Chemically Modified Polystyrene with a Synthesized N$_3$O$_2$ Schiff Base as a New Solid Phase Sorbent for on Line Preconcentration and Determination of Copper(II) in Water Samples by FAAS

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Abstract

This paper reports the synthesis and application of a new sorbent for on-line preconcentration of copper prior to its determination with atomic absorption spectrometry (AAS). The sorbent was prepared by immobilization of N,N-bis(naphthylideneimino)diethylenetriamine on chloromethylated polystyrene. Copper was sorbed on a mini-column packed with sorbent and subsequent eluted quantitatively by HCl and determined by flame atomic absorption spectrometry (FAAS). All variables were optimized for the quantitative preconcentration of copper ions and a study of interference level of various ions was also carried out. Under the optimum conditions, linear calibration graphs over the concentration ranges of 2.0-44.0 and 0.70-30.0 μg L$^{-1}$; detection limits of 1.4 and 0.46 μg L$^{-1}$; and enrichment factors of 80 and 183 were obtained for the preconcentration volumes of 10.0 and 25.0 mL of copper(II) solutions, respectively. Good relative standard deviations of 4.1 and 3.5% for ten replicate determinations of 10.0 and 30.0 µg L$^{-1}$ of copper were obtained, respectively.

Keywords:
Atomic absorption spectrometry; On-line preconcentration; Polystyrene; Schiff base; Copper(II)

1. Introduction

Copper is a micro-nutrient as well as a toxic element for living beings, depending up on the concentration level [1]. Low concentrations of copper are essential for plants and animals. However, high concentrations of copper are toxic for most aquatic plants and spineless marines [2]. Due to the great production and industrial use of copper, drinking water can be a potential source for an intense copper exposition. Copper is suspected to cause infant liver damages [3, 4] and after the mercury it is highly toxic for drinking water. Therefore, a precise, accurate and rapid measurement of copper is one of the most important interest targets in biological and environmental analytical chemistry.

The flame atomic absorption spectrometry (FAAS) technique is extensively employed for the quantification of metal species [5]. Despite the sensitivity and selectivity of FAAS, there is a great necessity for the preconcentration of trace metals prior their determination, basically due to their low concentrations or the matrix interferences in aqueous samples. In this regard, many preconcentration procedures including co-precipitation, liquid–liquid extraction, and cloud point extraction have been developed for the enrichment of trace metals prior their determination by AAS [6-8].

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Solid phase extraction (SPE) is another approach that offers a number of important benefits. It reduces solvent usage and exposure, disposal costs and extraction time for sample preparation. Consequently, in recent years SPE has been successfully used for the separation and sensitive determination of metal ions, mainly in water samples [9]. Bath mode of SPE is time consuming, require large sample or reagent volumes, and suffer from risks of contamination and analyte loss [10]. Using on-line techniques, the drawbacks of batch operation can be overcome to a great extent while preconcentration can be further enhanced [11]. Flow injection (FI) on-line separation and preconcentration coupled with the FAAS technique, with mini-columns containing an appropriate adsorbent, has been a much used method in the analytical determination of trace metals due to the low cost of this equipment and its high analytical velocity [12, 13]. The nature and property of the sorbent materials are very important in the solid phase extraction (SPE) methods [9]. Different sorbents have been successfully used for on-line column preconcentration and determination of copper individually or simultaneously with other heavy metals in various types of samples. Some of these are multi-walled carbon nanotubes (MWNTs) [14]; octadecyl functional groups bonded on silica gel and C-18 [15–20]; alumina coated [21, 22]; modified silica gel [23, 24]; synthetic zeolite [25] and knotted reactor [26-28]. Functionalized polymeric solid supports such as polystyrene-divinylbenzene (PS-DVB) polymer, Amberlite XAD-2 [29-31], XAD-4 [32] and polyurethane foam (PUF) [33, 34], are good alternatives to achieve very versatile systems for preconcentration and determination of copper in various samples. Some advantages of polymeric solid supports include low cost, simple preparation, high porosity and thus high available surface area, and stability in acidic or basic media [35].

Schiff base ligands are a category of important ligands with excellent coordinating ability toward a variety of metal ions. They have been used in various analytical investigations such as fabrication of ion selective electrodes [36, 37] and preconcentration and separation of trace amount of metal ions [38].

In the present study, a new sorbent was synthesized and applied for the on-line preconcentration and determination of traces of copper in the water samples. The chelating resin was prepared by chemically functionalization of chloromethylated polystyrene with N,N-bis(naphthylideneimino)diethylenetriamine (NAPdien) (Fig. 1). Studies confirmed the reliability of micro-column enrichment/separation packed with this newly synthesized sorbent for rapid FI–AAS preconcentration and determination of ultra-trace amounts of copper in various water samples.

![Fig. 1. Structure of PS-NAPdien resin.](image)

2. Material and methods

2.1. Reagents and solutions

Ultra-pure water from a Milli-Q water purification system (Millipore) was used to prepare all solutions. All chemicals were of analytical reagent grade and were provided by Merck or Fluka, and were used without previous purification.
Copper(II) stock solution (1000 mg L\(^{-1}\)) was prepared by dissolving 0.3840 g of Cu(NO\(_3\))\(_2\).3H\(_2\)O in a 100-mL volumetric. The obtained solution was standardized by known methods [39]. Working solutions were prepared daily from the stock solution by serial dilution with water.

Phosphate buffer solution was prepared by mixing appropriate volumes of 1.0 mol L\(^{-1}\) Na\(_2\)HPO\(_4\) and 1.0 mol L\(^{-1}\) KH\(_2\)PO\(_4\), and adjusting the pH to 7.0 using a pH-meter. Acetate Buffer solutions (pH = 3.0-5.5), phosphate buffer solutions (pH = 6.0-8.0), borate buffer solution (pH 9.0) and HCl 0.10 mol L\(^{-1}\) (for pH = 1.0-3.0) were used for the pH adjustment in the pH optimization experiments.

The HCl 2.0 mol L\(^{-1}\) as eluent solution was prepared by dilution 16.6 mL of concentrated hydrochloric acid (Merck) with ultra pure water in a 100-mL volumetric. The obtained solution was standardized against sodium carbonate. Other eluent solutions (nitric and sulfuric acid) were prepared by dilution appropriate volumes of their concentrated solutions.

Chloromethylated polystyrene (cross-linked with 2% divinylbenzene, 4-5% Cl content, 1.14-1.40 mmol g\(^{-1}\) Cl) was used in preparation of the sorbent. Other reagents such as 2-hydroxy-1-naphthaldehyde, diethylenetriamine and methanol were used for preparation of ligand NAPdien.

2.2. Preparation of the ligand NAPdien

The ligand NAPdien was prepared by the following literature procedure [40, 41]. 2-hydroxy-1-naphthaldehyde (12.2 g, 0.10 mol) was dissolved in 75 mL methanol, and to this was added a solution of diethylenetriamine (5.15 g, 0.050 mol) in 25 mL methanol. The reaction mixture was refluxed on a water bath for 1 h. After reducing the volume of the solvent to ca. 50 mL, the content was transferred into a beaker and excess solvent was evaporated under the current of air until the viscous yellow-red oil was obtained. This was further dried in vacuum. The purity of ligand was only checked by infrared spectroscopy, and electronic absorption spectra. IR(KBr): 3450, 2950, 2885, 1635, 1583, 1460, 1280, 1215, 1145, 1045, 845 and 750 cm\(^{-1}\). UV-Vis, \(\lambda_{\text{max}}(\text{nm})\): 400, 310, 285, 247, 220.

2.3. Preparation of polystyrene-N,N-bis(naphthylideneimino)diethylenetriamine (PS-NAPdien)

The immobilization of N,N-bis(naphthylideneimino)diethylenetriamine (NAPdien) on chloromethylated polystyrene was carried out according to the our previous reported procedure [42]. Successful functionalization of the polymer was confirmed by IR spectrum. IR (KBr): 3425, 3025, 2915, 1635, 1586, 1477, 1452, 1426, 1349, 1280, 1215, 1145, 1045, 845 and 750 cm\(^{-1}\). UV-Vis, \(\lambda_{\text{max}}(\text{nm})\): 400, 310, 285, 247, 220.

2.4. Preparation of mini-column

The mini-column was manufactured in the laboratory from polyethylene tubing of 8-cm length and 2.0-mm internal diameter, and packed with about 154 mg of the sorbent. Its ends were fitted with wool glass to retain the sorbent in the tube. The packed mini-column was initially washed with 2.0 mol L\(^{-1}\) HCl and then with water before use. Because of the long lifetime of the packing material, its performance was stable during all experiments.

2.5. Instrumentation

A schematic diagram of the flow manifold used is presented in Fig. 2. A variable flow-rate peristaltic pump with 12 channels (Hidolp, Model 5201) equipped with Tygon\textsuperscript{®} tubes was used to pump sample stream through the manifold. PTFE tubing was used for
manifold lines. The six-way rotary injection valve (Rheodyne, Model 5011) was used as a selection valve for the selection of sample or eluent streams. A mini-column (with 8 cm of length and i.d. = 2.0 mm) located between selection valve and FAAS. A Shimadzu Model AA-670 flame atomic absorption spectrometer with an air–acetylene flame was used for copper(II) determination. A copper hollow cathode lamp was used under the manufacture recommended conditions. Also the wavelength, slit width, and burner height had conventional values. The aspiration rate of the nebulizer was about 2.0 mL min⁻¹. IR spectra were recorded on a Shimadzu IR-470 spectrometer. Measurements of pH were made using a Metrohm 691 pH-meter equipped with a combined glass-saturated calomel electrode.

2.6. Preconcentration and determination procedure

The FI manifold used is presented in Fig. 2. The two-line FI manifold was used to preconcentration and determination of copper in real samples. The complete procedure has been consisted of two steps: loading (step 1) and elution (step 2). In the step 1 (Fig. 2a), the selection valve allowed a known volume (e.g. 10 mL) of the standard or sample solutions (buffered at pH= 7.0 with phosphate buffer) to pass through the mini-column at flow rate of 6.0 mL min⁻¹ for 100 s to load the sample on the mini-column packed with functionalized polystyrene. In the step 2 (Fig. 2b), the position of the selection valve was changed to flowing direction of the eluent solution and the eluent solution (2.0 mol L⁻¹ HCl) was passed through the mini-column at flow rate of 6.0 mL min⁻¹. The adsorbed copper on the mini column was eluted into the nebulizer of FAAS. Then the absorbance or peak heights of the transient signals were recorded.

![Fig.2. Schematic diagram of FI-manifold and the two operation sequences for copper(II) determination by FAAS. P: peristaltic pump; SV: selection valve; MC: mini-column; W: waste.](image-url)
3. Results and Discussion

With considering the selectivity of nitrogen/oxygen donor of \(N_xO_y\)-type of Schiff base ligands towards copper ions [43], we decided to examine the capability of polystyrene functionalized with \(N,N\)-bis(naphtilidineimino)diethylenetriamine (PS-NAPdien) (Fig. 1) as a new sorbent for the on line preconcentration and determination of copper ions using flow system. The immobilization reaction of NAPdien on the chloromethylated polystyrene polymer and characterization details has been reported in our previous paper [42]. However some IR spectral evidences clearly indicate the promotion of the ligand on the support via a covalent bond. These evidences are (i) the sharp C–Cl peak at 1264 cm\(^{-1}\) in chloromethylated polystyrene was practically omitted or was weak in the IR spectrum of the PS-NAPdien. (ii) the appearance of C=N bond of azomethine at 1629-1550 cm\(^{-1}\) and (ii) a medium intensity band due to stretching of C-N at 1193 cm\(^{-1}\) in the IR spectrum of the PS-NAPdien.

3.1. Investigation and Optimization of Variables

The main factors that affected the preconcentration process were pH of the sample solution, type and concentration of eluent, sample and eluent flow rates, volume of the sample loading, length of the mini-column and the salt effect. In order to establish the best chemical and flow conditions for deposition and elution of the analyte, the procedure was optimized by univariable method.

The effect of the sample pH on the sorption of copper(II) onto the column was studied by varying the pH of sample solution between 1.0 and 9.0. For this purpose, 5.0 mL of 20.0 \(\mu\)g L\(^{-1}\) copper(II) solutions buffered at different pH were enriched at a flow rate of 2.0 mL min\(^{-1}\). The results (Fig. 3) show that the optimum pH falls in the range of 6.0-8.0. Thus all sample solutions were buffered at pH= 7.0 by phosphate buffer solution with final concentration of 0.040 mol L\(^{-1}\).

![Graph](image)

**Fig. 3.** Effect of sample solution acidity on the absorbance.
Conditions: preconcentration of 5.0 mL of 20.0 \(\mu\)g L\(^{-1}\) Cu(II) solution with flow rate of 2.0 mL min\(^{-1}\) on a 4.0 cm mini-column and elution with 2.0 mol L\(^{-1}\) HCl with flow rate of 2.0 mL min\(^{-1}\).
Preliminary experiments showed that elution of sorbed copper ions could be done by breaking the metal-chelate bond in acidic media. For the selection of the best eluent, various mineral acids such as nitric acid, hydrochloric acid, and sulfuric acid with the same hydronium ion concentration of 2.0 mol L⁻¹ were tested. The results obtained show that sulfuric acid can not quantitatively strip the sorbed copper ions (recovery percent about 70%). Hydrochloric acid and nitric acid gave the higher sensitivity and recovery (83% for HCl and 80% for HNO₃). So hydrochloric acid was chosen as the eluent for this purpose.

The effect of eluent concentration on the absorption signal of copper was examined in the range 0.20–3.0 mol L⁻¹. Concentrations higher than 3.0 mol L⁻¹ were not studied since different parts of the spectrometer nebulizer could be affected. The results (Fig. 4) showed that the absorbance increased as the HCl concentration increased up to 1.8 mol L⁻¹ and then remained constant with further increase in the eluent concentration. Thus for insure quantitative elution of adsorbed copper, HCl concentration of 2.0 mol L⁻¹ was chosen for subsequent studies.

![Fig. 4. Effect of eluent concentration on the absorbance. Conditions: preconcentration of 5.0 mL of 20.0 μg L⁻¹ Cu(II) solution buffered at pH= 7.0 with flow rate of 2.0 mL min⁻¹ on a 4.0 cm mini-column and elution with flow rate of 2.0 mL min⁻¹.](image)

In on-line solid phase extraction systems, the sample and eluent flow rates are the most important parameters, since they regulate maximum mass transfer from liquid to solid-phase, elution efficiency and analytical throughput. The influences of the sample and eluent solutions flow rates were investigated in the range of 1.0 and 7.0 mL min⁻¹ by passing aliquots of 5.0 mL of 20.0 μg L⁻¹ copper ion solutions at pH of 7.0 through a 4 cm packed column containing sorbent. The results show that the absorbance was increased by increasing the flow rate of the sample solution up to 2.5 mL min⁻¹ and then was level off. However, for the flow rates of eluent solution, the maximum desorption values (~84%) were obtained in the flow rate of 3.0–7.0 mL min⁻¹. For decreasing loading time and increasing sampling
frequency, the flow rate of 6.0 mL min\(^{-1}\) was selected for both the sample and eluent solutions.

The effect of sample volume (loading time) on the absorption signal was tested in the range of 6-50 mL of 20.0 μg L\(^{-1}\) copper(II) solutions (1-8.3 min loading times) with a sample flow rate of 6.0 mL min\(^{-1}\). The results obtained for preconcentration of different volumes of 20.0 μg L\(^{-1}\) copper(II) solution are shown in Fig. 5. As shown in Fig. 5, the signal increased linearly by increasing the sample volume up to 25.0 mL, which means that the retention efficiency was constant within this time interval and a higher sample volume (up to 25.0 mL with loading time of 4.2 min) can be employed for samples with low concentration of copper. In addition, the recovery studies were carried out over the whole tested sample volumes range. The results show that the recovery is constant and high (~83%) up to 25.0 mL loading volume and then decrease with increasing sample volume. However, we used sample volumes of 10.0 and 25.0 mL for construction of two different calibration graphs.

![Fig. 5. Effect of preconcentration volume on the absorbance.](image)

**Fig. 5.** Effect of preconcentration volume on the absorbance.
Conditions: preconcentration of 20.0 μg L\(^{-1}\) Cu(II) solution buffered at pH = 7.0 with flow rate of 6.0 mL min\(^{-1}\) on a 4.0 cm mini-column and elution with HCl 2.0 mol L\(^{-1}\) with flow rate of 6.0 mL min\(^{-1}\).

The effect of length of the mini-column on the deposition efficiency of 0.2 μg copper(II) from 10 mL of sample solution was investigated in the range of 2.0-10.0 cm (containing 38-220 mg of sorbent) using mini-columns with the same inner diameters. It was found that that the retention efficiency of column increased up to 7.0 cm and then remained constant. Thus a mini-column with length of 8.0 cm (containing 154 mg of sorbent) was selected for sufficient sorption (recovery of 99.3%) of different amounts of copper from 10 mL solution.

The effect of ionic strength (salt effect) on the performance of the optimized analytical procedure was studied using KNO\(_3\) in the concentration range of 0.00-0.60 mol L\(^{-1}\). The results obtained show that the presence of salts even at high concentration has not considerable effect on the analytical signal and recovery of copper(II).
3.2. Analytical parameters

Under the optimum conditions (pH 7.0, sample and eluent flow rates of 6.0 mL min\(^{-1}\) and elution with 2.0 mol L\(^{-1}\) HCl), some analytical parameters of FI-online preconcentration system were studied.

Preconcentration factor (CF) was evaluated from the ration of two different concentrations with same analytical signal as below [44]:

\[
CF = \frac{C_1}{C_2}
\] (1)

where \(C_1\) is a concentration, which have a direct nebulization signal equal to the preconcentration/elution analytical signal of \(C_2\). Fig. 6 shows the signals obtained from preconcentration of 10 mL of 12.5 μg L\(^{-1}\) of copper(II) solution and direct pneumatic nebulization of acidic solution of 1.0 mg L\(^{-1}\) copper(II). According to the results a preconcentration factor of about 80 was achieved. The preconcentration factor, calculated as the ratio of the slopes of the calibration graphs with and without preconcentration, was 75.

![Fig. 6. Absorbance-time response for (a) sequential preconcentration and elution of Cu(II) solution (10 mL, 12.5 μg L\(^{-1}\), pH 7.0), and (b) conventional nebulization of 1.0 mg L\(^{-1}\) acidic Cu(II) solution.](image)

The recovery was defined as the ratio between the analyte mass in the original sample solution and that in the concentrate after elution. For recovery test, 10.0 mL of a 40.0 μg L\(^{-1}\) copper solution was percolated through the column. The elution was performed and the concentrate containing the analyte was collected in 1.0 mL and the copper in this solution was directly determined by FAAS. Under optimum condition a recovery of 99.5% was obtained.

The lifetime of the mini-column packed with NAPdien was determined by 500 replicate (maximum tested) measurements of the analytical signal for preconcentration and elution of 10 mL 20.0 μg L\(^{-1}\) copper(II) standard solutions. No significant loss or gain in the analytical signal was observed during this measurement time. Because of the very long lifetime of the packing material, the column did not need any regeneration or repacking during all experiments.

The sorption capacity of the PS-NAPdien sorbent for the retention of copper was also determined. In this study, a column containing 80 mg of PS-NAPdien resin was used and a large volume of 1.0 mg L\(^{-1}\) copper solution was passed through the column. The effluent was collected in 5 mL fractions and their direct nebulization analytical signal detected until the analytical signal was reached to its expected maximum value. The results demonstrated that the sorbent has a sorption capacity of 3.5 mg g\(^{-1}\) of dry resin.
Using a manifold presented in Fig. 2 under the optimum conditions, two linear calibration graphs were found for preconcentration of and determination of 10.0 and 25.0 mL of copper(II) solution with different copper(II) concentrations. When 10.0 mL of sample volume (preconcentration time of 100 s) was employed, a linear calibration curve in the concentration range of 2.0–44.0 μg L⁻¹ Cu(II) with regression equations of $A = 3.38 \times 10^{-3} C_{\text{Cu(II)}} + 0.004$ ($r= 9990$, $n= 16$) was obtained. For preconcentration of 25.0 mL of sample solution, the relation between absorbance and copper(II) concentration was linear in the range of 0.70–30.0 μg L⁻¹ copper(II) with linear equation of $A = 9.11 \times 10^{-3} C_{\text{Cu(II)}} + 0.005$ ($r= 9984$, $n= 10$), where $A$ is absorbance and $C_{\text{Cu(II)}}$ is copper(II) concentration in μg L⁻¹.

The $3\sigma$ limits of detection 1.4 and 0.46 μg L⁻¹ were found for preconcentration volumes of 10.0 mL and 25.0 mL, respectively. In the detection limit study, ten replicate preconcentration of 10.0 and 20.0 mL blank solutions (a mixture of buffer and distilled water) were performed according to the proposed procedure (Section 2.6) and the corresponding blank signal standard deviations were used for calculation of detection limit using $DL = 3S_b/m$, where $S_b$ is standard deviation of blank and $m$ is the calibration sensitivity. The relative standard deviations of 4.1 and 3.5% for ten replicate determinations of 10.0 and 30.0 μg L⁻¹ of copper were obtained, respectively. The sampling frequency was found to be about 30 h⁻¹ for preconcentration of 10.0 mL of sample solutions.

3.3. Field flow preconcentration studies

Most of the analytical procedures involve several stages including the sampling, storage and analyte determination thus a loss of the analyte or sample contamination is encountered in each stage. In order to avoid this drawback the on line mini-column field preconcentration (sampling) technique was proposed. In this technique flow systems are used to process the water samples at the sampling site and trace elements of interest are immobilized on mini-columns. These mini-columns are returned to the laboratory where they are directly inserted into a flow system for on-line elution and quantitative analysis [45]. With respect to intrinsic advantages of field preconcentration technique, we decide to study the performance of the PS-NAPdien as a sorbent in the field preconcentration of copper(II) ions at the obtained optimum conditions. In this study, the flow manifold (Fig. 2a) was modified by addition of a new line containing buffer stream for online mixing of the buffer solution with the sample solution before passing through the mini-column in the preconcentration step. Under the optimum conditions of pH 7.0, sample and eluent flow rates of 6.0 mL min⁻¹ and elution with 2.0 M HCl. Some calibration columns were prepared in the laboratory by pumping 10.0 mL of tap water samples containing different concentrations of copper(II) with flow rate of 6.0 mL min⁻¹ through the 8 cm mini-column filled with PS-NAPdien. After loading, the mini-column was washed with water and, the residual internal fluid was drawn off with an air stream in order to remove the washing solution. The dry mini-columns were disconnected from the flow preconcentration system and keep in room conditions for 36 h. Blanks columns were prepared in the same manner but using the appropriate water at pH 7.0. After 36 h, columns were inserted in flow system (Fig. 2b) and eluted with HCl 2.0 M and corresponding signals were recorded. The obtained results show that in the field preconcentration strategy the calibration graph is linear in the range 5.0–50.0 μg L⁻¹ of copper(II) with regression equation of $A = 1.75 \times 10^{-3} C_{\text{Cu(II)}} + 0.002$ ($r= 9975$, $n= 6$). The $3\sigma$ detection limit of 3.5 μg L⁻¹ was found for preconcentration of 10.0 mL sample solution. The relative standard deviation for ten replicate determinations of 30.0 μg L⁻¹ of copper was 4.3%.

3.5. Selectivity

In order to assess the possible analytical application of the described procedure, the effects of various substances present in the matrix of real samples on the determination of
copper(II) were investigated. Synthetic mixtures of solutions containing 20.0 μg L\(^{-1}\) of copper(II) and various excess amounts of diverse ions were used as sample. The tolerance limit was defined as the concentration of the added ions causing a change in the recovery more than ±5%. The results obtained in these experiments (Table 1) demonstrate that the presence of large amounts (8-20 mg L\(^{-1}\)) of alkali, alkaline earth, and transition metals in the sample had no significant effect on the preconcentration of copper. Only Fe\(^{3+}\) and Hg\(^{2+}\) caused variation in the copper(II) signal at low concentrations. In the presence of 20 mg L\(^{-1}\) citrate ion, Fe\(^{3+}\) does not interfere up to 4 mg L\(^{-1}\) (200-fold). Thus the analysis of water samples was carried out in the presence of 20 mg L\(^{-1}\) of citrate ion. The interference effect of Hg\(^{2+}\) can be reduced up to 20 mg L\(^{-1}\) (1000-fold) using 20 mg L\(^{-1}\) tartarate ion.

**Table 1. Interferences for the determination of copper(II) (20.0 μg L\(^{-1}\))**

<table>
<thead>
<tr>
<th>Species</th>
<th>Tolerance limit (μg L(^{-1}))</th>
</tr>
</thead>
</table>
| K\(^{+}\), Na\(^{+}\), Mg\(^{2+}\), Ba\(^{2+}\), Sr\(^{2+}\), NH\(_4\)\(^{+}\), Ni\(^{2+}\), As\(^{3+}\), Co\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), MoO\(_4^{2-}\), F\(^{-}\), Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), SO\(_4^{2-}\), SO\(_3^{2-}\), S\(_2\)O\(_3^{2-}\), PO\(_4^{3-}\), C\(_2\)O\(_4^{2-}\), NO\(_2^{-}\), SCN\(^{-}\), Citrate, Tartarate | 20000
| Pb\(^{2+}\)                | 16000                            |
| Ag\(^{+}\), Mn\(^{2+}\)    | 12000                            |
| Al\(^{3+}\), Cr\(^{3+}\)   | 8000                             |
| EDTA                      | 1000                             |
| Hg\(^{2+}\), Fe\(^{3+}\)  | 5                                |

a: maximum limit tested.

### 3.6. Evaluation of method by water sample analysis

The proposed procedure was applied to the determination of copper(II) in water and salt samples. The analyte was enriched in the preconcentration system shown in Fig.1, utilizing the optimized variables and a preconcentration time of 100 s. For removal the probably interference of iron, citrate ion with final concentration of 20 mg L\(^{-1}\) was added to all samples analyzed. The accuracy of the method was investigated through the recovery test with adding known amounts of analyte to the aqueous matrices. In Table 2, the results of the recovery test are given. As seen in Table 2, the efficiency of the on-line preconcentration system was very good for all samples analyzed. The recoveries were between 94.0 and 106%, which indicating that the matrix effect was not significant. To test the 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 μg L\(^{-1}\) was analyzed. Comparison of copper concentration found (97.3 ± 0.1 μg L\(^{-1}\)) and true value proved good accuracy of the method.

### 4. Conclusion

The capability of a new functionalized polymer containing N,N-bis(naphtilidineimino) diethylenetriamine (PS-NAPdien) beads as a new sorbent for FI on-line preconcentration coupled with FAAS for trace copper determination was successfully evaluated and demonstrated. 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 figures of merit of the present method and some recently selected on-line solid phase extraction preconcentration FAAS methods [16, 46-56] are given in Table 3. By comparing the data in Table 3, it is clear that the detection limit of the proposed method is better than those obtained with other sorbent materials [47, 48, 50, 52, 54-56]. Some of
these methods have better detection limits [46, 49, 51] but they need very large sample volumes, and so this method may have high sample consumption and sampling frequencies.

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu(II) added</th>
<th>Cu(II) found</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water(I)</td>
<td>-</td>
<td>&lt;DL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.0040</td>
<td>0.0038 (±0.0002)</td>
<td>95.0</td>
</tr>
<tr>
<td></td>
<td>0.024</td>
<td>0.025 (±0.003)</td>
<td>104.2</td>
</tr>
<tr>
<td>Tap water(II)</td>
<td>-</td>
<td>&lt;DL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.016</td>
<td>0.017 (±0.001)</td>
<td>106.2</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
<td>0.021 (±0.002)</td>
<td>105.0</td>
</tr>
<tr>
<td>Spring water</td>
<td>-</td>
<td>&lt;DL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.0050</td>
<td>0.0051 (±0.0003)</td>
<td>102.0</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>0.025 (±0.001)</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>0.033</td>
<td>0.032 (±0.002)</td>
<td>97.0</td>
</tr>
<tr>
<td>Bottled natural mineral water</td>
<td>-</td>
<td>&lt;DL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.013</td>
<td>0.014 (±0.001)</td>
<td>107.7</td>
</tr>
<tr>
<td></td>
<td>0.017</td>
<td>0.018 (±0.001)</td>
<td>105.9</td>
</tr>
<tr>
<td>0.50 M NaCl solution</td>
<td>-</td>
<td>&lt;DL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.0060</td>
<td>0.0063 (±0.0004)</td>
<td>105.0</td>
</tr>
<tr>
<td></td>
<td>0.010</td>
<td>0.0094 (±0.0003)</td>
<td>94.0</td>
</tr>
<tr>
<td></td>
<td>0.014</td>
<td>0.014 (±0.001)</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>0.018</td>
<td>0.019 (±0.002)</td>
<td>105.6</td>
</tr>
<tr>
<td></td>
<td>0.026</td>
<td>0.026 (±0.001)</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>0.030</td>
<td>0.030 (±0.001)</td>
<td>100.0</td>
</tr>
</tbody>
</table>

### Table 3. The figures of merit of the present method and some newly reported SPE-AAS methods

<table>
<thead>
<tr>
<th>Support</th>
<th>Modifier (ligand)</th>
<th>Eluent</th>
<th>Sample volume (mL)</th>
<th>PF</th>
<th>DL (µg L⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowex Optipore SD-2</td>
<td>5-methyl-4-(2-thiazolylazo) resorcinol</td>
<td>HNO₃</td>
<td>250</td>
<td>50</td>
<td>1.03</td>
<td>46</td>
</tr>
<tr>
<td>Polyethylenimine</td>
<td>-----</td>
<td>-----</td>
<td>10</td>
<td>2</td>
<td>5.2</td>
<td>47</td>
</tr>
<tr>
<td>Silica gel</td>
<td>3-(1-imidazolyl)propyl</td>
<td>HNO₃</td>
<td>11.25</td>
<td>42.2</td>
<td>0.4</td>
<td>16</td>
</tr>
<tr>
<td>Octadecyl silica</td>
<td>Bis(3-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine</td>
<td>HNO₃</td>
<td>2000</td>
<td>400</td>
<td>2.4</td>
<td>48</td>
</tr>
<tr>
<td>Analcime zeolite</td>
<td>pyrocatechol violet</td>
<td>HNO₃</td>
<td>1000</td>
<td>200</td>
<td>0.05</td>
<td>49</td>
</tr>
<tr>
<td>Chromosorb 105</td>
<td>pyrocatechol violet</td>
<td>HCl</td>
<td>30</td>
<td>60</td>
<td>1.67</td>
<td>50</td>
</tr>
<tr>
<td>Octadecyl silica</td>
<td>bis-(3-methoxy salicylaldehyde)-1,6-diaminohexane</td>
<td>EDTA</td>
<td>1000</td>
<td>100</td>
<td>0.03</td>
<td>51</td>
</tr>
<tr>
<td>Amberlite XAD-2</td>
<td>1,10-phenanthroline</td>
<td>Ethanol</td>
<td>1000</td>
<td>100</td>
<td>3.9</td>
<td>52</td>
</tr>
<tr>
<td>Syrene imprinted polymer</td>
<td>2,2′-[ethane-1,2-diylbis(nitrilo(E)methylidylen)]bis(6-allyl-4-methoxyphenol)</td>
<td>HNO₃</td>
<td>2.0</td>
<td>5.8</td>
<td>1.07</td>
<td>53</td>
</tr>
</tbody>
</table>
Table 3 (continued)

<table>
<thead>
<tr>
<th>Support</th>
<th>Modifier (ligand)</th>
<th>Eluent</th>
<th>Samle volume (mL)</th>
<th>PF</th>
<th>DL  (μg L⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syrene imprinted polymer</td>
<td>2,2'-[ethane-1,2-diylbis(nitrilo(E)methylylidene)]bis(6-allyl-4-methoxyphenol)</td>
<td>HNO₃</td>
<td>2.0</td>
<td>5.8</td>
<td>1.07</td>
<td>53</td>
</tr>
<tr>
<td>Peat</td>
<td>-----</td>
<td>HNO₃</td>
<td>13.6</td>
<td>16</td>
<td>3</td>
<td>54</td>
</tr>
<tr>
<td>Sepabeads</td>
<td>N¹, N²-bis(4-fluorobenzylidene)ethane-1,2-diamine</td>
<td>HNO₃</td>
<td>1500</td>
<td>188</td>
<td>1.6</td>
<td>55</td>
</tr>
<tr>
<td>Multi-walled carbon nanotubes</td>
<td>-----</td>
<td>HNO₃</td>
<td>600</td>
<td>60</td>
<td>1.46</td>
<td>56</td>
</tr>
<tr>
<td>Chloromethylated polystyrene</td>
<td>Bis(naphthilidinimino)diethylenetriamine</td>
<td>HCl</td>
<td>10</td>
<td>80</td>
<td>1.4</td>
<td>This work</td>
</tr>
</tbody>
</table>

Acknowledgement

The authors are thankful to the Shahrood University of Technology Research Council for the support of this work.

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