

Synthesis and application of chloromethylated polystyrene modified with 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone (PPDOT) as a new sorbent for the on-line preconcentration and determination of copper in water, soil, and food samples by FAAS

Mansour Arab Chamjangali*, Ghadamali Bagherian, Ali Mokhlesian, Bahram Bahramian

College of Chemistry, Shahrood University of Technology, P.O. Box 36155-316, Shahrood, Iran

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ABSTRACT

In this paper, we report a simple and sensitive on-line solid phase extraction system for the preconcentration and determination of Cu(II) by flame atomic absorption spectrometry (FAAS). This method is based upon the on-line retention of copper at pH 5.0 on a minicolumn packed with chloromethylated polystyrene modified by 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone (PPDOT) as a new solid-phase extraction (SPE) sorbent. The retained Cu(II) ions were eluted with 1.0 M HNO₃, and transported directly to FAAS for determination. Several chemical and flow variables were studied and optimized for a quantitative preconcentration and determination of copper(II). At the optimized conditions, for preconcentration of 10.0 mL of a sample solution, a linear calibration graph was obtained over the concentration range of 3.00–120.0 μg L⁻¹ for Cu(II). The limit of detection (3σ), limit of quantification (10σ), and enrichment factor are 0.56 μg L⁻¹, 2.0 μg L⁻¹ and 41, respectively. The relative standard deviation (*n* = 6) at 20 μg L⁻¹ of Cu(II) is 2.0%. This method could be applied for determination of trace amounts of Cu(II) in water, soil, and food samples with satisfactory results.

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1. Introduction

Due to the great production and industrial use of copper, water can be a potential source for an intense copper exposition. A copper concentration more than 1 μg mL⁻¹ can impart a bitter taste to water. Copper concentration in potable water is usually very low ($\leq 20 \mu\text{g L}^{-1}$) [1]. Copper content in lake and river waters varies in the range of 0.5–1000 μg L⁻¹ with an average value of 10 μg L⁻¹ [2].

Copper is an essential micronutrient required for normal metabolism of many living organisms only at low levels, nearly to 40 μg L⁻¹ [3,4]. While copper is essential, it can be toxic at a high level. A large oral dose of copper is suspected to cause infant liver damage, and after mercury it is highly toxic for drinking water [5,6]. Copper can inhibit the activity of dihydrophilhydratase, an enzyme involved in haemopoiesis. Symptoms of copper poisoning are very similar to those produced by arsenic [7]. Therefore, the precise and accurate determination of trace amounts of copper is an important part of the studies in analytical chemistry.

Flame atomic absorption spectrometry (FAAS) and spectrophotometry are relatively simple and available techniques in many routine laboratories for copper determination [8–10]. However, direct determination of trace amounts of copper in complicated materials is usually difficult owing to matrix interferences and/or insufficient detection power. To solve these problems, preconcentration and matrix elimination is usually required. In the last few years many efforts have been made in the analytical chemistry area for developing selective and sensitive methodologies suitable for trace determination of copper individually or simultaneously with other heavy metals in different matrices. In this context, flow injection analysis (FIA) systems have been successfully coupled with solid-phase extraction (SPE) for preconcentration/separation of copper with several types of modified and non-modified solid sorbents. Some of these are multi-walled carbon nanotubes (MWNts) [11], octadecyl functional groups bonded to silica gel and C-18 [12–17], alumina coated [18,19], modified silica gel [20,21], synthetic zeolite [22], and knotted reactor [23–25]. Another approach employed in on-line SPE systems is the application of functionalized polymeric resins. In this case, some functionalized polymeric solid supports such as polystyrene-divinylbenzene (PS-DVB) polymer, Amberlite XAD-2 [26–28], XAD-4 [29], and polyurethane foam (PUF) [30,31] are good alternatives to achieve very versatile sys-

* Corresponding author. Tel.: +98 273 3395441.

E-mail addresses: marab@shahroodut.ac.ir, arabe51@yahoo.com (M.A. Chamjangali).

tems for preconcentration and determination of copper in various samples.

Polystyrene is another class of hydrophobic polymer materials with advantages of low cost, high porosity and thus highly available surface area, and stability in acidic or basic media. In our previous works we reported the application of functionalized polystyrene with an N_3O_2 Schiff base as an efficient solid-phase sorbent for the on-line preconcentration and determination of Cd(II) and Co(II) [32,33].

1-Phenyl-1,2-propanedione-2-oxime thiosemicarbazone (PPDOT) is a chromogenic reagent reacting with the following heavy metal ions: Cu(II), Ni(II), Co(II), Zn(II), Fe(II), Fe(III), and Ag(I) [34]. PPDOT has been used as a chelating reagent in UV-visible spectrophotometric determination of Ni(II), Co(II), and Cu(II) [34,35]. Considering the well-documented selectivity of the ligand PPDOT towards copper ions [35], here we report a rapid, highly selective, and efficient on-line separation and preconcentration system for determination of traces of copper in water, soil, and food samples. In this approach, chloromethylated polystyrene functionalized with PPDOT is used as solid phase. To the best of our knowledge, this is the first report on the use of polystyrene functionalized with PPDOT as a sorbent in the solid phase preconcentration and determination of metal ions.

2. Experimental

2.1. Apparatus

The flow system (Fig. 1) comprised a variable speed 12-channel peristaltic pump (Heidolph, Model 5201) equipped with Tygon tubes. A home-made polyethylene column (2.5 mm i.d., 9.0 cm long), and a six-way rotary injection valve (Rheodyne, Model 5011) were used. Other parts of the system were connected using PTFE tubing (1.3 mm i.d.), provided from Supelco. All atomic absorption measurements were performed on a Shimadzu Model AA-670 flame atomic absorption spectrometer equipped with an air-acetylene flame and a copper hollow cathode lamp. The equipment was operated at the standard conditions recommended by the manufacturer. The wavelength, slit width, and burner height had conventional values. The aspiration rate of the nebulizer was about 3.0 mL min^{-1} . A CHN analyzer Perkin Elmer (Model 2400, Series II) was used to determine the C, H, and N percentages of the modified chloromethylated polystyrene. FT-IR spectra ($4000\text{--}500 \text{ cm}^{-1}$; KBr pellets) were recorded on a Bruker Model vertex 70) FT-IR spectrophotometer. A Philips scanning electron microscope (Model XL-30) was used to record the surface images. To record the UV-visible spectra, a Shimadzu UV-160 spectrophotometer with 1.0 cm quartz cells was used. The pH measurements were performed using a Metrohm (Model 691) digital pH-meter equipped with a combined glass-Ag/AgCl electrode.

2.2. Reagents and solutions

All the chemicals used were of analytical reagent grade, manufactured by Merck. To prepare the solutions, doubly distilled water was used. 1.0 g L^{-1} of Cu(II) stock solution was prepared by dissolving appropriate amount of copper nitrate in a 100-mL volumetric flask. The solution obtained was standardized by a known method [36]. Working standard solutions of copper(II) were prepared by appropriate dilution of the stock solution. Phosphate buffer solutions with the pH range of 3.0–9.0 were prepared by mixing appropriate volumes of the solutions H_3PO_4 (1.0 M), NaH_2PO_4 (1.0 M), and K_2HPO_4 (1.0 M). Citrate buffer solution of pH

5.0 was prepared by mixing sodium hydroxide (1.0 M) and citric acid (1.0 M). Acetate buffer solution of pH 5.0 was prepared by mixing sodium hydroxide (1.0 M) and acetic acid (1.0 M). The pH values for all the buffer solutions were controlled using a pH-meter during their preparation. The eluent solution, 1.0 M HNO_3 , was prepared by appropriate dilution of concentrated nitric acid (Merck) with water. Chloromethylated polystyrene (cross-linked with 2% divinylbenzene, 4–5% Cl content, 1.14–1.40 mmol Cl/g) was purchased from Merck and used for preparation of the sorbent.

2.3. Preparation of PPDOT

The ligand PPDOT was prepared according to a previously reported procedure [34]. It was a yellow-colored solid with a decomposition temperature of 190°C . It was slightly soluble in water and soluble in dimethyl formamide (DMF) and ethylenediamine. The structural formula of PPDOT prepared was confirmed by the IR spectra obtained using a potassium bromide disc. The IR spectral data shows characteristic absorption bands in wave number, cm^{-1} , corresponding to the following functional groups: --OH (3410), --NH (3342 and 3245), --C=N (1615), and --C=S (1204).

2.4. Preparation of chloromethylated polystyrene functionalized with PPDOT (PS-PPDOT)

5.0 mmol of PPDOT was added to a 250-mL round bottom flask equipped with a magnetic stirrer bar containing 100 mL of DMF and chloromethylated polystyrene (2 g, 1.25 mmol/g of Cl). The reaction mixture was stirred for 24 h at 100°C . After cooling, the reaction mixture was filtered and washed thoroughly with DMF, and dried in vacuum for 12 h. The resin obtained was characterized by FT-IR spectroscopy, elemental analysis, and SEM images.

2.5. Preparation of microcolumn

The microcolumn used for preconcentration of analyte was prepared by packing 240 mg of PS-PPDOT resin into a glass tube with 2.5 mm i.d. and 9.0 cm length. After packing, the two ends of column were blocked by glass wool. The column prepared was washed with HNO_3 (2.0 M) and then with water before use.

2.6. General procedure for on-line preconcentration and determination

Preconcentration and determination of Cu(II) was carried out using a three line FI-manifold (Fig. 1) and a three-step procedure. At the preconcentration step (Fig. 1a), a stream of the sample was selected by rotation of valve V_1 and an aliquot of 10.0 mL of sample or standard solution containing Cu(II) and buffered at pH 5.0 was passed through a 9.0 cm minicolumn packed with 240 mg of PS-PPDOT at flow rate of 2.5 mL min^{-1} for 240 s, and copper ions were adsorbed on the sorbent. In the washing step (Fig. 1b), selection valve V_1 was rotated to another position, and doubly distilled water was directed to the minicolumn at flow rate of 2.5 mL min^{-1} for 20 s in order to remove the contaminants weakly adsorbed on the sorbent. In the third step (Fig. 1c), selection valve V_2 was rotated, and a stream of HNO_3 (1.0 M) was directed to the minicolumn at the flow rate of 3.0 mL min^{-1} for 20 s for quantitative elution of adsorbed Cu(II). The eluted Cu(II) ions were continuously transported to FAAS, and the transient signal was recorded. Peak height (absorbance) of the recorded peak was used for quantification of Cu(II).

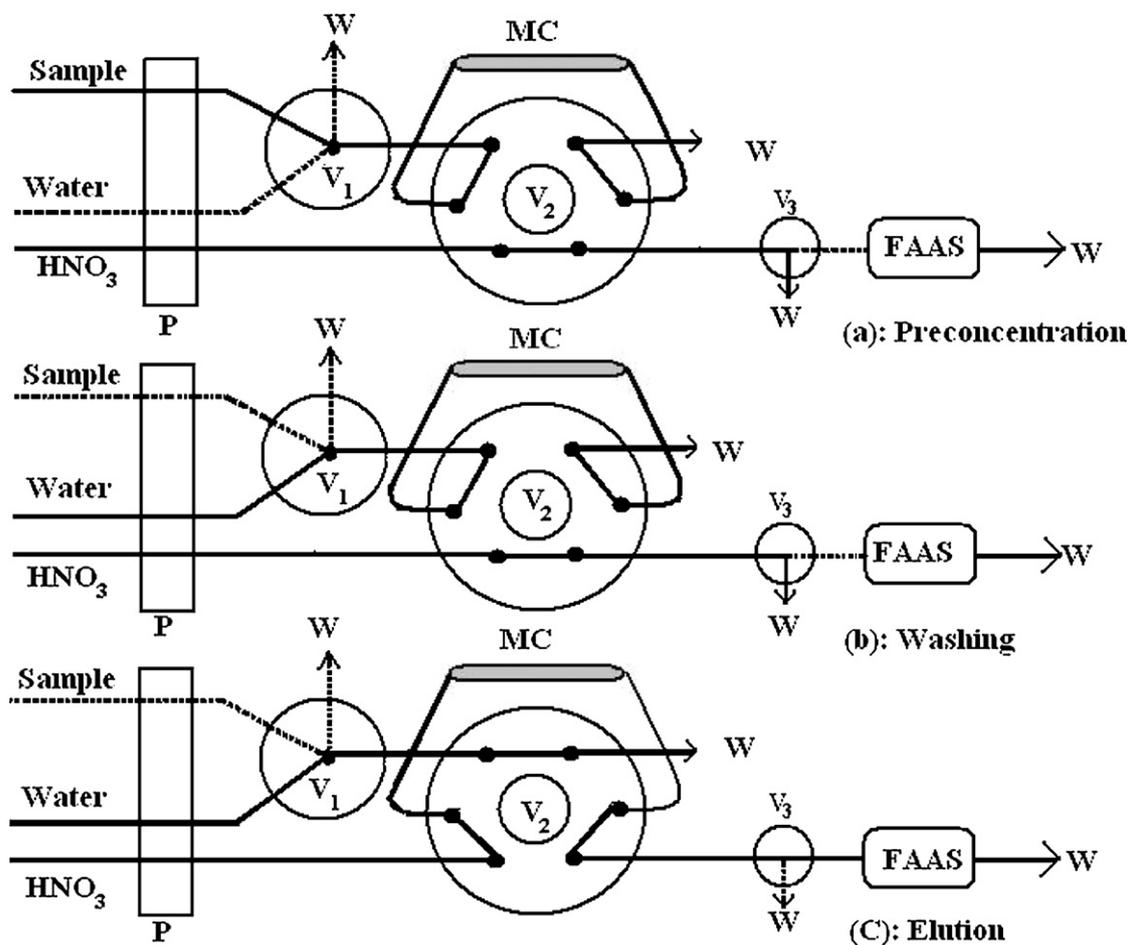


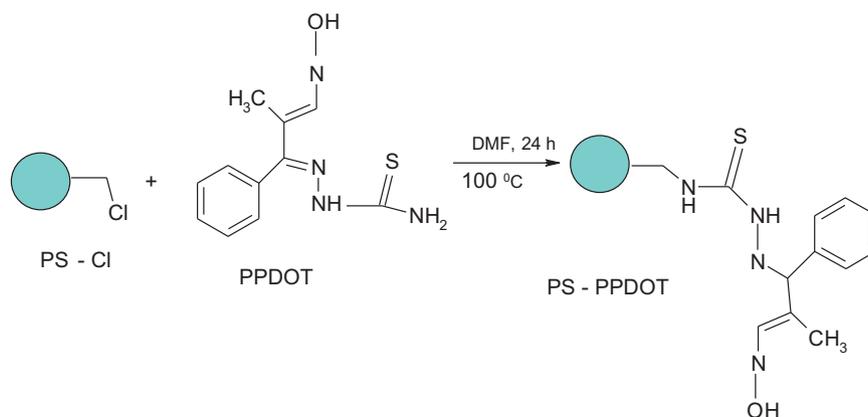
Fig. 1. Schematic diagram for FI-manifold: (a) preconcentration, (b) washing, and (c) elution steps. P: peristaltic pump, V_1 , V_2 and V_3 , selection valves, and W: waste.

2.7. Recovery study

For recovery test, 10.0 mL of a $20.0 \mu\text{g L}^{-1}$ Cu(II) solution was enriched under the optimum conditions using manifold, as shown in Fig. 1. Elution was performed by passing HNO_3 (1.0 M) through the microcolumn. Exactly 1.0 mL of the concentrate containing eluted Cu(II) ions was continuously collected at the end of column. The copper in this solution was then determined by direct aspiration to FAAS. The recovery was defined as the ratio between the copper mass in the concentrate after elution and that in the original sample solution.

3. Results and discussion

It is well-known that PPDOT has a high selectivity towards copper ions due to the larger formation constant of Cu(II)-PPDOT complex ($K_f = 8.25 \times 10^7$) [34]. In addition, chloromethylated polystyrene (2% DVB) as a SPE solid support is a good alternative polymeric material due to its inexpensiveness, ready availability, mechanical robustness, and satisfactory functionalization ability [32,33]. Thus we decided to examine capability of polystyrene functionalized with PPDOT (PS-PPDOT) as a new sorbent for the on-line preconcentration and determination of copper ions. The



Scheme 1. Synthesis of PS-PPDOT resin, and its proposed structure.

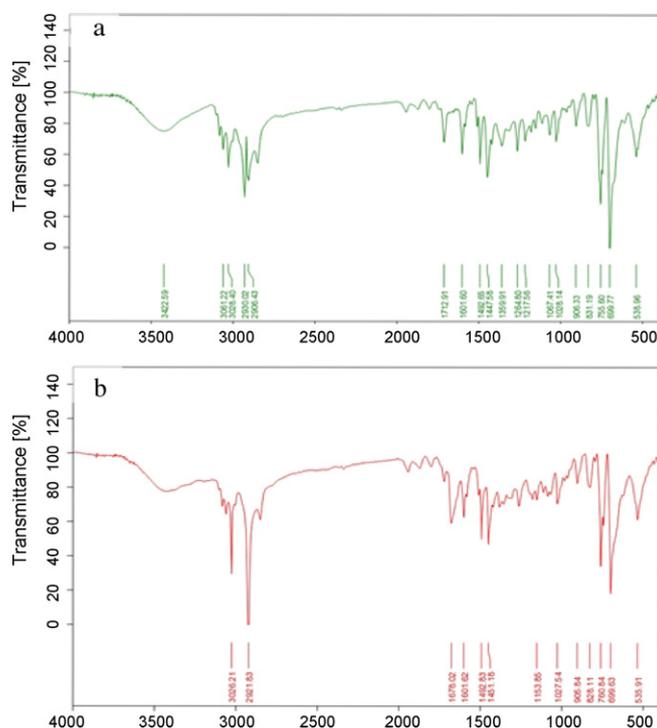


Fig. 2. IR spectra for (a) PS-Cl and (b) PS-PPDOT.

resin could easily be synthesized through the reaction shown in Scheme 1.

In this approach, PPDOT is attached via a covalent bond to a pendant chloromethyl group on the surface of the polymer resin particles. The results obtained from elemental analysis shows the nitrogen content of PS-PPDOT to be about 4.76%, which indicates that about 65% of the total chlorines are substituted by amines. To follow the reaction, FT-IR spectra of the starting polymer (PS-Cl) and product (PS-PPDOT) were recorded (Fig. 2). Comparing the IR spectra for the starting polymer (Fig. 2a) and PS-PPDOT resin (Fig. 2b) indicates that the peak located at 1264 cm^{-1} , corresponding to vibration of C-Cl bond in $-\text{CH}_2\text{Cl}$ groups in the starting polymer, is seen as a very weak band in the IR spectrum of PS-PPDOT. In addition, vibration bands for azomethine C=N bond ($\nu = 1678\text{ cm}^{-1}$) appears in the IR spectrum of PS-PPDOT. These data confirm the immobilization of PPDOT on the polymeric support via a covalent bond. SEMs were recorded for a single bead of pure PS-Cl (Fig. 3a) and the polymer-anchored ligand (PS-PPDOT) (Fig. 3b) in order to observe the morphological changes. As expected, the pure polystyrene bead had a smooth surface, while the PS-PPDOT bead showed roughening of the top layer, which is another evidence for the loading of the ligand on the support.

3.1. Optimization of variables

3.1.1. Effect of pH and buffer type

The pH of the solutions has a critical role in the complex formation reaction between Cu(II) and PPDOT on the surface of polystyrene. Effect of pH on the sorption of copper was investigated in the pH range of 3.0–9.0 using phosphate buffers. The pH values for sample solutions containing $20.0\text{ }\mu\text{g L}^{-1}$ Cu(II) were adjusted at desired values using suitable phosphate buffer solutions. Then 10.0 mL of sample solutions were passed through a 5.0 cm minicolumn packed with PS-PPDOT resins (140 mg) with a flow rate of 3.0 mL min^{-1} . The adsorbed Cu(II) was eluted by a stream of HNO_3 (2.0 M) with a flow rate of 3.0 mL min^{-1} . According to the results shown in Fig. 4, maximum absorbance and sorption efficiency of

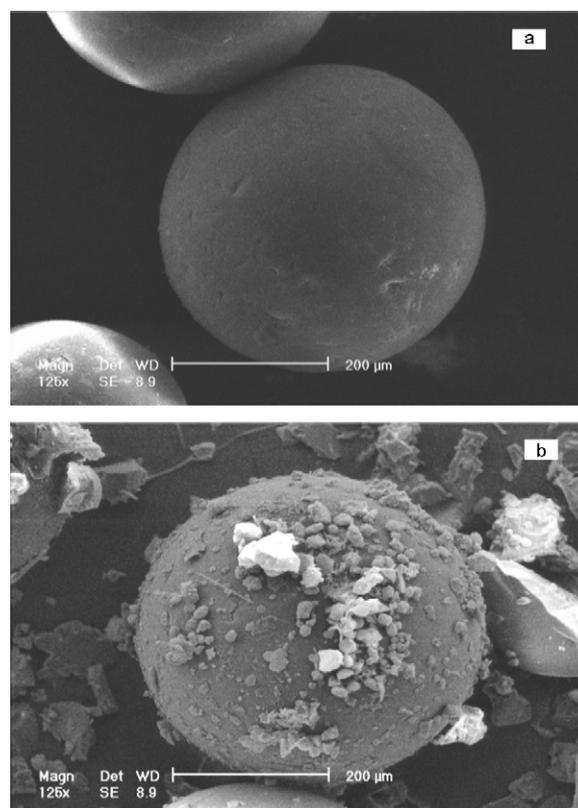


Fig. 3. SEM images for (a) pure chloromethylated polystyrene and (b) polymer-anchored ligand (PS-PPDOT).

PS-PPDOT was achieved at pH 5.0. The decrease in the efficiency at pH values higher and lower than 5.0 is probably due to non-complete complex formation between copper ions and PS-PPDOT. At pH values lower than 4.8, electron donor groups in PPDOT are protonated, and at pH values higher than 5.2, the possible formation of hydroxy species of Cu(II) compete with the formation of Cu(II)-PPDOT complex. Effect of buffer composition on absorbance signal was also investigated using the acetate, citrate, and phosphate buffer solutions with the same pH of 5.0. The results show that among the citrate, acetate, and phosphate buffers, the acetate buffer has maximum sensitivity and recovery. Citrate buffer causes

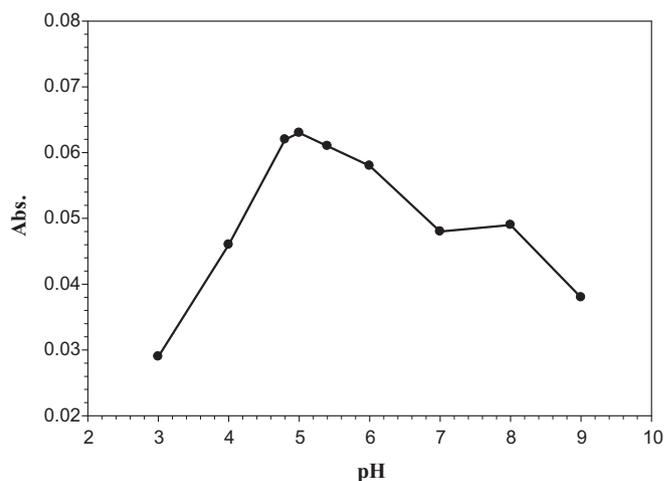


Fig. 4. Effect of pH on the sensitivity. Conditions: pre-concentration of 10.0 mL of $20.0\text{ }\mu\text{g L}^{-1}$ Cu(II) solution with flow rate of 3.0 mL min^{-1} on a 5.0 cm minicolumn and elution with HNO_3 (2.0 M) with flow rate of 3.0 mL min^{-1} .

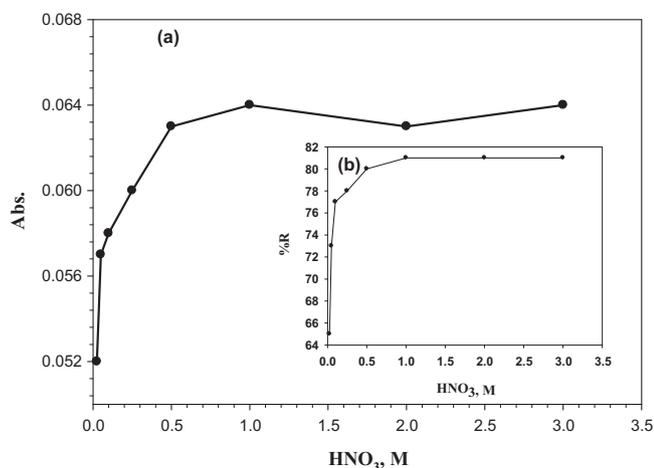


Fig. 5. Effect of eluent concentration on the (a) absorbance and (b) recovery. Conditions: preconcentration of 10.0 mL of $20.0 \mu\text{g L}^{-1}$ Cu(II) solution buffered at pH = 5.0 with flow rate of 3.0 mL min^{-1} on a 5.0 cm minicolumn and elution with HNO_3 at flow rate of 3.0 mL min^{-1} .

about 75% reduction in the analytical signal (with respect to the acetate buffer) due to the formation of copper–citrate complexes of Cu(II). On the other hand, phosphate ions compete with the complex formation reaction through the possible formation of a precipitate, leading to a sensible signal depression ($\sim 15\%$). Thus all sample and standard solutions were buffered at pH 5.0 by addition of 5.0 mL of the acetate buffer to 50 mL of sample solutions.

3.1.2. Type and concentration of eluent

Preliminary experiments showed that elution of adsorbed copper ions could be done by breaking the metal–chelate bond in acidic media. To choose the eluent, sulfuric acid, hydrochloric acid, and nitric acid with the same hydronium ion concentration of 2.0 M were used for desorption of the copper ions. The results showed that all the tested mineral acids had the same elution ability and sensitivity. Since nitrate ion is chemically inert relative to sulfate and chloride ions, nitric acid was selected as the eluent for elution of Cu(II) from the minicolumn. The effect of nitric acid concentration was studied in the range of 0.025–3.0 M. According to the results shown in Fig. 5, with increase in the nitric acid concentration up to 0.50 M, both absorbance and recovery values increase and then remain constant at higher concentrations. Thus nitric acid (1.0 M) was chosen as eluent in order to ensure complete elution of the total Cu(II) retained from minicolumn even at high concentrations of copper.

3.1.3. Influence of sample rate flow

Influence of sample flow rate on the on-line solid phase extraction systems is very important, because it regulates the maximum mass transfer from liquid to solid phase. Thus the influence of this parameter had to be studied carefully in order to regulate an optimum sample flow rate that permits a maximum mass transfer from liquid to solid phase without loss of analytical throughput. Effect of the sample flow rate was checked from 1.2 to 5.6 mL min^{-1} . According to the results (Fig. 6), it is clear that the absorbance signals are constant in the range of 1.0–2.5 mL min^{-1} . On the other hand, a graduate decrease in the response and retention efficiency is observable when the sample flow rate increases more than 2.5 mL min^{-1} . This is due to this fact that the kinetic of the complex formation of Cu(II) is not very fast, and contact times associated with applying flow rates higher than 2.5 mL min^{-1} are not sufficient for complete sorption of Cu(II). Therefore, for the sample precon-

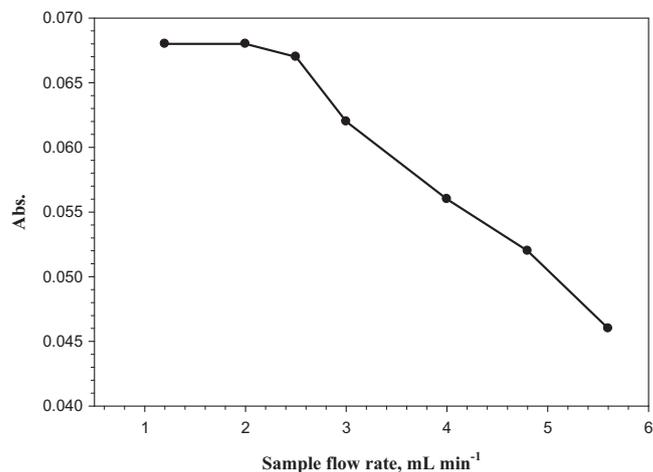


Fig. 6. Effect of sample flow rate on the sensitivity. Conditions: preconcentration of 10.0 mL of $20.0 \mu\text{g L}^{-1}$ Cu(II) solutions buffered at pH = 5.0 on a 5.0 cm minicolumn and elution with HNO_3 (1.0 M) at flow rate of 3.0 mL min^{-1} .

centration step, a flow rate of 2.5 mL min^{-1} was selected as the best one.

3.1.4. Influence of nitric acid (eluent) flow rate

Influence of nitric acid (eluent) flow rate on the analyte desorption from the minicolumn was investigated within the range of 1.2– 5.5 mL min^{-1} . As shown in Fig. 7, maximum absorbance is achieved within the range of 2.0– 3.5 mL min^{-1} . The decrease in the analytical signal at eluent flow rates higher than 3.5 mL min^{-1} is probably due to slow elution kinetic. However, because of the compatibility between the elution and nebulization flow rates, a flow rate of 3.0 mL min^{-1} was selected for elution of the adsorbed Cu(II).

3.1.5. Effect of amount of sorbent

Effect of the amount of sorbent on the analytical signal was evaluated at different values between 56 and 240 mg of the sorbent. In this study, 10.0 mL of sample solutions containing $20.0 \mu\text{g L}^{-1}$ of Cu(II) was passed through columns packed with different amounts of resin at flow rate of 2.5 mL min^{-1} . The retained Cu(II) ions

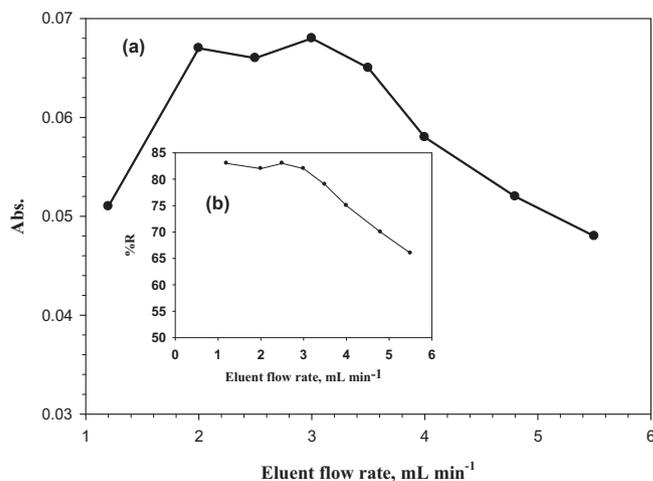


Fig. 7. Effect of eluent flow rate on the (a) absorbance and (b) recovery. Conditions: preconcentration of 10.0 mL of $20.0 \mu\text{g L}^{-1}$ Cu(II) solutions buffered at pH = 5.0 with flow rate of 2.5 mL min^{-1} on a 5.0 cm minicolumn and elution with HNO_3 (1.0 M).

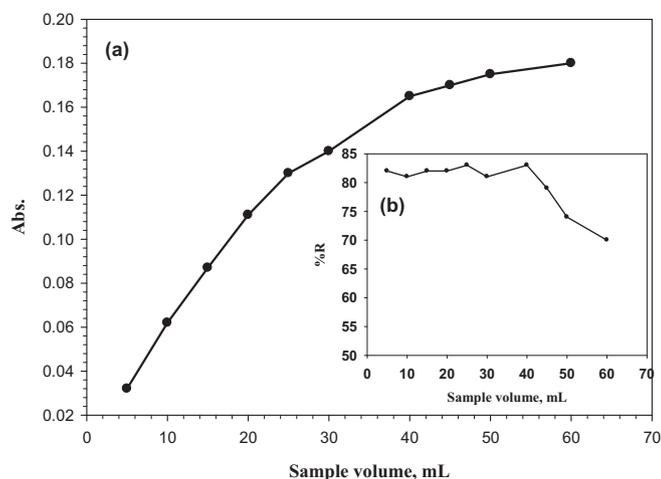


Fig. 8. Effect of preconcentration volume on the (a) absorbance and (b) recovery. Conditions: preconcentration of $10.0 \mu\text{g L}^{-1}$ Cu(II) solution buffered at pH = 5.0 with flow rate of 2.5 mL min^{-1} on a 9.0 cm minicolumn and elution with HNO_3 (1.0 M) at flow rate of 3.0 mL min^{-1} .

were desorbed by elution with nitric acid (1.0 M) at flow rate of 3.0 mL min^{-1} . The results obtained showed a progressive increase in the retention of analyte (recovery) up to 140 mg of sorbent. Above 140 mg , the recovery was high ($\sim 83\%$) and constant. In the amounts lower than 140 mg , the sorbent was insufficient for complete retention of Cu(II) ions, and about 140 mg of the sorbent was enough to retain $0.20 \mu\text{g}$ of Cu(II) ions from 10.0 mL of sample solutions. However, 240 mg of resin (corresponding to 9.0 cm packed length of column) was used in order to ensure maximum retention of copper ions at higher concentrations.

3.1.6. Effect of sample volume (loading time)

Effect of sample volume (loading time) on the absorption signal was tested in the range of 5.0 – 60.0 mL for $20.0 \mu\text{g L}^{-1}$ of Cu(II) solution (2 – 24 min loading times) with a sample flow rate of 2.5 mL min^{-1} . The results obtained for preconcentration of different volumes of Cu(II) solution (Fig. 8) show that the signal increases linearly with increase in the sample loading time up to 16 min , which means that the retention efficiency is constant within this time interval of 5 – 16 min , and then decreases with increase in the loading time. Thus longer loading times up to 16 min (40.0 mL sample volume) can be employed for samples with low concentration of copper. However, as a compromise between sensitivity and sampling frequency, 4.0 min loading time (10.0 mL sample volume) was chosen for subsequent studies.

3.1.7. Salt (ionic strength) effect

In order to find the effect of ionic strength on the retention of Cu(II) and analytical signal, the influence of KNO_3 (as an inert electrolyte) concentration on the sensitivity was investigated. For this purpose, the optimized parameters were used for preconcentration of 10.0 mL of Cu(II) solutions with concentration of $20.0 \mu\text{g mL}^{-1}$ containing different amounts of KNO_3 in the concentration range of 0.00 – 0.30 M . The results obtained show that the presence of salts even at a high concentration does not have a considerable effect on the analytical signal and recovery of Cu(II).

3.2. Analytical performance

Under the optimum conditions, linear calibration graphs were obtained in the concentration range of 3.00 – $120.0 \mu\text{g L}^{-1}$. The calibration equation was $A = -0.001 + 3.241 C_{\text{Cu}}$ ($r = 0.9997$, $n = 11$),

where A is absorbance, and C_{Cu} is Cu(II) concentration in $\mu\text{g L}^{-1}$. The detection limit was calculated by $3S_b/m$, where S_b is the standard deviation of the blank measurements, and m is the slope of calibration curve. For ten replicate measurements of blank, a detection limit of $0.56 \mu\text{g L}^{-1}$ was found. The limit of determination (LOD) was calculated to be $2.0 \mu\text{g L}^{-1}$ by taking ten times of blank standard deviation. Precision of the proposed method was determined as 5.0 , 2.0 , and 1.6% for six replicated determinations of solutions containing 4.0 , 20.0 , and $100.0 \mu\text{g mL}^{-1}$ of copper(II), respectively. For preconcentration of 10.0 mL of sample solution, the enrichment factor of 41 was calculated as the ratio of the calibration graph slope obtained with preconcentration ($A = -0.001 + 3.241 C_{\text{Cu}}$) to the calibration graphs slope without preconcentration ($A = -0.004 + 0.0782 C_{\text{Cu}}$). The consumptive index was defined as the consumed sample volume in mL per unit of preconcentration factor [37]. Considering enrichment factor of 41 for preconcentration of 10.0 mL of sample solution, a consumptive index of 0.40 was calculated. The sampling frequency for a 240 s loading time and 30 s elution time was 13 h^{-1} . Lifetime of the minicolumn packed with PS-PPDOT was also studied. From the 100 (maximum tested) retention and elution cycle, it was found that the resin was usable with the same efficiency and capacity, indicating no appreciable loss of multiactive chelating sites. Thus lifetime of the sorbent was very long and the minicolumn packed with PS-PPDOT had a constant performance during all experiments, and so there was no need for any regeneration or repacking.

3.3. Maximum recovery and sorbent capacity

The recovery was defined as the ratio between the copper mass in the concentrate after elution and that in the original sample solution. According to the recovery study procedure (Section 2.7), a maximum recovery of 82.5% was found for preconcentration of 10.0 mL of sample solution containing $0.20 \mu\text{g}$ Cu(II).

Maximum adsorption capacity of the sorbent was studied by a batch procedure. In this study, 100 mL of an aqueous solution (buffered at pH 5.0) containing 2.0 mg L^{-1} of Cu(II) was stirred in contact with 100 mg of functionalized chloromethylated polystyrene for 45 min . After equilibration and maximum adsorption, the amount of Cu(II) remained in solution was determined by direct aspiration to AAS, and the difference between the initial and remaining amounts of copper was calculated. According to the results obtained, a maximum absorption capacity of $820 \mu\text{g}$ of Cu per gram of resin was obtained.

3.4. Interference study

In order to identify the potential interferences in the preconcentration and determination of copper using the proposed resin, the effect of some potentially foreign ions, which may be present in real samples, was evaluated. In this investigation, various excess amounts of diverse ions were added to the solution containing $20.0 \mu\text{g L}^{-1}$ of copper, and the proposed procedure was applied. The tolerance limit of a foreign ion was taken as the value that resulted in deviation of absorbance value more than $\pm 3S$ (S is the standard deviation of five replicate determinations of absorbance for $20.0 \mu\text{g L}^{-1}$ of copper solution). The results obtained are summarized in Table 1. These results show that most ions do not interfere with determination of Cu(II) even at high concentrations. Only Hg^{2+} and Fe^{3+} interfere with the determination of Cu(II) due to complex formation with PPDOT. In the presence of 100 mg L^{-1} of SCN^- (as masking agent), the interference effects of Hg^{2+} and Fe^{3+} can be reduced up to 100 -fold and 500 -fold, respectively. Thus analyses of

Table 1
Effect of some foreign ions on the determination of copper(II) ($20.0 \mu\text{g L}^{-1}$).

Species	Tolerance limit ($W_{\text{Ion(II)}}/W_{\text{Cu(II)}}$)	Error in absorbance (%)
K ⁺	10,000	0.0
Na ⁺	10,000	-3.1
F ⁻	10,000	0.0
Mg ²⁺	10,000	+4.5
Ca ²⁺	10,000	+4.8
NO ₃ ⁻	10,000	+1.1
CO ₃ ²⁻	5000	-5.0
SO ₄ ²⁻	5000	-3.0
Cd ²⁺	5000	+4.7
Fe ²⁺	5000	-2.8
Zn ²⁺	5000	-5.0
Mn ²⁺	5000	-4.6
Cr ³⁺	5000	-4.8
Pb ²⁺	5000	+2.3
Ba ²⁺	5000	+3.1
Cr ⁶⁺	5000	0.0
SCN ⁻	5000	-0.80
NH ₄ ⁺	5000	+2.1
I ⁻	5000	-3.6
Br ⁻	5000	+2.1
Cl ⁻	5000	-2.0
PO ₄ ³⁻	2500	-3.8
Co ²⁺	1000	-4.5
Ag ⁺	1000	+0.70
Al ³⁺	1000	-4.6
Ni ²⁺	1000	-0.77
Citrate	250	-5.1
Fe ³⁺	100(500 [*])	-12.3(-4.3 [*])
Hg ²⁺	5(100 [*])	-11.5(-3.8 [*])
EDTA	5	-3.8

^{*} Tolerance limits after treatment with 100 mg L^{-1} thiocyanate ions.

water and soil samples were carried out in the presence of about 50 mg L^{-1} of SCN⁻ as masking agent.

3.5. Analysis of real samples

3.5.1. Analysis of certified reference material

To test validation of the proposed method, standard water sample with composition adequate to SPS-SW2 (Reference Material for Measurement of Elements in Surface Waters, Spectrapure Standards AS, Oslo, Norway) with copper concentration of $100 \mu\text{g L}^{-1}$ was analyzed. Comparison of the copper concentration found ($98.8 \pm 0.2 \mu\text{g L}^{-1}$) with the true value proved good accuracy of the method.

3.5.2. Analysis of water samples

The proposed method was applied to determination of copper in tap water (Shahrood, Iran), spring water (Abshar Spring, Shahrood, Iran), and bottled mineral water (Kohrang Co., Iran). To prevent from the possible interference of iron(III) ions, water samples were treated with thiocyanate ions (50 mg L^{-1}) as masking agent. For all water samples, spiking and recovery experiments were carried out. Each spiked sample was analyzed using standard addition method by the proposed procedure. The results are listed in Table 2. Satisfactory recoveries were obtained for spiked copper ions, which confirm accuracy of the method.

3.5.3. Analysis of soil samples

In this study, soil samples were collected from flower gardens at Shahrood University of Technology, Shahrood, Iran. For digestion of samples, 20.0 g of dry soil sample was put in a beaker, and then 20 mL of distilled deionized water, 12 mL of HNO₃ (65%), and 3 mL of H₂O₂ (30%) were added to the beaker. The suspension was stirred and heated during stirring until its volume decreased to about half. The suspension obtained was then filtered through a

Table 2
Results for determination of Cu(II) in different water samples.

Sample	Added ($\mu\text{g L}^{-1}$)	Found [*] ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water	–	N.D	–
	10.0	10.1(± 0.2)	101
	100.0	98.4(± 0.4)	98.4
Bottled mineral water	–	N.D	–
	10.0	9.97(± 0.2)	99.7
	40.0	38.5(± 0.9)	96.3
Spring water	–	N.D	–
	10.0	9.81(± 0.3)	98.1
	50.0	50.1(± 1)	100.2

^{*} Numbers in parentheses are standard deviations for three replicate determinations.

Table 3
Results for determination of Cu(II) in soil samples.

No	Added ($\mu\text{g L}^{-1}$)	Found [*] ($\mu\text{g L}^{-1}$)	Recovery (%)	Content in soil ($\mu\text{g g}^{-1}$) [*]
1	–	6.3(± 0.3)	–	3.94(± 0.19)
2	20.0	26.0(± 0.4)	98.5	
3	60.0	64.8(± 0.9)	97.5	

^{*} Numbers in parentheses are standard deviation for three replicate determinations.

Table 4
Results for determination of Cu(II) in milk samples.

No	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Content in milk ($\mu\text{g mL}^{-1}$) [*]
1	–	12.2(± 0.7)	–	0.15(± 0.09)
2	20.0	31.5(± 0.7)	96.5	
3	50.0	53.3(± 0.9)	97.5	

^{*} Numbers in parentheses are standard deviation for three replicate determinations.

cellulose membrane filter (Millipore) of pore size $0.45 \mu\text{m}$, and made up to 500 mL in a volumetric flask with distilled water. Then 2.0 mL of the solution was added to a 50-mL volumetric flask, neutralized by adding dilute KOH, and buffered at pH 5.0, to which an appropriate volume of thiocyanate ion solution added to give the final concentration of 50 mg L^{-1} , and finally, this was diluted with distilled water. Some 10.0 mL aliquots of the resulting solution was used for determination of Cu(II) by applying the proposed procedure. The results obtained are summarized in Table 3. There is a good agreement between the results obtained and true spiked values at 95% confidence level (*t*-test).

3.5.4. Analysis of milk samples

An aliquot of 10.0 mL of bottled milk sample (Parishad Co.) was placed in a 100-mL beaker, and 10 mL of 65% HNO₃ and 3 mL of 30% H₂O₂ were added. Content of the beaker was heated on a hot plate at 100°C for 40 min, and then the semi-residue mass was dissolved in 10 mL of 1.0 M HCl. The clarified solution obtained was neutralized by adding dilute KOH, and diluted up to 50 mL in a volumetric flask. Then 20.0 mL of the solution was added to a 50-mL volumetric flask, buffered at pH 5.0, and finally diluted with distilled water. Some 10.0 mL aliquots of the resulting solution was used for determination of Cu(II) by applying the proposed procedure. The results (Table 4) show that, in all cases, the copper recovery is almost quantitative.

Table 5
Figures of merit for some recently reported methods for the determination of Cu(II).

Support	Modifier/ligand	Eluent	V (mL) ^a	PF ^b	DL (μg L ⁻¹) ^c	Ref.
Styrene-divinylbenzene resin	(S)-2-[hydroxy-bis-(4-vinyl-phenyl)-methyl]-pyrrolidine-1-carboxylic acid ethyl ester	HCl	13.2	21	1.1	[38]
Silica gel	Zirconium(IV) phosphate	HNO ₃	300	30	1.1	[39]
Polyurethane foam	Ammonium pyrrolidine dithiocarbamate	IBMK	12	170	0.2	[30]
Polychlorotrifluoroethyl	Diethyldithiophosphate	IBMK	17.4	250	0.07	[40]
Dowex Optipore SD-2	5-Methyl-4-(2-thiazolylazo) resorcinol	HNO ₃	250	50	10.2	[41]
Octadecyl Silica	Bis-(5-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine	HNO ₃	2000	400	2.4	[7]
Analcime zeolite	Pyrocatechol violet	HNO ₃	1000	200	0.05	[42]
Chromosorb 105	pyrocatechol violet	HCl	30	60	1.67	[43]
Octadecyl silica	Bis-(3-methoxy salicylaldehyde)-1,6-ohexane	EDTA	1000	100	0.03	[44]
Amberlite XAD-2	1,10-Phenanthroline	Ethanol	1000	100	3.9	[45]
Styrene imprinted polymer	2,2'-(Ethane-1,2-diylbis(nitrilo(E)methylidene))bis-(6-allyl-4-methoxyphenol)	HNO ₃	2	58	1.07	[46]
Sepabeads	N ¹ ,N ² -bis-(4-fluorobenzylidene)ethane-1,2-diamine	HNO ₃	1500	188	1.6	[47]
PVC	2-Phenyl-1H-benzo[d]imidazole (PHBI)	HNO ₃	450	90	0.95	[48]
Polyethylenimine	–	–	10	2	5.2	[49]
Peat	–	HNO ₃	13.6	16	3	[50]
Multi-walled carbon nanotubes	–	HNO ₃	600	60	1.46	[51]
Polystyrene	1-Phenyl-1,2-propanedione-2-oxime thiosemicarbazone	HNO ₃	10	40	0.59	This work

^aV: sample volume; ^bPF: preconcentration factor; ^cDL: detection limit.

4. Conclusion

A fast, sensitive, and selective method for extraction, preconcentration, and determination of copper ions in real samples was introduced. The method is based on SPE of copper with PS-PPDOT resin as a new selective SPE sorbent. The proposed sorbent possesses some distinct advantages including simple preparation method, high stability (it can remain stable in strongly acidic and basic media), and infinite lifetime. The retained copper was eluted with a preconcentration factor of 41. Finally, the method was used for extraction and determination of copper in tap, spring and mineral water, soil, and milk samples with satisfactory results. Figures of merit for the proposed method and some recently reported on-line solid-phase extraction preconcentration FAAS methods [7,38–51] are given in Table 5. By comparing the data in this table, it is clear that detection limit for the proposed method is better than those obtained with other sorbent materials [7,38,39,41,43,45–51]. Although some of these methods have better detection limits [30,40,42,44], they need very large sample volumes [42,44], and so this method may have high sample consumption.

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