



## Preconcentration and determination of Cu(II) in a fresh water sample using modified silica gel as a solid-phase extraction adsorbent

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### ABSTRACT

A method was developed to attach 4-amino-2-mercaptopyrimidine (AMP) onto silica gel surface and to determine trace metals. The surface functionalization reaction was performed with a silylant agent, chloropropyltrimethoxysilane (Si-CPTS), and the product, Si-AMP, was characterized by FT-IR and elemental analysis to evaluate the surface modification. The functionalized silica was applied in the sorption of Cu(II) ions from an aqueous medium. The series of adsorption isotherms were adjusted to a modified Langmuir equation and the maximum number of moles of adsorbed copper was  $0.447 \text{ mmol g}^{-1}$ . The modified material was placed in a preconcentration system, where it reached an approximately 20-fold enrichment factor using 5 mg of Si-AMP. The proposed method was applied in the preconcentration and determination of Cu(II) in a fresh water sample from the Paraná river and was validated through a comparative analysis of a standard reference material (1643e).

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### 1. Introduction

In the last two decades, metal ions have been the focus of numerous studies of contaminants in aquatic environments. Their occurrence has raised major public health concerns due to their increasing presence in aquatic compartments and organisms [1–3]. Numerous harmful health effects, such as high blood pressure, and kidney and nervous system impairment, have been imputed to metal ions such as cadmium and lead, and all these metals, including copper, are considered toxic to aquatic biota [3]. In response to these concerns, several research groups have focused on the development of adsorbent materials that can be applied in combination with techniques such as atomic absorption spectrometry (AAS) and inductively coupled plasma optical emission (ICP OES) [4–10]. In general, these materials must be susceptible to surface modifications through chemical reactions with silica, cellulose, etc. Among the many types of solid phases used in solid-phase extraction (SPE), silica gel is the most common due to its advantageous characteristics of thermal stability, no swelling and hydroxyl reactive

groups [11,12]. To achieve considerable metal sorption capacity, molecules with basic centers are attached onto the surfaces of materials directly or through a silylant agent [13–16]. The basic centers consist of oxygen, nitrogen, sulfur, and other atoms that can act as electron-pair donors to coordinate metals ions in solution. The selectivity of the modified surface toward metal ions depends on several factors such as the size of the modifier, activity of the loaded group, and the characteristics of soft and hard acids and bases [4,14,15,17–19].

In this work, the chelating molecule 4-amino-2-mercaptopyrimidine (AMP) was attached onto a silica gel surface through an organosilane reaction, and characterized by FT-IR spectroscopy and elemental analysis. The material was applied in the extraction and preconcentration of Cu(II) in a fresh water sample taken from the Paraná river, Ilha Solteira, SP, Brazil. The sampling point was chosen taking into account the high Cu(II) concentration in surface sediment determined in previous work [20]. The accuracy of the proposed method was evaluated by comparison against a certified reference material (SRM 1643e).

### 2. Materials and methods

#### 2.1. Preparation of 4-amino-2-mercaptopyrimidine modified silica gel

Silica gel (Merck-60,  $\text{Ø} = 40 \mu\text{m}$ ) was previously activated at 423 K under vacuum for 24 h. 5 g of activated silica gel

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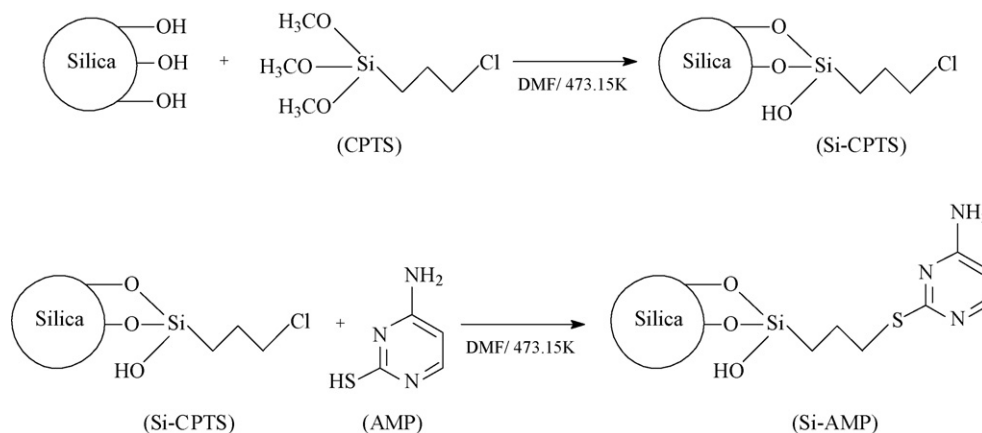


Fig. 1. Two-step functionalization reaction of silica gel with 4-amino-2-mercaptopyrimidine molecule ligand.

was suspended in 30 mL of dimethylformamide (DMF) under reflux, mechanical stirring and nitrogen atmosphere. 3.4 mL of 3-chloropropyltrimethoxysilane (Aldrich – Analytical grade) was then added to this suspension and the mixture was kept under reflux for 72 h. The reaction product was filtered, washed with acetone and ethanol and then dried.

The resulting solid, called Si-CPTS, was suspended in 30 mL of DMF under reflux, mechanical stirring and nitrogen atmosphere. 2.4 g of the 4-amino-2-mercaptopyrimidine molecule ligand was added to this mixture and the reaction was performed for 72 h at 423 K. The resulting product, called Si-AMP, was washed with acetone and ethanol. The two-step reaction is depicted in Fig. 1.

## 2.2. Instrumentation

The amount of molecule ligand (AMP) attached to the silica surface was determined using a Thermo Finnigan Flash 1112 Series EA CHNS elemental analyzer. Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were recorded on a Nicolet Nexus 670 spectrometer equipped with a Smart Collector, using 200 scans and  $4\text{ cm}^{-1}$  resolution. The metals were determined using a Perkin Elmer Analyst 700 atomic absorption spectrometer in the flame mode (FAAS).

## 2.3. Batch procedure

An aliquot of metal salt solution ( $5.0 \times 10^{-3}\text{ mol L}^{-1}$ ) and 0.05 mg of Si-AMP were placed in a 250 mL conical flask and the mixture was kept under mechanical stirring. This batch procedure was performed using different stirring times (1–40 min), pH (1–6) and different aliquots of metal salt solution (5–50 mL). The supernatant concentration of Cu(II) was determined directly by FAAS after stepwise dilution, and the number of divalent metal moles separated by unit mass of Si-AMP,  $N_f$  ( $\text{mmol g}^{-1}$ ) was calculated based on the following equation:

$$N_f = \frac{n_i - n_s}{m}, \quad (1)$$

where  $n_i$  is the initial mole number of the metal ion in solution phase,  $n_s$  is the metal mole number at equilibrium after adsorption, and  $m$  is the mass (g) of adsorbent (Si-AMP).

## 2.4. Preconcentration procedure

Before placing the sample in the system, it was subjected to an optimization procedure, in which the investigated parameters were eluant concentrations ranging from 0.5 to 2.0  $\text{mol L}^{-1}$  of chloric acid, and sample and eluant flow rates of 0.5–3.0  $\text{mL min}^{-1}$ . All

the parameters were optimized using 1.0 mL of eluant, and the preconcentration volume was 20.0 mL of Cu(II) solution at  $0.05\text{ mg L}^{-1}$ . The eluate was collected in polyethylene flasks, followed by Cu(II) determination by flame atomic absorption spectrometry. The Si-AMP column was prepared by packing 5.0 mg of material in a tygon tube with 2.86 mm of internal diameter.

## 2.5. Preparation of fresh water sample and certified reference material

The river water sample was previously filtered through a  $0.45\text{ }\mu\text{m}$  membrane, after which 50 mL was transferred to a conical flask and kept on a hot plate until it dried. The resulting residue was then dissolved in a solution prepared with 5 mL of concentrated nitric acid and 500  $\mu\text{L}$  of hydrogen peroxide kept at  $100^\circ\text{C}$  for 30 min. The digested water sample was adjusted to pH 5 by adding a sodium hydroxide solution, after which the extract was transferred to a 50 mL volumetric flask. The results were compared with those obtained by graphite furnace atomic absorption spectrometry (GFAAS) to estimate the contribution of dissolved organic substances that can be associated with copper ions [21]. In addition, to certify the method using a continuous flow, aliquots of 20.0 mL of SRM material were subjected to the preconcentration system and the eluates collected were analyzed by flame atomic absorption spectrometry.

## 3. Results

### 3.1. Characterization

The 4-amino-2-mercaptopyrimidine compound was chosen for anchorage onto the silica surface due to the potential evidenced by its nitrogenated and sulfurated groups. The percentage of nitrogen determined by elemental analysis for Si-AMP was found to be 1.03. Based on this value, the concentration of molecule ligand anchored to the silica surface was calculated as  $0.245\text{ mmol g}^{-1}$  of material. The infrared spectra of solid samples shown in Fig. 2 confirmed the functionalization reaction of the silica surface by the AMP molecule ligand. The main changes observed in the Si-AMP spectrum in the region of  $3338\text{ cm}^{-1}$  were attributed to the N–H stretching mode from primary amine bonded to a carbon atom in the aromatic ring, while those at  $1588$  and  $1540\text{ cm}^{-1}$  were attributed to the N–H bending (scissoring) vibrations of primary amines. C–N stretching vibration from nitrogen atom in the aromatic ring could not be detected due to silica matrix absorption. Other absorption bands, which appeared in the region of  $2900$  and  $2850\text{ cm}^{-1}$ , were attributed respectively to asymmetrical ( $\nu_{\text{as}}\text{CH}_2$ ) and sym-

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