Eurasian Journal of Analytical Chemistry

Eurasian J Anal Chem 6(3): 173-188, 2011

Chemically Modified Polystyrene with a Synthesized N_3O_2 Schiff Base as a New Solid Phase Sorbent for on Line Preconcentration and Determination of Copper(II) in Water Samples by FAAS

Mansour Arab Chamjangali *, **Soheila Kalvani, and Bahram Bahramian**

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

Received: *26/07/2010;* ***Accepted:*** *13/04/2011*

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 $\mu g\ L^{-1}$; detection limits of 1.4 and 0.46 $\mu g\ L^{-1}$; 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 $\mu g\ L^{-1}$ 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].

---

* **Corresponding Author**
E-mail: marab@shahroodut.ac.ir

ISSN: 1306-3057

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-diviylbenzene (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.

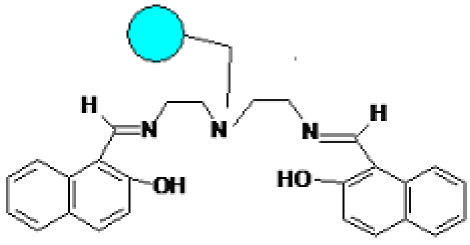


Fig. 1. Structure of PS-NAPdien resin.

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 $Cu(NO_3)_2.3H_2O$ 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_2HPO_4 and 1.0 mol L^{-1} KH_2PO_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, λ_{max}(nm): 400, 310,285, 247, 220.

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

The immobilization of N,N-bis(naphtilidineimino)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, 1210, 1150, 1070, 1050, 985, 905, 865, 845, 750,697, 563 and 490 cm^{-1}.

2.4. Preparation of mini-column

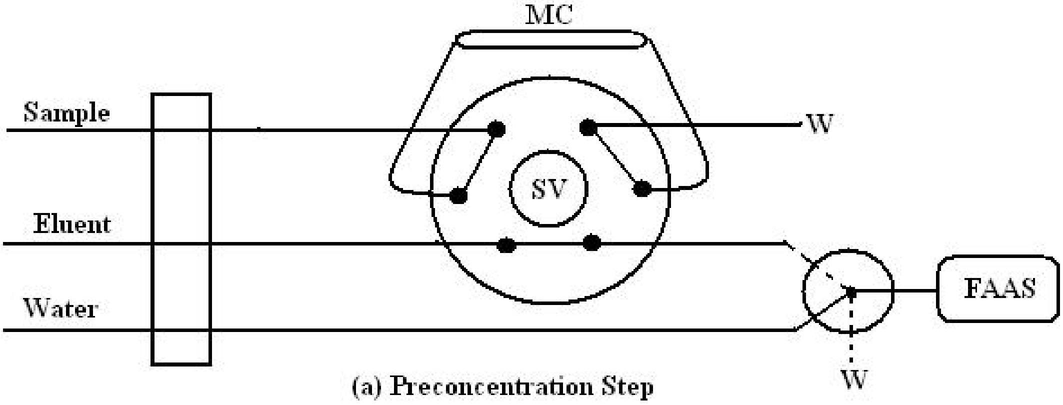
The mini-column was manufactured in the laboratory from polyethylene tubing of 8-cm length and 2.0-mm internal diameter, and packed with about 154 mg of the sorbent. Its ends were fitted with wool glass to retain the sorbent in the tube. The packed mini-column was initially washed with 2.0 mol L^{-1} 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

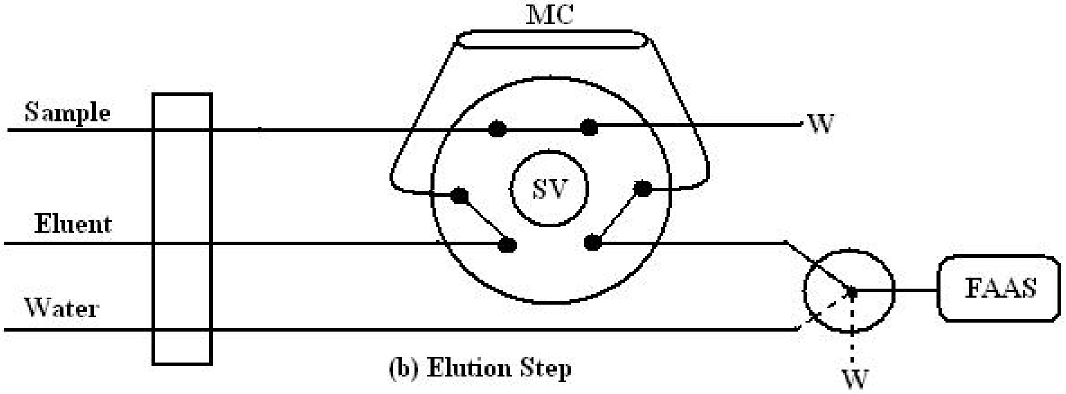
A schematic diagram of the flow manifold used is presented in Fig. 2. A variable flow-rate peristaltic pump with 12 channels (Hidolph, Model 5201) equipped with Tygon® tubes was used to pump sample stream through the manifold. PTFE tubing was used for manifold lines. The six-way rotary injection valve (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.



(a) Preconcentration Step



(b) Elution Step

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.

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 (iii) 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 μg 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}.

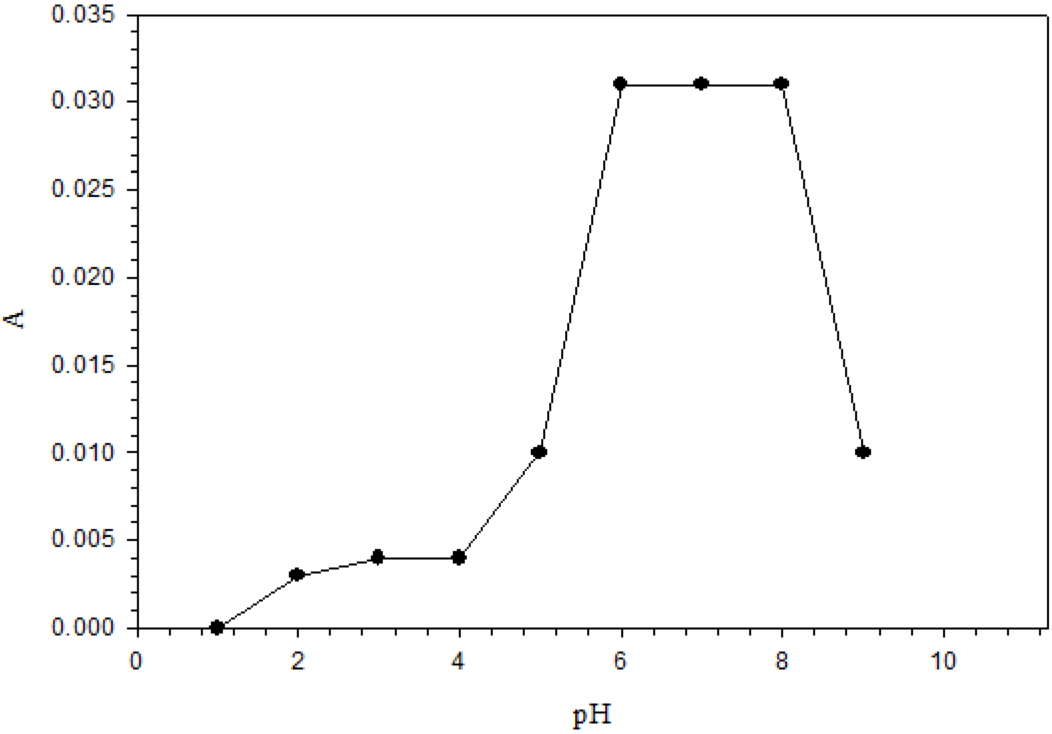


Fig. 3. Effect of sample solution acidity on the absorbance.
Conditions: preconcentration of 5.0 mL of 20.0 μg L^{-1} Cu(II) solution with flow rate of 2.0 mL min^{-1} on a 4.0 cm mini-column and elution with 2.0 mol L^{-1} HCl with flow rate of 2.0 mL min^{-1}.

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 HNO_3). 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.

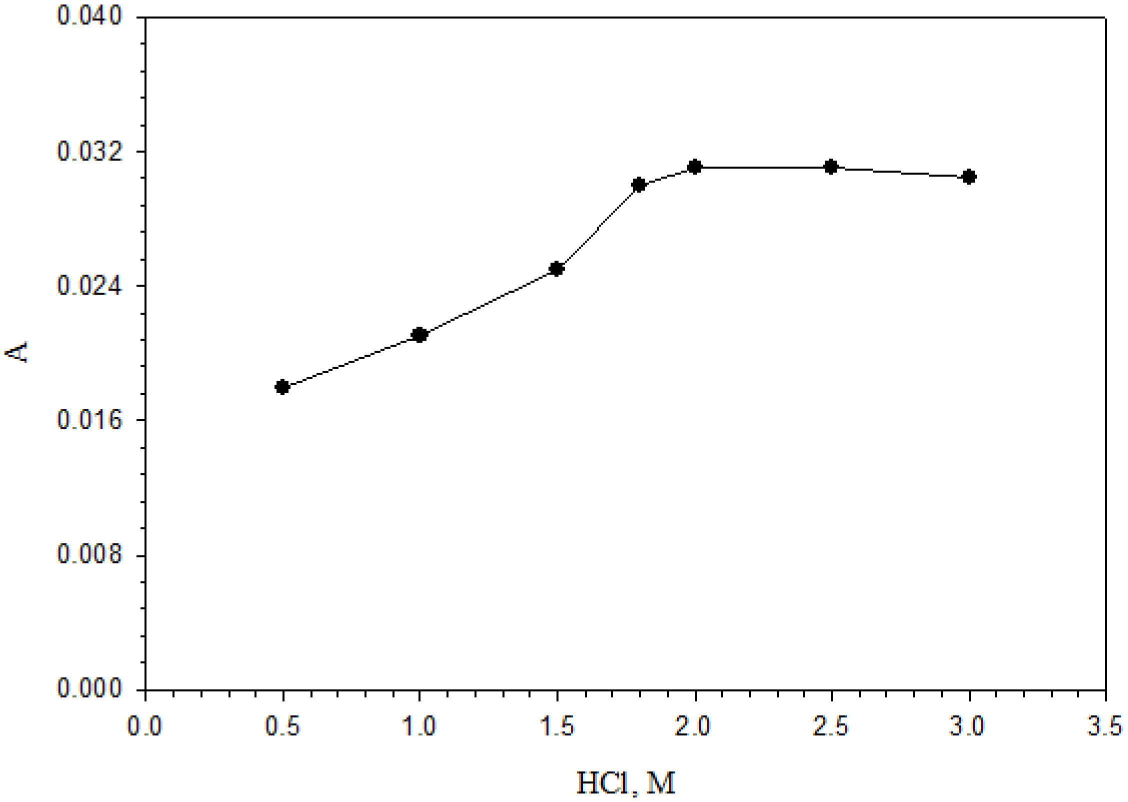


Fig. 4. Effect of eluent concentration on the absorbance.

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}.

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.

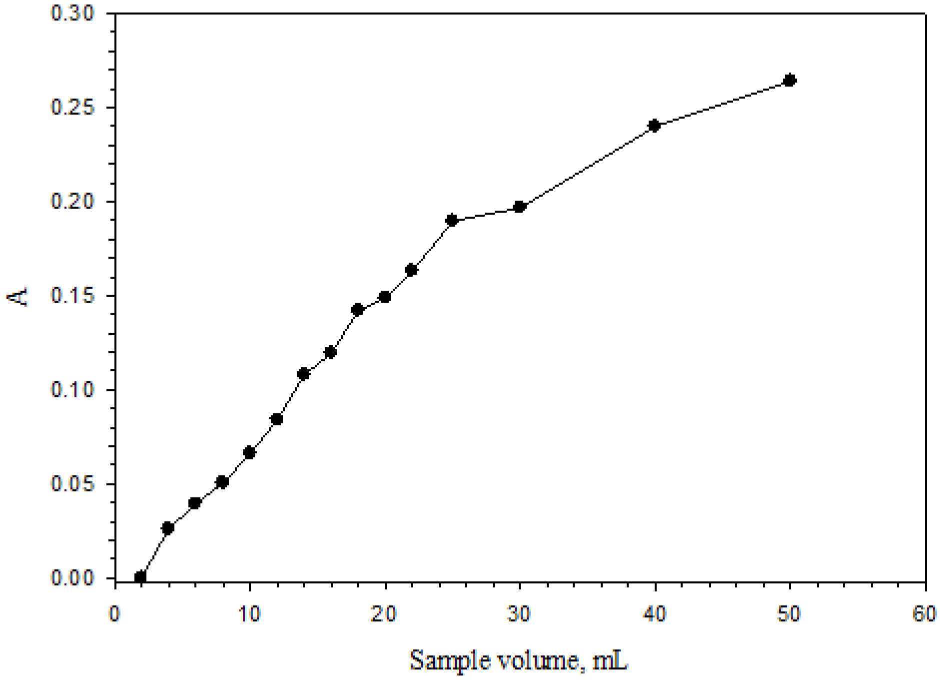


Fig. 5. Effect of preconcentration volume on the absorbance.
Conditions: preconcentration of 20.0 μg L^{-1} Cu(II) solution buffered at pH= 7.0 with flow rate of 6.0 mL min^{-1} on a 4.0 cm mini-column and elution with HCl 2.0 mol L^{-1} with flow rate of 6.0 mL min^{-1}.

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]:

$$CF = \frac{C_1}{C_2} \tag{1}$$

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.

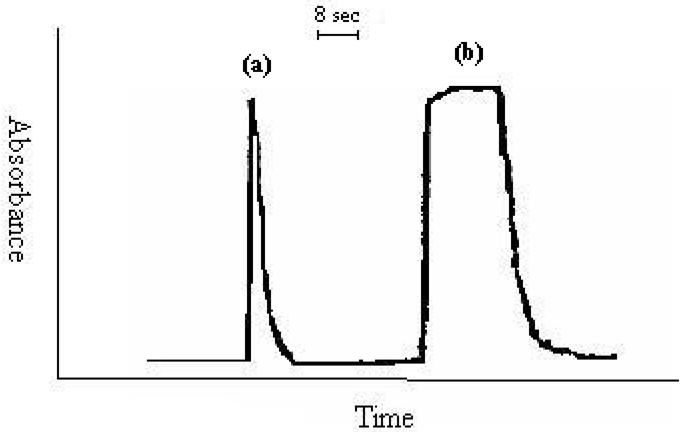


Fig. 6. Absorbance-time response for (a) sequential preconcentration and elution of Cu(II) solution (10 mL, 12.5 μg L^{-1}, pH 7.0), and (b) conventional nebulization of 1.0 mg L^{-1} acidic Cu(II) solution.

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 $A= 3.38 \times 10^{-3} C_{Cu(II)} + 0.004$ (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 $A= 9.11 \times 10^{-3} C_{Cu(II)} + 0.005$ (r= 9984, n= 10), where A is absorbance and $C_{Cu(II)}$ is copper(II) concentration in μg L^{-1}.

The 3σ 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 $A= 1.75 \times 10^{-3} C_{Cu(II)} + 0.002$ (r= 9975, n= 6). The 3σ 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})

Species	Tolerence limit (μg L^{-1})
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-}, $S_2O_3^{2-}$, PO_4^{3-}, $C_2O_4^{2-}$, NO_2^-, SCN^-, Citrate, Tartarate	20000[a]
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

Sample	Cu(II) added (μg mL^{-1})	Cu(II) found (μg mL^{-1})	Recovery (%)
Tap water(I)	-	<DL	-
	0.0040	0.0038 (±0.0002)	95.0
	0.024	0.025 (±0.003)	104.2
Tap water(II)	-	<DL	-
	0.016	0.017 (±0.001)	106.2
	0.020	0.021 (±0.002)	105.0
Spring water	-	<DL	-
	0.0050	0.0051 (±0.0003)	102.0
	0.025	0.025 (±0.001)	99.8
	0.033	0.032 (±0.002)	97.0
Bottled natural mineral water	-	<DL	-
	0.013	0.014 (±0.001)	107.7
	0.017	0.018 (±0.001)	105.9
0.50 M NaCl solution	-	<DL	-
	0.0060	0.0063 (±0.0004)	105.0
	0.010	0.0094 (±0.0003)	94.0
	0.014	0.014 (±0.001)	100.0
	0.018	0.019 (±0.002)	105.6
	0.026	0.026 (±0.001)	100.0
	0.030	0.030 (±0.001)	100.0

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

Support	Modifier (ligand)	Eluent	Samle volume (mL)	PF	DL (μg L^{-1})	Ref
Dowex Optipore SD-2	5-methyl-4-(2-thiazolylazo) resorcinol	HNO_3	250	50	1.03	46
Polyethylenimine	-----	-----	10	2	5.2	47
Silica gel	3-(1-imidazolyl)propyl	HNO_3	11.25	42.2	0.4	16
Octadecyl silica	Bis(5-bromo-2-hydroxybenzaldehyde) -1,2-propanediimine	HNO_3	2000	400	2.4	48
Analcime zeolite	pyrocatechol violet	HNO_3	1000	200	0.05	49
Chromosorb 105	pyrocatechol violet	HCl	30	60	1.67	50
Octadecyl silica	bis-(3-methoxy salicylaldehyde)-1,6-diaminohexane	EDTA	1000	100	0.03	51
Amberlite XAD-2	1,10-phenanthroline	Ethanol	1000	100	3.9	52
Syrene imprinted polymer	2,2′-[ethane-1,2-diylbis(nitrilo(E)methylylidene)]bis(6-allyl-4-methoxyphenol)	HNO3	2.0	5.8	1.07	53

Table 3 (continued)

Support	Modifier (ligand)	Eluent	Samle volume (mL)	PF	DL (μg L^{-1})	Ref
Syrene imprinted polymer	2,2′-[ethane-1,2-diylbis(nitrilo(E)methylylidene)]bis(6-allyl-4-methoxyphenol)	HNO_3	2.0	5.8	1.07	53
Peat	-----	HNO_3	13.6	16	3	54
Sepabeads	N^1, N^2-bis(4-fluorobenzylidene)ethane-1,2-diamine	HNO_3	1500	188	1.6	55
Multi-walled carbon nanotubes	-----	HNO_3	600	60	1.46	56
Chloromethylated polystyrene	Bis(naphtilidineimino) diethylenetriamine	HCl	10	80	1.4	This work

Acknowledgement

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

References

1. Sharma B K (1997) Environmental Chemistry Goel Publishing House Meerut, India.
2. Moore J W, Ramamoorthy S (1984) Heavy Metals in Natural Waters Springer-Verlag, New York.
3. Förstner U, Wittmann G T (1981) Metal pollution in the aquatic environment Springer, Berlin.
4. Dieter H H, Schimmelpfennig W, Meyer E, Tabert M (1999) Early childhood cirrhoses (ECC) in Germany between 1982 and 1994 with special consideration of copper etiology. Eur J Med Res 4:233
5. Tao G, Fang Z, Baasner J, Welts B (2003) Flow injection on-line dilution for flame atomic absorption spectrometry by micro-sample introduction and dispersion using syringe pumps. Anal Chim Acta 481:273
6. Bezerra M A, Arruda M A Z, Ferreira S L C (2005) Cloud Point Extraction Review. Appl Spectrosc Rev 40:269.
7. Stalikas C D (2002) Micelle-mediated extraction as a tool for separation and preconcentration in metal analysis. Trends Anal Chem 21:343.
8. Miró M, Frenzel W (2004) Automated membrane-based sampling and sample preparation exploiting flow-injection analysis. Trends Anal Chem 23:624.
9. Camel V (2003) Solid phase extraction of trace elements. Spectrochim Acta Part B 58:1177
10. Liu P, Su Z, Wu X, Pu Q (2002) Application of isodiphenylthiourea immobilized silica gel to flow injection on-line microcolumn preconcentration and separation coupled with flame atomic absorption spectrometry for interference-free determination of trace silver, gold, palladium and platinum in geological and metallurgical samples. J Anal At Spectrom 17:125
11. Fang Z (1995) Flow Injection Atomic Absorption Spectrometry, John Wiley and Sons Ltd, West Sussex, England.

12. Zhang S, Pu Q, Liu P, Sun Q, Su Z (2002) Synthesis of amidinothioureido-silica gel and its application to flame atomic absorption spectrometric determination of silver, gold and palladium with on-line preconcentration and separation. Anal Chim Acta 452:223
13. Ferreira S L C, Lemos V A, Santelli RE, Ganzarolli E, Curtius AJ (2001) An automated on-line flow system for the pre-concentration and determination of lead by flame atomic absorption spectrometry. Microchem J 68:41
14. Liang H D, Han D M (2006) Multi-walled carbon nanotubes as sorbent for flow injection on-line microcolumn preconcentration coupled with flame atomic absorption spectrometry for determination of cadmium and copper. Anal Lett 39:2285
15. Fang Z, Guo T, Welz B (1991) Determination of cadmium, lead and copper in water samples by flame atomic-absorption spectrometry with preconcentration by flow-injection on-line sorbent extraction. Talanta 38:613
16. Xu S, Sperling M, Welz B (1992) Flame atomic absorption spectrometric determination of cadmium and copper in biological reference materials using on-line sorbent extraction preconcentration. Fresenius J Anal Chem 344:535
17. Ma R, Van Mol W, Adams F (1994) Determination of cadmium, copper and lead in environmental samples An evaluation of flowinjection on-line sorbent extraction for flame atomic absorption spectrometry. Anal Chim Acta 285:33
18. Ali A, Yin X, Shen H, Ye Y, Gu X (1999) 1,10-Phenanthroline as a complexing agent for on-line sorbent extraction/preconcentration for flow injection-flame atomic absorption spectrometry. Anal Chim Acta 392:283
19. da Silva E L, Martins A O, Valentini A, de Favere V T, Carasek E (2004) Application of silica gel organofunctionalized with 3-(1-imidazolyl)propyl in an on-line preconcentration system for the determination of copper by FAAS. Talanta 64:181
20. Gu X, Xu G M, Ye Y X, Yin X F (2000) Copper determination by flow injection on-line sorbent preconcentration coupled with flame atomic absorption spectrometry using 1,10-phenanthroline. Lab Robotics Automat 12:97
21. Dadfarnia S, Shabani A M H, Tamaddon F, Rezaei M (2005) Immobilized salen (N,N-bis(salicylidene) ethylenediamine) as a complexing agent for on-line sorbent extraction/preconcentration and flowinjection–flame atomic absorption spectrometry. Anal Chim Acta 539:69
22. Dadfarnia S, Salmanzadeh A M, Shabani A H M (2002) Immobilized 1,5-diphenylcarbazone as a complexing agent for on-line trace enrichment and determination of copper by flow injection-atomic absorption spectroscopy. J Anal At Spectro 17:1434
23. da Silva E L, Ganzarolli E M, Carasek E (2004) Use of Nb2O5–SiO2 in an automated on-line preconcentration system for determination of copper and cadmium by FAAS. Talanta 62:727
24. Lemos V A, Teixeira L S G,, Bezerra M A, Costa A C S, Castro J T, Cardoso L A M de Jesus D S, Santos E S, Baliza P X, Santos L N (2008) Materials for solid-phase extraction of trace elements. Appl Spectrosc Rev 43:303

25. de Pena Y P, Lopez W, Burguera J L, Burguera M, Gallignani M, Brunetto R, Carrero P, Rondon C, Imbert F (2000) Synthetic zeolites as sorbent material for on-line preconcentration of copper traces and its determination using flame atomic absorption spectrometry. Anal Chim Acta 403:249
26. Chen H, Xu S, Fang Z (1994) Determination of copper in water and rice samples by flame atomic absorption spectrometry with flow-injection on-line adsorption preconcentration using a knotted reactor. Anal Chim Acta 298:167
27. Li Y, Jiang Y, Ping Yan X (2004) Further study on a flowinjection on-line multiplexed sorption preconcentration coupledwithflameatomic absorption spectrometry for trace element determination. Talanta 64:758
28. Yan X P, Li Y, Jiang Y (2002) A flow injection on-line displacement/sorption preconcentration and separation technique coupled with flame atomic absorption spectrometry for the determination of trace copper in complicated matrices. J Anal At Spectro 17:610
29. Ferreira S, Lemos V A, Moreira B C, Spinola Costa A C, Santelli R E (2000) An on-line continuous flow system for copper enrichment and determination by flame atomic absorption spectroscopy. Anal Chim Acta 403:259
30. Lemos V A, Baliza P X (2005) Amberlite XAD-2 functionalized with 2-aminothiophenol as a new sorbent for on-line preconcentration of cadmium and copper. Talanta 67:564
31. Cassella R J, Magalhaes O I B, Couto M T, Lima E L S, Neves M A F S, Coutinho F M B (2005) Synthesis and application of a functionalized resin for flow injection/FAAS copper determination in waters. Talanta 67:121
32. Yebra M C, Carro N, Enriquez M F (2001) A Moreno-Cid A Garcia, Field sample preconcentration of copper in sea water using chelating minicolumns subsequently incorporated on a flow-injection–flame atomic absorption spectrometry system. Analyst 126:933
33. Anthemidis A N, Zachariadis G A, Stratis J A (2002) On-line preconcnetration and determination of copper, lead and chromium(VI) using unloaded polyurethane foam packed column by flame atomic absorption spectrometry in natural waters and biological samples. Talanta 58:831
34. Lemos V A, de Jesus A A, Gama E M, David G T, Yamaki R T (2005) On-line solid phase extraction and determination of copper in food samples using polyurethane foam loaded with Me-BTANC. Anal Lett 38:683
35. Akelah A, Moet A (1990) Functionalized Polymers and their Applications, Chapman and Hall, Great Britain.
36. Mashhadizadeh M H, Pour Taheri E, Sheikhshoaie I (2007) A novel Mn2+ membrane electrode based on a recently synthesized Schiff base. Talanta 72:1088
37. Sadeghi S, Fathi F, Esmaeili A A, Naeimi H (2006) Novel triiodide ion-selective polymeric membrane electrodes based on some transition metal-Schiff base complexes. Sens Actuators B114:928
38. Ziyadanoğullar B, Ceviziçi D, Temel H, Ziyadanoğullar R (2008) Synthesis, characterization and structure effects on preconcentration and extraction of N,N′-bis-(salicylaldehydene)-1,4-bis-(p-aminophenoxy) butane towards some divalent cations. J Hazard Mater 150:285

39. Vogel A I (2000) A Text Book of Quantitative Chemical Analysis sixth ed. Longmans, London.

40. Coleman W M, Boggess R K, Hughes J W, Taylor L T (1981) Electrochemical studies of manganese(II) complexes containing pentadentate ligands with O_2N_3, O_3N_2, and O_2SN_2 donor sets. Inorg Chem 20:700

41. Benabdallah T, Al-taiar A H, Reffas H (2004) Spectrophotometric studies of the behaviour of multidentate schiff base ligands with copper(II) in methanol solution. S Afr J Chem 57:33

42. Arab Chamjangali M, Talebzadeh Farooji S, Bahramian B (2010) Application of chloromethylated polystyrene functionalized with N,N-bis (naphthylideneimino) diethylenetriamine in an on-line preconcentration system for the determination of cadmium by FAAS. J Hazard Mater 174:843.

43. Hancock R D, Martell A E (1989) Ligand design for selective complexation of metal ions in aqueous solution. Chem Rev 89:1875

44. Pinto C G, Pavon J L P, Cordero B M, Beato E R, Sanchez S S (1996) Cloud point preconcentration and flame atomic absorption spectrometry: application to the determination of cadmium. J Anal At Spect 11:37

45. Ma R, Woods G, McLeod C W (1999) Flow Analysis with Atomic Spectrometric Detectors, Anal Spectrosc Library, Vol. 9, Elsevier, Amsterdam, 1999, p 439.

46. Tuzen M, Soylak M, Citak D, Ferreira HS, Korn M G A, Bezerra M A (2009) A preconcentration system for determination of copper and nickel in water and food samples employing flame atomic absorption spectrometry. J Hazard Mater 162:1041.

47. Sabermahani F, Taher M A (2006) Application of a new water-soluble polyethylenimine polymer sorbent for simultaneous separation and preconcentration of trace amounts of copper and manganese and their determination by atomic absorption spectrophotometry. Anal Chim Acta 565:152

48. Fathi S A M, Yaftian M R (2008) Enrichment of trace amounts of copper(II) ions in water samples using octadecyl silica disks modified by a Schiff base ionophore prior to flame atomic absorption spectrometric determination. J Hazard Mater 164:133

49. Afzali D, Mostafavi A, Taher M A, Moradian A (2007) Flame atomic absorption spectrometry determination of trace amounts of copper after separation and preconcentration onto TDMBAC-treated analcime pyrocatechol-immobilized. Talanta 71:971

50. Buke B, Divrikli U, Soylak M, Elci L (2009) On-line preconcentration of copper as its pyrocatechol violet complex on Chromosorb 105 for flame atomic absorption spectrometric determinations. J Hazard Mater 163:1298.

51. Mashhadizadeh M H, Pesteh M, Talakesh M, Sheikhshoaie I, Ardakani M M, Karimi M A (2008) Solid phase extraction of copper(II) by sorption on octadecyl silica membrane disk modified with a new Schiff base and determination with atomic absorption spectrometry. Spectrochim Acta Part B 63:885

52. Castro Martha T P O, Baccan N (2005) Application of factorial design in optimization of preconcentration procedure for copper determination in soft drink by flame atomic absorption spectrometry. Talanta 65:1264.

53. Tobiasz A, Walas S, Trzewik B, Grzybek P, Zaitz M M, Gawin M, Mrowiec H (2009) Cu(II)-imprinted styrene–divinylbenzene beads as a new sorbent for flow injection-flame atomic absorption determination of copper. Microchem J 93:87.
54. Gonzales A P S, Firmino M A, Nomura C S, Rocha F R P, Oliveira P V, Gaubeur I (2009) Peat as a natural solid-phase for copper preconcentration and determination in a multicommuted flow system coupled to flame atomic absorption spectrometry. Anal. Chim. Acta 636:198.
55. Ghaedi M, Shabani R, Shokrollahi A, Montazerozohori M, Sahraiean A, Soylak M (2009) Preconcentration and separation of trace amount of copper (II) on N1, N2-bis(4-fluorobenzylidene)ethane-1,2-diamine loaded on Sepabeads SP70. J Hazard Mater 170:169.
56. Soylak M, Ercan O (2009) Selective separation and preconcentration of copper (II) in environmental samples by the solid phase extraction on multi-walled carbon nanotubes. J Hazard Mater 168:1527.