



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

S.A.M. Fathi, M.R. Yaftian*

Department of Chemistry, Faculty of Science, Zanjan University, PO Box 45195-313 Zanjan, Iran

ARTICLE INFO

Article history:

Received 14 December 2007

Received in revised form 9 July 2008

Accepted 31 July 2008

Available online 6 August 2008

Keywords:

Copper(II)

Solid phase extraction

Preconcentration

Schiff base

ABSTRACT

Bis(5-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine is synthesized by the reaction of 5-bromo-2-hydroxybenzaldehyde and 1,2-diaminopropane in ethanol. This ligand is used as a modifier of octadecyl silica disks for preconcentration of trace amounts of copper(II) ions, followed by nitric acid elution and flame atomic absorption spectrometric (FAAS) determination. The effect of parameters influencing the extraction efficiency, i.e. pH of the sample solutions, amount of the Schiff base, type and volume of stripping reagent, sample and eluent flow rates were evaluated. Under optimum experimental conditions, the capacity of the membrane disks modified by 4 mg of the ligand was found to be 247.7 (± 2.1) μg of copper. The detection limit and the concentration factor of the presented method are 2.4 ng/l and greater than 400, respectively. The method was applied to the extraction, recovery and detection of copper in different synthetic and water samples.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Copper is known as an important element in industry and biological systems as well. It is an essential nutrient to all high plants and animals. Copper is found in the bloodstream of animals, as a co-factor in various enzymes. This element can be also poisonous and even fatal to organisms. A concentration more than 1 $\mu\text{g}/\text{ml}$ can impart a bitter taste to water. Large oral doses can cause vomiting and may eventually cause liver damage. Copper concentration in potable water is usually very low ($\leq 20 \mu\text{g}/\text{l}$) [1]. The concentration of copper in lakes and rivers ranges from 0.5 to 1000 $\mu\text{g}/\text{l}$ with an average concentration of 10 $\mu\text{g}/\text{l}$. In groundwater the average of copper concentration (5 $\mu\text{g}/\text{l}$) is similar to that in lakes and rivers. Some groundwater contains up to 2800 $\mu\text{g}/\text{l}$, that is above the standard level for drinking water [2]. Copper can inhibit the activity of dihydrophil hydratase, an enzyme involved in haemopoiesis. Symptoms of copper poisoning are very similar to those produced by arsenic. Fatal cases are generally terminated by convulsions, palsy, and insensibility. Therefore, a precise, accurate and rapid measurement of copper is much interest.

Flame and graphite furnace atomic absorption spectrometry [3] and spectrophotometric methods [4] are known as the most

common methods for determination of copper in various samples. However, these methods suffer from their insufficient sensitivity for very low concentration of the metal in environmental and biological samples. To overcome such problems, an enrichment and matrix elimination step is sometimes required before applying the above-mentioned techniques. Various separation and preconcentration methods have been proposed to achieve these goals. Among them are solvent extraction [5], cloud point extraction [6], membrane filtration [7], ion exchange [8] and coprecipitation [9] techniques.

Solid phase extraction (SPE) is an alternative technique for liquid–liquid extraction for preconcentration purposes. It reduces the disposal costs, extraction time, and consumption of hazardous organic solvents [10,11]. Octadecyl-bonded silica disks modified by suitable ionophores have been successfully applied for solid phase extraction, separation, preconcentration and determination of different metal ions [12]. Undoubtedly, modifiers (ligands) play a crucial role in the success of such method.

Owing to their coordinating ability with a variety of metal ions, Schiff base ligands have been involved in various analytical investigations for many years. They are a category of important sensory molecules for fabricating cation- [13] and anion- [14] selective electrodes. Shemirani et al. [15] have studied the application of bis(2-methoxybenzaldehyde)ethylenediimine as a complexing agent for Cr(III) ions and a subsequent entrapment of this complex in surfactant micelles for enrichment and separation of chromium ions. In addition, various Schiff base ligands of type N_2O_2 were used

* Corresponding author. Tel.: +98 241 5152581; fax: +98 241 2283203.
E-mail address: yaftian@znu.ac.ir (M.R. Yaftian).

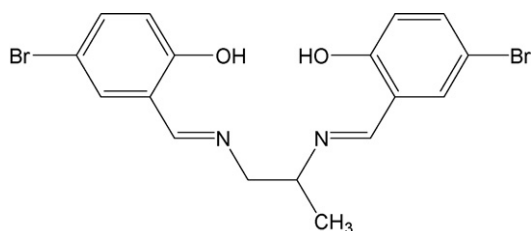


Fig. 1. Chemical structure of bis(5-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine (L).

as extractants in solvent extraction studies [16]. These molecules have been also used as modifier of octadecyl silica disks for pre-concentration and separation of trace amount of metal ions [17].

Considering the well documented selectivity of nitrogen/oxygen donor ligands towards copper ions [18] and in continuation to our recent studies on the complexive, extractive and analytical applications of N_xO_y -type of Schiff base ligands [19–21], here we report a rapid, highly sensitive and efficient method for the extraction and concentration of trace amounts of Cu(II) ions from aqueous media using octadecyl silica membrane disks modified with a new N_2O_2 -type Schiff base ligand called bis(5-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine (Fig. 1) and its determination by atomic absorption spectrometry.

2. Experimental

2.1. Reagents

Ethanol (Merck), 5-bromo-2-hydroxybenzaldehyde and 1,2-diaminopropane (Across) were used for the synthesis of bis(5-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine. Hydrochloric, nitric, sulfuric, acetic, formic (Merck), phosphoric (Fluka) acids, methanol (Aldrich), metal salts (Merck) were analytical grade. The stock solution of Cu^{2+} was prepared by dissolving an appropriate amount of copper nitrate in distilled water. This solution was standardized by complex formation titration. Working solutions were prepared by appropriate dilution of the stock solution.

2.2. Apparatus

1H NMR measurements were performed on a FT-Bruker (AVC 250 MHz) spectrometer and data was referenced relative to residual protonated solvent (7.26 ppm for $CDCl_3$). FT-IR spectrum was recorded on a Unicam (Matson 1000) spectrometer. A Varian (220AA) flame atomic absorption spectrometer (air/acetylene flame) was used for metal ions determinations. A Metrohm (model 780) digital pH meter equipped with a combined glass electrode was used for the pH adjustments.

2.3. Synthesis of

bis(5-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine (L)

A solution of 5-bromo-2-hydroxybenzaldehyde (0.7300 g, 4 mmol) in EtOH (30 ml) was refluxed with 1,2-diaminopropane (0.1500 g, 1.4 mmol) for 2 h. The yellow precipitate was filtered off and recrystallized twice from ethanol. The purity of the product was checked by thin layer chromatography. Yield, 0.6100 g (69%). UV-vis (CH_2Cl_2): 235, 338 nm. IR (KBr): $\nu_{O-H} = 3438.4\text{ cm}^{-1}$, $\nu_{C-H} = 2923\text{ cm}^{-1}$, $\nu_{C=N} = 1630.7\text{ cm}^{-1}$, $\nu_{C=C} = 1576.9\text{ cm}^{-1}$, $\nu_{C=O} = 1192.3\text{ cm}^{-1}$. 1H NMR ($CDCl_3$): δ (ppm) 1.38 (d, 3H, $NCH(CH_3)CH_2N$), 3.73 (m, $NCH(CH_3)CH_2N$), 3.86 (m, 1H, $NCH(CH_3)CH_2N$), 6.81–7.38 (m, 6H, ArH), 8.23 (s, $CHNCH_2CH(CH_3)N$), 13.19 (s, 2H, OH).

2.4. Solvent extraction procedure

The solvent extraction experiment was performed, using equal volumes (10 ml) of the organic (0.01 M of the Schiff base in dichloromethane) and aqueous (1×10^{-4} M of metal ions in 0.1 M sodium chloride) phases, in stoppered glass tubes at room temperature. The pH of the aqueous solutions was adjusted using NaOH/HCl solutions. The extraction equilibrium appeared to be attained after 30 min of continuous stirring. This was confirmed by measuring the copper concentration in the organic phase after 10, 20, 30 and 40 min of stirring, which was found to be 90, 98, 97.8 and 98%, respectively. After separation of the phases, the concentration of the metal ions remaining in the aqueous phase was measured by atomic absorption spectrometry.

2.5. Preparation of the SPE disks and extraction procedure

The applied procedure is similar to that reported by Shamsipur et al. [12]. Extraction experiments were performed with Empore membrane disks (47 mm diameter and 0.5 mm thick) containing octadecyl-bonded silica (8 μm particles, 6 nm pore size). The disks were used in conjunction with a standard Millipore 47 mm filtration apparatus connected to a water aspirator. After placing the membrane disk in the filtration apparatus, 10 ml methanol was poured onto the disk and drawn through it by applying a slight vacuum. The conditioning of disks was performed by pouring 10 ml methanol onto the disk. A low vacuum was applied until the solvent surface almost reaches the surface of the disk. Then, 20 ml water was introduced onto the disk and was passed through the disk and it was then dried under vacuum for 5 min. A solution of 4 mg of the ligand in 3 ml methanol was introduced onto the disk. The solution was allowed to penetrate inside the membrane. The modified disk was placed into an oven and the solvent was evaporated at 70 °C. The general procedure for the extraction of copper ions on the modified membrane was as follows: the disk was washed by passing 25 ml water and then, the sample solution was passed through the disk. After extraction, the adsorbed copper complex was stripped by 5 ml nitric acid solution (0.5 M) for determination by AAS method.

3. Results and discussion

Lipophilic nature of a modifier (ligand) affects the efficiency of solid phase extraction processes. In order to examine this characteristic, the distribution of the studied ligand (L) between water and dichloromethane was determined as a function of the aqueous phase pH in the range 2–11. The results revealed the highly lipophilic nature of the ligand because it remains, almost, completely in the organic phase at whole examined pH range.

The selectivity of the studied Schiff base was checked by performing competitive extraction experiment of Cu^{2+} , Cd^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} and Pb^{2+} ions (each 1×10^{-4} M) from aqueous solution (pH 5.5) into dichloromethane solution of the ligand (0.01 M). The order and extraction percentage of the verified ions was found to be as follow: Cu^{2+} (97.6%) \gg Cd^{2+} (16.9%) $>$ Zn^{2+} (8.4%) $>$ Co^{2+} (1.2%) $>$ Ni^{2+} ($<1\%$) \approx Pb^{2+} ($<1\%$). The results show an adequate selectivity of the ligand towards copper ions. This outcome provokes us to examine the efficiency of bis(5-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine as a suitable reagent for pre-concentration of Cu^{2+} ions by using it as a modifier of octadecyl-bonded silica membrane disks in solid phase extraction.

Table 1

Effect of different stripping acid solutions (5 ml) on the recovery of copper complexed on the modified octadecyl silica disks by 4 mg of L

Acid concentration (M)	Copper recovery (%) ^a		
	HNO ₃	HCl	H ₂ SO ₄
0.1	3.4	1.0	1.1
0.2	11.2	1.8	3.7
0.3	29.6	3.0	4.0
0.4	99.7	14.3	5.4
0.5	100.2	26.6	41.2

The sample solutions were buffered at pH of 7, strippant flow rate was 10 ml/min.

^a $\sigma_{N-1} \leq 1.6\%$.

We report recently [21] the extractive properties of *N,N'*-bis(1'-hydroxy-2'-acetonaphthone)propylenediamine, a similar ligand to the Schiff base studied in the present study, towards copper ions. The results consist with a cation exchange mechanism with the formation of a 1:1 (metal to ligand) stoichiometry. By analogy, one can propose a 1:1 stoichiometry for the complexed copper ions by L.

3.1. Selection of stripping reagent

After extraction of 5 μg of copper from a 50 ml sample solution (buffered at pH 7) by a disk modified with 4 mg of L, the complexed ions were stripped with 5 ml of different acids (HNO₃, HCl and H₂SO₄). In this step of the study the eluent flow rate was 10 ml/min. The results are regrouped in Table 1. It is seen that 5 ml of nitric acid 0.4–0.5 M can stripped quantitatively the copper ions from the disks. Therefore, 5 ml of 0.5 M nitric acid was used for further works.

3.2. Effect of pH

The influence of pH of the sample solutions on the extraction efficiency was studied in the pH range 2.0–8.0. The pH of solutions was adjusted by buffer solutions prepared from the mixture of phosphoric, formic or acetate acids and sodium hydroxide. The results (Fig. 2) indicate that the amount of copper retained on the disk is nearly independent on pH of the sample solutions in the range 6.0–8.0. Higher pH values (>8) were not tested because the possibility of hydrolysis of octadecyl silica in the disks.

3.3. Optimization of amount of the ligand

In order to determine the optimum amount of the studied Schiff base (L) for a quantitative extraction, a series of extraction experiments of 5 μg copper ion from 50 ml aqueous solutions at pH 7 (using phosphate buffer) and a flow rate of 30 ml/min were conducted as a function of the quantity of ligand in the range 0–8 mg (Fig. 3). As seen, the extraction of copper ions is quantitative using above 3 mg of the ligand. We modified the disks with 4 mg of the Schiff base for carrying out the subsequent SPE experiments. It is noteworthy that, there was no detectable amount of copper retained by the unmodified disk.

3.4. Influence of flow rate on the extraction efficiency

The influence of the sample flow rate through the modified membrane disks on the extraction of copper ions was studied. In this investigation the flow rate of samples was varied as 2, 7, 30 and 75 ml/min. The obtained results are given in Table 2. It is seen that the extraction efficiency of the method is not influenced by the flow rates of sample solutions. It was also found that, the recovery of copper ions does not depend on the elution flow

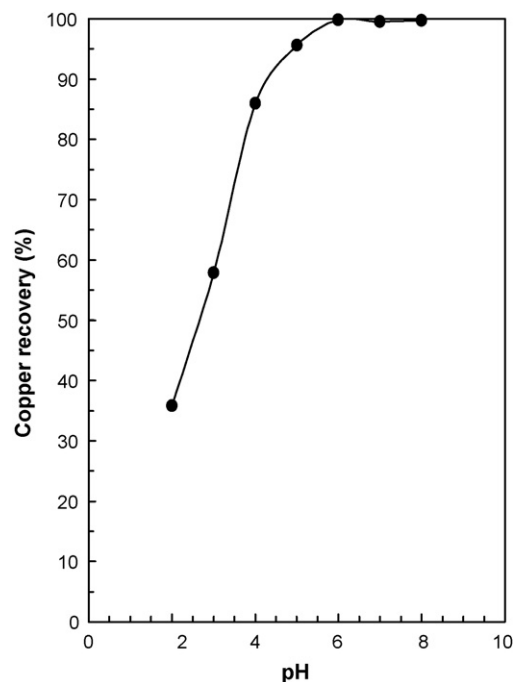


Fig. 2. Effect of the sample pH on the extraction of copper. Experimental conditions: 5 μg Cu in 50 ml solutions at different pH; octadecyl silica disk modified by 6 mg of L; sample solution and strippant (5 ml, HNO₃ 0.5 M) flow rate, 30 and 10 ml/min, respectively. $\sigma_{N-1} \leq 1.3\%$.

rates in the range of 1–28 ml/min (Table 2). The results reflect the fast complexation–decomplexation reactions of Cu(II) ions with the studied Schiff base. Based on these results, we used flow rates 30 and 10 ml/min for extraction and stripping steps, respectively.

3.5. Retention capacity of the modified disk

The maximum capacity of the membrane disk modified by 4 mg of the Schiff base was determined by passing 50 ml portions of an

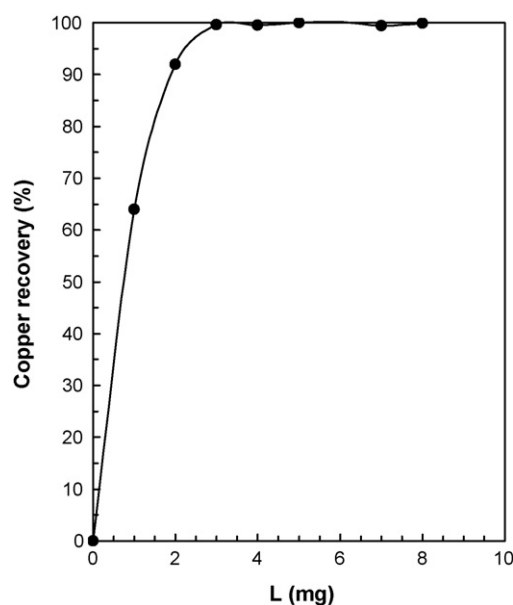


Fig. 3. Variation of copper recovery as a function of amount of the Schiff base on the disks. Extraction experiment: 5 μg of copper in aqueous solution (50 ml, pH 7); sample flow rate 30 ml/min, stripping agent 5 ml HNO₃ (0.5 M). $\sigma_{N-1} \leq 1.8\%$.

Table 2
Results of the investigation of sample and stripping solutions flow rates on the extraction and recovery of copper

Process	Extraction	Flow rate (ml/min)	2	7	30	75
		Extraction (%)	99.8	100.1	100.2	100.1
Stripping	Stripping	Flow rate (ml/min)	1	4	9	28
		Recovery (%)	100.4	99.8	101.0	100.2

$\sigma_{N-1} \leq 2\%$ for three replicate experiments.

aqueous solution containing 500 μg copper through the disk, followed by determination of the retained metal ions by flame atomic absorption spectrometry (FAAS). The maximum capacity was found to be 247.7 (± 2.1) μg of copper.

3.6. Break-through volume

The break-through volume of the method was determined by passing the sample solutions containing 5 μg of copper in 25, 50, 100, 250, 500, 1000 and 2000 ml buffered at pH 7 through modified disks with 4 mg of L followed by stripping of copper from the disk by 5 ml solution of 0.5 M nitric acid. The results showed that the extraction by modified membrane disks was found to be quantitative at least up to 2000 ml. Thus the break-through volume of the method is greater than 2000 ml. This means that a concentration factor of higher than 400 can be achieved.

For comparison, the concentration factor of the proposed method and that previously reported are given in Table 3. It is seen that, the concentration factor of the proposed method in this work is superior to that of the most other reported methods [7,11,22,24].

3.7. Limit of detection

The limit of detection (LOD) of the proposed method for determination of copper was studied under the optimal experimental conditions. The LOD obtained based on 3σ [12,17] of blank is 2.4 ng/l.

The capability of the modified disks with 4 mg of the studied Schiff base for a quantitative retention of different amounts of copper ion in 1000 ml of buffered solution (pH 7) was assessed. It was found that solutions containing 0.1–80 μg of Cu(II) ions can be quantitatively extracted by the disk.

3.8. Extraction of Cu^{2+} ions from synthetic samples

In order to evaluate the preconcentration and determination of Cu^{2+} ions from their mixtures with diverse metal ions, an aliquot of aqueous solution (50 ml) containing 5 μg of copper ion and other ions (see Table 4) was taken and the recommended procedure was followed. The results show that the presence of the tested ions does not affect the recovery of copper ions in the examined mixtures and a quantitative recovery of copper ions can be achieved by the modified disk.

Table 3
Comparison of concentration factor found for copper enrichment in this work with those reported previously

Concentration factor	Reference
25	[22]
60	[7]
100	[24]
330	[11]
400	[23]
>400	This work

Table 4
Separation of copper from synthetic samples

Added cation (M^{n+})	Amount taken (each ion, mg)	Copper recovery (%)
Na^+	10	100.2 (± 1.5)
K^+	10	99.7 (± 1.2)
Ca^{2+}	10	98.9 (± 1.6)
Mg^{2+}	10	100.1 (± 1.4)
Ni^{2+}	1	99.8 (± 1.5)
Co^{2+}	1	99.2 (± 1.3)
Zn^{2+}	1	99.1 (± 1.4)
Pb^{2+}	1	98.9 (± 1.6)
Cd^{2+}	0.5	98.3 (± 1.5)
Na^+ , K^+ , Ca^{2+} , Mg^{2+}	6	100.2 (± 1.3)
Ni^{2+} , Co^{2+} , Zn^{2+} , Pb^{2+}	0.4	99.0 (± 1.3)
Na^+ , Ca^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+}	5 and 0.5 ^a	100.4 (± 1.5)

Initial samples contained 5 μg Cu^{2+} and different amounts of various ions in 50 ml aqueous solution buffered at pH 7.

^a Taken amount of Na^+ and Ca^{2+} was 5 mg, and that of Pb^{2+} , Zn^{2+} and Cd^{2+} ions was 0.5 mg.

Table 5
Recovery of copper added to 1000 ml of different water samples

Sample	Added copper (μg)	Copper recovery ($\mu\text{g/l}$)
Snow water	0	0.18 (± 0.04)
	5	5.19 (± 0.021)
Tap water	0	2.19 (± 0.03)
	5	7.09 (± 0.02)
Mineral water	0	1.62 (± 0.07)
	5	6.59 (± 0.02)

3.9. Analytical application of the proposed method

To assess the applicability of the method to real samples, it was applied to the extraction and determination of copper from different water samples (Table 5). Tap water (Zanjan city, 25 December 2007), snow water (Zanjan city, 9 January 2007) and a regional trade mark mineral water samples were analyzed. As can be seen from Table 5, the copper ions can be quantitatively recovered from the water samples used.

4. Conclusions

The proposed SPE is accurate, precise, inexpensive and rapid method for enrichment and determination of trace amount of copper ions. A preconcentration factor of >400 was achieved by this method which allows to determine the copper content in highly diluted samples by conventional flame atomic absorption spectrometry. It is found that, the modified disks with 4 mg of bis(5-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine can quantitatively extract 0.1–80 μg copper ion from 1000 ml of buffered solution (pH 7).

References

- [1] Y. Yamini, J. Hassan, M.H. Karbasi, Solid-phase extraction of copper with cupron on octadecyl silica cartridge and its determination with atomic absorption, *Microchim. Acta* 148 (2004) 305–309.

- [2] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological profile for copper, 2004, GA, USA, Department of Health and Human Service, Public Health Service, <http://www.atsdr.cdc.gov>.
- [3] B. Welz, Atomic Absorption Spectroscopy, VCH, Amsterdam, 1985.
- [4] Standard Methods for Examination of Water and Waste Water, 19th ed., American Public Health Association, Washington, DC, 1995.
- [5] R. Saran, T.S.B. Baul, R. Srinivas, D.T. Khathing, Simultaneous determination of trace heavy-metals in waters by atomic-absorption spectrometry after preconcentration by solvent-extraction, *Anal. Lett.* 25 (1992) 1545–11360.
- [6] A. Bavili Tabrizi, Development of a cloud point extraction-spectrofluorimetric method for trace copper(II) determination in water samples and parenteral solutions, *J. Hazard. Mater.* B139 (2007) 260–264.
- [7] U. Divrikli, A.A. Kartal, M. Soylak, L. Elic, Preconcentration of Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) ions in environmental samples by membrane filtration prior to their flame atomic absorption spectrometric determinations, *J. Hazard. Mater.* 145 (2007) 459–464.
- [8] K. Ohzeki, M. Minorikawa, F. Yokota, I. Nukatsuka, R. Ishida, Enrichment of trace amounts of copper as chelate compounds using a finely divided ion-exchange resin, *Analyst* 15 (1990) 23–28.
- [9] M. Soylak, S. Saracoglu, U. Divrikli, L. Elci, Coprecipitation of heavy metals with erbium hydroxide for their flame atomic absorption spectrometric determinations in environmental samples, *Talanta* 66 (2005) 1098–1102.
- [10] M. Tuzen, K. Parlar, M. Soylak, Enrichment/separation of cadmium(II) and lead(II) in environmental samples by solid phase extraction, *J. Hazard. Mater.* B121 (2005) 79–87.
- [11] M. Ghaedi, F. Ahmadi, M. Soylak, Preconcentration and separation of nickel, copper and cobalt using solid phase extraction and their determination in some real samples, *J. Hazard. Mater.* 147 (2007) 226–231.
- [12] M. Shamsipur, A.R. Ghiasvand, H. Sharghi, H. Naeimi, Solid phase extraction of ultra trace copper(II) using octadecyl silica membrane disks modified by a naphthol-derivative Schiff's base, *Anal. Chim. Acta* 408 (2000) 271–277.
- [13] M.H. Mashhadizadeh, E. Pour Taheri, I. Sheikhshoae, A novel Mn²⁺ membrane electrode based on a recently synthesized Schiff base, *Talanta* 72 (2007) 1088–1092.
- [14] S. Sadeghi, F. Fathi, A.A. Esmaeili, H. Naeimi, Novel triiodide ion-selective polymeric membrane electrodes based on some transition metal-Schiff base complexes, *Sens. Actuators B* 114 (2006) 928–935.
- [15] F. Shemirani, S. Dehghan Abkenar, A.A. Mirroshandel, M. Salavati Niasari, R. Rahnama Kozania, Preconcentration and speciation of chromium ion water samples by atomic absorption spectrometry after cloud-point extraction, *Anal. Sci.* 19 (2003) 1453–1456.
- [16] S. Oshima, N. Hirayama, K. Kubono, H. Kokusen, T. Honjo, Ion-pair extraction behavior of divalent transition metal cations as charged complexes with *N,N'*-bis(2-pyridylmethylidene)-1,2-diiminoethane and its analogues, *Anal. Chim. Acta* 441 (2001) 157–164.
- [17] T. Shamspur, M.H. Mashhadizadeh, I. Sheikhshoae, Flame atomic absorption spectrometric determination of silver ion after preconcentration on octadecyl silica membrane disk modified with bis[5-((4-nitrophenyl) azosalicylaldehyde)] as a new Schiff base ligand, *J. Anal. At. Spectrom.* 18 (2003) 1407–1410.
- [18] R.D. Hancock, A.E. Martell, Ligand design for selective complexation of metal ions in aqueous solution, *Chem. Rev.* 89 (1989) 1875–1914.
- [19] M.R. Yaftian, S. Rayati, R. Safarbal, N. Torabi, H.R. Khavasi, A new tetradentate N₂O₂-type Schiff base ligand. Synthesis, extractive properties towards transition metal ions and X-ray crystal structure of its nickel complex, *Trans. Met. Chem.* 32 (2007) 374–378.
- [20] Z. Pilehvari, M.R. Yaftian, S. Rayati, M. Parinejad, A novel wire-type lead-selective electrode based on bis (1'-hydroxy-2'-acetonephthone)-2,2'-diiminodiethylamine, *Ann. Chim.* 97 (2007) 747–757.
- [21] D. Emadi, M.R. Yaftian, S. Rayati, *N,N'*-Bis(1'-hydroxy-2'-acetonephthone) propylenediamine: synthesis, extractive properties, and use as an ionophore in a Cu(II)-selective potentiometric sensor, *Turk. J. Chem.* 31 (2007) 423–433.
- [22] S. Hutchinson, G.A. Kearney, E. Horne, B. Lynch, J.D. Glennon, M.A. McKervey, S.J. Harris, Solid phase extraction of metal ions using immobilized calixarene tetrahydroxamates, *Anal. Chim. Acta* 291 (1994) 269–275.
- [23] M.R. Ganjali, Z. Gjasemi, M. Salavati-Niasari, L. Haji-gha babaei, Solid phase extraction and flame atomic absorption determination of copper, *Chem. Anal. (Warsaw)* 47 (2002) 619–626.
- [24] Y. Yamini, A. Tamaddon, Solid-phase extraction and spectrophotometric determination of trace amounts of copper in water samples, *Talanta* 49 (1999) 119–124.