), copper(II), lead(II) and manganese(II) ions. The influence of chemicals (sample pH, nitric acid concentration) and flow (sample and eluent flow rates) variables that could affect the performance of this system were investigated and optimized. This system was then applied to the analysis of natural water and acid digests of cereal samples. The method developed was validated by analyzing several certified reference materials.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent grade. Ultra-pure water with a resistivity of 18.2 MΩ cm was used for dilutions. The laboratory glassware used was soaked in 10% (v/v) nitric acid overnight and then rinsed several times with ultra-pure water before use. Stock solutions (1000 mg L^{-1}) of the analytes were prepared by dissolving appropriate amounts of nitrate salts in 1% HNO_3. These stock standards were then used to prepare calibration standards by serial dilution on a daily basis prior to use. Ammonium acetate buffer solution (pH 7.0) was prepared using pure acetic acid (Riedel-de Haen, 100%) and ammonium acetate (Sigma–Aldrich, >98%). Ammoniacal buffer solution (pH 9.0) was prepared using pure ammonium chloride (Sigma–Aldrich, >99.5%) and ammonia solution (Riedel-de Haen, 26%). Amberlite XAD-4 and sodium hydroxide from Fluka, 2,6-pyridinedicarboxaldehyde, tin (II) chloride and ethanol obtained from Sigma–Aldrich and nitric acid, sulfuric acid and hydrochloric acid obtained from Merck were used for the synthesis of the modified resin. Five certified reference materials were used in this study. These were an aqueous standard QCS-19 (High Purity Standard, Charleston, USA), rice flour unpolished high level of Cd (NIES 10c) (National Institute for Environmental Studies NIES, Japan), wheat flour (NBS 1567a) (National Bureau of Standards, USA), estuarine water (SLEW-3) and a riverine water (SRLS-5) (both National Research Council, Canada).

2.2. Instruments

A Perkin Elmer AAnalyst 200 flame atomic absorption spectrometer equipped with appropriate hollow cathode lamps and an air-acetylene flame (air and acetylene flow rate 10 L min^{-1} and 2.5 L min^{-1}, respectively) as the atomiser was used as the detector throughout. The wavelengths used for monitoring Cd, Pb, Cu, Mn and Co were 228.80, 283.31, 324.75, 279.48 and 240.73 nm, respectively. Infrared (IR) spectra were recorded using a Perkin Elmer Spectrum 65 FT-IR spectrometer. A digital pH-meter (Hanna Instruments model HI 4522, Romania) with a combined glass electrode was used for all pH measurements. The flow rate of samples and eluents through the columns was controlled using a peristaltic pump (Watson Marlow 323 SD, Falmouth, UK).

2.3. Synthesis of the 2,6-pyridinedicarboxaldehyde functionalized Amberlite XAD-4

The 2,6-pyridinedicarboxaldehyde functionalized Amberlite XAD-4 resin was synthesized by nitrating 5 g of Amberlite XAD-4 copolymer with a mixture of 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4 with constant stirring in a 60 °C water bath for 1 h. The reaction mixture was poured into ice–water and the nitrated resin filtered off and then washed with ultra-pure water until the effluents reached neutral pH. The nitrated resin was refluxed at 90 °C for 10 h with a mixture of 40 g of $SnCl_2$, 45 mL of concentrated HCl and 50 mL of ethanol. The product was filtered off, washed with ultra-pure water and then with 2 M NaOH to release the amino polymer through the reaction shown below (Kara et al., 2005).

$$(RNH_3)_2SnCl_6 + 8OH^- \rightarrow 2RNH_2 + SnO_3^{2-} + 6Cl^- + 5H_2O$$

The amino polymer (2.5 g) was refluxed with 1 g of 2,6-pyridinedicarboxaldehyde in 100 mL of ethanol for 4 h. The modified resin was filtered off and washed with ethanol. The repeat unit of the 2,6-pyridinedicarboxaldehyde functionalized Amberlite XAD-4 is shown in Fig. 1.

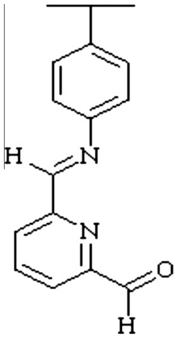

Fig. 1. Structure of 2,6-pyridinedicarboxaldehyde functionalized Amberlite XAD-4.