



Polyurethane foam functionalized with phenylfluorone for online preconcentration and determination of copper and cadmium in water samples by flame atomic absorption spectrometry

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ABSTRACT

In this work, a polyurethane foam (PUF) functionalized with phenylfluorone (PUF-PF) was packed in a minicolumn and used as an on-line preconcentration system for cadmium and copper determination in water samples. The experimental conditions (both chemical and physical) were optimized to achieve the highest sensitivity. A study of possible ion interference on the retention of cadmium and copper was also performed. The enrichment factors obtained were 14 and 16 for copper and cadmium, respectively, using a preconcentration time of 1 min. The proposed system allowed the determination of metals with limits of detection (3σ) of 0.8 and 0.3 $\mu\text{g L}^{-1}$ for Cu(II) and Cd(II), respectively. The precision of the procedures was also calculated as 7.6% for Cu(II) (at 25 $\mu\text{g L}^{-1}$) and 4.0% for Cd(II) (at 10 $\mu\text{g L}^{-1}$). The limits of quantification obtained were 2.6 and 0.8 $\mu\text{g L}^{-1}$ for Cu(II) and Cd(II), respectively. Cadmium and copper contents in water samples (from rivers and swimming pools) were determined by applying the proposed procedure. In these samples, recovery tests were conducted in order to evaluate the accuracy of the method; the recovery percentages varied between 83 and 109%.

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1. Introduction

Metals are some of the main causes of pollution in fresh waters and may be introduced into water ecosystems by natural or artificial means. Natural means include rain and the release/conveyance of bedrock or other soil compartments, while artificial means include anthropogenic sources, sewers *in natura* in urban centers, industrial wastes, agricultural activities and wastes from mineral and digging sites [1].

The quality of hydrological resources is of great importance in providing data relevant to environmental contamination [2]. In this sense, the resolution no. 357 from the Brazilian Council of Environment (CONAMA) [3] defines fresh water as water with salinity equal to or lower than 0.5‰ and establishes the maximum acceptable limit of copper and cadmium in these waters the range of 9.0 to 13.0 $\mu\text{g L}^{-1}$ and 1.0 to 10.0 $\mu\text{g L}^{-1}$, respectively, according to the water body classification.

In Brazil, pool waters are regulated by other agency, the Brazilian National Agency of Sanitary Inspection (ANVISA), which has established limits for physicochemical parameters such as pH, purity and the concentration of residual chloride in order to maintain the quality of pool waters [4]. ANVISA does not regulate the concentration of metals present in such an environment. Therefore, the results found in this paper

assessing copper and cadmium concentrations in pool water were related to the maximum limits stipulated by Brazilian Council of Environment (CONAMA) resolution no. 357 (2005) [3] for recreational waters involving primary contact, such as swimming, water-skiing and diving, where the possibility of human ingestion of water is high. For this type of classification, the maximum concentrations allowed are 9.0 $\mu\text{g L}^{-1}$ and 1.0 $\mu\text{g L}^{-1}$ for copper and cadmium, respectively. In this context, it is of scientific, environmental and social importance to develop methodologies for the determination of trace concentrations of cadmium and copper in river and pool water samples.

The main objectives of solid phase extraction (SPE) are the removal of interferents from the source, and the preconcentration and isolation of analytes. It is one of the most commonly used techniques for extraction and/or preconcentration of different analytes, allowing their quantification in very low concentrations using different analytical techniques such as high performance liquid chromatography (HPLC), flame atomic absorption spectrometry (FAAS) or inductively coupled plasma optical emission spectrometry (ICP OES), among others [5].

The conventional SPE manual procedures, although efficient, are usually slow and tedious, and require large quantities of samples and reagents. Besides, these methods are, in general, susceptible to contamination and analyte loss. Therefore, the search for alternatives with a lower environmental impact has included the application of techniques such as flow injection analysis (FIA) that has many positive qualities,

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such as low consumption of reagents, minimal production of waste and reduced human participation [6].

Many systems for on-line preconcentration systems using PUF as a sorbent have been proposed since 1998 [7]. Several papers report the use of impregnated/functionalized PUF in on-line systems and the coupling with techniques such as molecular absorption spectrophotometry [8–9], FAAS [10–16] and ICP OES [17–21]. The polyurethane foam structure allows its easy use as a sorbent in preconcentration on-line systems and provides advantages over other adsorbents such as lower resistance to flow, lower pressure, lower risk of leaks, easy disposal, low cost and good resistance to changes in pH [16].

This paper presents the development of a method for Cu(II) and Cd(II) determination in samples of river and swimming pool waters using FAAS after on-line preconcentration on polyurethane foam functionalized with phenylfluorone.

2. Experimental

2.1. Apparatus

A Varian model AA240FS (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer was used for the determination of cadmium and copper. Cadmium and copper hollow cathode lamps were run at 4.0 mA of current, which was the condition suggested by the manufacturer. Cadmium signals were measured at 288.8 nm, using a spectral bandwidth of 0.5 nm, and copper signals were measured at 324.8 nm, also using a spectral bandwidth of 0.5 nm. An air (13.5 L min⁻¹)/acetylene (2.0 L min⁻¹) flame was employed and the background correction was performed with a deuterium lamp. Peak height was used as the quantitative variable.

An Agilent Cary 5000 spectrophotometer (Palo Alto, CA, USA) and an Agilent Cary 630 Fourier Transform Infrared Spectrometer (Palo Alto, CA, USA) were employed for the acquisition of diffuse reflectance and infrared spectrum of the functionalized foam, respectively. The FTIR spectrum was obtained with an attenuated total reflection (ATR) accessory.

A Gilson Minipuls 3 peristaltic pump (Villiers-le Bel, France) furnished with Tygon™ tubes was used to propel all solutions. A six-way manual valve from Rheodyne, model 5041, was used to select preconcentration/elution steps.

A Digimed (São Paulo, Brazil) pH meter, model DM-22, equipped with a combined glass electrode, was employed to measure the pH of the solutions.

2.2. Reagents and solutions

All solutions used in this work were prepared with analytical grade reagents used without further purification. Ultrapure water with resistivity of 18.2 MΩ cm, obtained using a Direct-Q 3 system from Millipore (Milford, MA, USA), was used in the preparation of all solutions.

The 1000 mg L⁻¹ copper and cadmium stock solutions were supplied by Tedia (Fairfield, OH, USA). Standard solutions with different concentrations were prepared by appropriate dilution of the stock solutions just before use.

To elute the metals from the solid phase, a 1.0 mol L⁻¹ hydrochloric acid solution was prepared from the dilution of the concentrated acid (Tedia, Fairfield, OH, USA) in ultrapure water.

For the functionalization reaction of PUF, a 7.0 mol L⁻¹ sodium nitrite (Sigma-Aldrich, St Louis, MO, USA) and a 0.07 mol L⁻¹ phenylfluorone (Acros Organics, Saint Louis, EUA) solutions were prepared from dissolution of the reagents in ultrapure water and a 1.0 mol L⁻¹ sodium hydroxide solution (Vetec, Duque de Caxias, RJ, Brazil), respectively. Solutions of hydrochloric acid were also prepared at the concentrations of 6.0 mol L⁻¹ and 0.1 mol L⁻¹ by dilution of the concentrated HCl (Tedia, Fairfield, OH, USA) in ultrapure water.

A 0.1 mol L⁻¹ Britton Robinson buffer solution was prepared by dissolving 1.54 g of boric acid (Caledon, Georgetown, ON, Canada), 1.40 mL of acetic acid (Vetec, Duque de Caxias, RJ, Brazil) and 1.70 mL of phosphoric acid (Vetec, Duque de Caxias, RJ, Brazil) in approximately 200 mL of ultrapure water. Afterwards, the pH of the solution was adjusted to 9.0 by adding NaOH 6 mol L⁻¹ (Vetec, Duque de Caxias, RJ, Brazil), and the volume was completed to 250 mL in a volumetric flask. In order to perform the pH study, the same procedure was performed to adjust the pH in the range of 4 to 10.

2.3. Synthesis of polyurethane foam functionalized with phenylfluorone

One gram of foam was soaked in a 6.0 mol L⁻¹ hydrochloric acid solution for 60 min to liberate the maximum number of free amino groups (-NH₂) by the hydrolysis of free isocyanate groups (-NCO) present in the foam. Then, after the foam was washed with water, it was placed in a 0.1 mol L⁻¹ HCl solution (100 mL) and then cooled in an ice bath. The foam was diazotized by the drop wise addition of 10 mL of a 7 mol L⁻¹ of sodium nitrite solution to the cold solution containing the foam, and stirred vigorously until a yellow color appeared due to the formation of diazonium chloride. Then, it was left for 60 min at a temperature below 3 °C. Next, 10 mL of a 0.07 mol L⁻¹ phenylfluorone solution in 1.0 mol L⁻¹ NaOH was added gradually with continuous stirring while keeping the solution cooled below 3 °C. The color of the foam turned red. The red foam was placed in a fridge for 24 h. Finally, the sorbent was washed with ultrapure water and then left at room temperature in a dry and clean place free from dust. In basic medium, the foam bonded with phenylfluorone had a purple color. However, in acidic medium, it had a dark red color [22].

2.4. Minicolumn preparation

The minicolumn was prepared using a 3.0 cm long Tygon™ tube with a diameter of 0.5 cm. The minicolumn was filled with 40 mg of PUF functionalized with phenylfluorone (PUF-PF). Only one minicolumn was used throughout the experiments reported in this work.

2.5. Sample preparation

All samples were collected in low-density polyethylene flasks, acidified to pH 2.0 with nitric acid and stored in a refrigerator (temperature of 4 °C) to avoid changes in their physicochemical properties. At the time of measurement, an aliquot of the sample (49 mL) was transferred to a 50 mL volumetric flask, which was completed with 1.0 mL of buffer solution (pH 9.0).

2.6. Flow injection system

A diagram of the on-line preconcentration system is shown in Fig. 1. The flow system was made up of a peristaltic pump fitted with Tygon™ tubes, a six-way valve and a minicolumn packed with polyurethane foam resin functionalized with phenylfluorone, coupled to a flame atomic absorption spectrometer.

A sample solution (S) containing Cd(II) and Cu(II) was pumped at 8.0 mL min⁻¹ through the minicolumn that retained the metallic cations. By switching the injection valve, a stream of 1.0 mol L⁻¹ hydrochloric acid (E) that flowed at 6.0 mL min⁻¹ displaced the Cd(II) and Cu(II) ions from solid phase. The eluate was taken directly to the nebulizer of the spectrometer. It was not necessary to recondition the minicolumn at the end of each cycle since the samples were buffered before preconcentration.

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