Solid phase extraction of copper(II) ions using C18-silica disks modified by oxime ligands

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A B S T R A C T

5-Tert-butyl-2-hydroxy-benzaldehyde oxime (L_1) and 3,5- di-tert-butyl-2-hydroxy-benzaldehyde oxime (L_2) are synthesized and characterized by conventional spectroscopic methods. These ligands are used as modifier of octadecyl silica membrane disks for separation and pre-concentration of trace amounts of copper(II) ions, followed by sulfuric or nitric acid elution and flame atomic absorption spectrometric (FAAS) determination. The effect of parameters influencing the extraction efficiency i.e. pH of sample solutions, amount of the oxime, type and volume of eluent, sample solution and eluent flow rates were evaluated. Under optimum experimental conditions, the maximum capacity of the membrane disks modified by 6 mg of L_1 or 4 mg of L_2 was found to be 284.7 ($\pm$2.8) μg of copper and 382.5 ($\pm$3.1) μg of copper, respectively. The detection limits of the presented methods are 0.29 ng ml^{-1} for L_1 and 0.25 ng ml^{-1} for L_2. The enrichment factors are greater than 400 for both cases. These methods were successfully applied to the extraction, recovery and detection of copper in different water samples.

1. Introduction

Among the chemical species copper has a biological action at low doses and a toxic effect when ingested in larger quantities. A concentration more than 1μg ml^{-1} of copper 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 μg l^{-1}) [1]. A high concentration of copper in foods originates mainly from fungicide residues containing this metal used in agriculture and from water plumbing. The determination of trace levels of copper is important because it could catalyze oxidation of fatty acid chains, exerting a deleterious influence on shelf life and nutritional value [2].

Conventional ways for measurement of copper are flame [3] and electrothermal [4] atomic absorption spectrometry, and spectrophotometric [5] methods. Frequently, a separation and pre-concentration step are required for the determination of ultra-trace amounts of copper, because the matrix of samples may cause serious interference and also because the amount of the metal present in samples may be close to or even below the detection limit of these methods [6].

Solid phase extraction (SPE) has been applied as the excellent extraction and enrichment procedures, and it becomes an interesting technique in the cleanup of complex samples, by the matrix removal of the interfering compounds, to increase the overall sensitivity and selectivity of analytical methods [7].

Application of modified disks is known as the relatively newest alternative in the field of solid phase extraction techniques. A relatively simple alternative for preparation of the SPE disks is based upon the impregnation of suitable reagents on octadecyl disks, which are successfully used for the separation and sensitive determination of various metal ions [8].

Ionophoric properties of Schiff base and oxime compounds have been extensively studied because of their specific and selective reactions with metal ions. These compounds are able to form stable complexes with several transition metal ions, particularly with copper(II) ions [9]. An oxime is one in a class of chemical compounds with the general formula R_1R_2CNOH, where R_1 is an organic side chain and R_2 is either hydrogen, forming an aldoxime, or another organic group, forming a ketoxime [10].

We have used successfully Schiff base ionophores as disk modifier for SPE and cloud point extraction of copper ions in previous works [11,12]. In this study we report a rapid, selective, highly sensitive and efficient method for the extraction and pre-concentration of trace amounts of copper(II) ions from aqueous media using octadecyl silica membrane disks modified with two synthesized oximes (Fig. 1) called 5-tert-butyl-2-hydroxy-benzaldehyde oxime (L_1) and 3,5- di-tert-butyl-2-hydroxy-benzaldehyde oxime (L_2) and its determination by FAAS. To the best of our knowledge this is the first application of these oximes for pre-concentration of trace amounts of copper(II) ions in aqueous samples.

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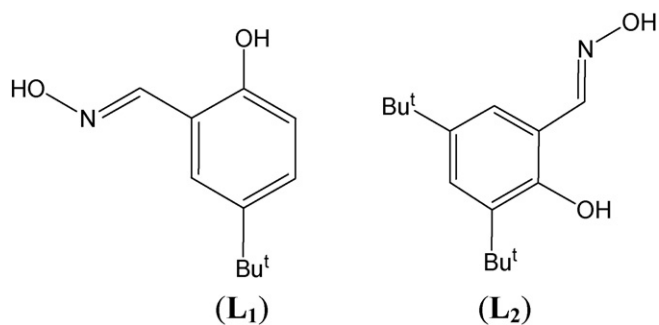E-mail addresses: yaftian@znu.ac.ir, mryaftian@yahoo.com (M.R. Yaftian).

Fig. 1. Chemical structure of 5-tert-butyl-2-hydroxy-benzaldehyde oxime (**L$_1$**) and 3,5- di-tert-butyl-2-hydroxy-benzaldehyde oxime (**L$_2$**).

2. Experimental

2.1. Reagents

Ethanol, 4-tert-butylphenol (Fluka), 2,4-di-tert-butylphenol, sodium hydroxide, chloroform, hydroxylammonium chloride and sodium acetate (Merck) were used for the synthesis of **L$_1$** and **L$_2$**. Hydrochloric, nitric, sulfuric, acetic, formic (Merck), phosphoric (Fluka) acids and methanol (Merck) were the highest purity. Metal salts were analytical grade and purchased from Merck chemical company. The stock solution of Cu^{2+} was prepared by dissolving an appropriate amount of copper nitrate. This solution was standardized by complex formation titration. Working solutions were prepared by appropriate dilution of the stock solution.

2.2. Apparatus

^{1}H 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 (220 AA) 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 the oximes

The studied oximes were synthesized based on the well known method of Reimer–Tiemann for preparation of corresponding salicylaldehyde derivatives, in the first step, and the reaction with hydroxylamine hydrochlorides and sodium acetate, in the second step.
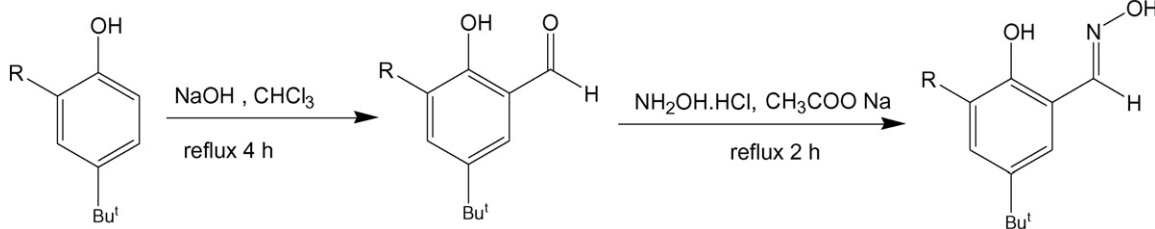
21 ml of distilled water and $CHCl_3$ (4.2 ml) for 4 h. The productions of this step (salicylaldehyde) separated by column chromatography and their purity were checked by thin layer chromatography. Yield: 2.500 g (50%) and 3.500 g (70%) for **L$_1$** and **L$_2$** respectively.

The produced salicylaldehydes that were refluxed with hydroxylammonium chloride (4.000 g, 28.7 mmol) and sodium acetate (8.000 g, 97.5 mmol) in water for 2 h. The final productions were extracted by ethyl acetate (yield: about 90% for both oximes).

Characterizations spectra for **L$_1$**: UV–vis. (CH_2Cl_2): 260 nm, IR (KBr): $\nu_{O-H} = 3353.8\ cm^{-1}$, $\nu_{C-H} = 2969.0\ cm^{-1}$, $\nu_{C=N} = 1500.0\ cm^{-1}$, $\nu_{C=C} = 1469.2,\ 1630.7\ cm^{-1}$, $\nu_{C-O} = 1261.0\ cm^{-1}$. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.29 (s, 9H,CH_3), 6.8, 7.18, 7.33 (d, 3H, ArH), 8.26 (s, 1H, ArCHNOH), 8.50 (s, 2H, OH) and about **L$_2$**: UV–vis. (CH_2Cl_2): 260 nm, IR (KBr): $\nu_{O-H} = 3438\ cm^{-1}$, $\nu_{C-H} = 2953\ cm^{-1}$, $\nu_{C=N} = 1469\ cm^{-1}$, $\nu_{C=C} = 1446,\ 1638\ cm^{-1}$, $\nu_{C-O} = 1246\ cm^{-1}$. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.29, 1.45 (s, 18H,CH_3), 7.03–7.38 (d, 2H, ArH), 8.26 (s, 1H, ArCHNOH), 10.14 (s, 2H, OH).

2.4. Solvent extraction procedure

The solvent extraction experiments were performed using equal volumes (10 ml) of the organic (5×10^{-3} M of the oxime in dichloromethane) and aqueous phases (1×10^{-4} M of metal ions in 0.1 M sodium chloride) phases, in stoppered glass tubes at 25 °C. The pH of aqueous solution was adjusted using NaOH/HCl solutions. The extraction equilibrium appeared to be attained after 30 min of continuous stirring. After separation of the phases, the concentration of the metal ions remaining in the aqueous phase was measured by atomic absorption spectrophotometry.

2.5. Preparation of the SPE disks and extraction procedure

The applied procedure is similar to that reported elsewhere [11]. 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 the disk 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 drawn through the disk and it was then dried under vacuum for 5 min. A solution of 6 mg of **L$_1$** or 4 mg of **L$_2$** in 3 ml methanol was introduced onto the disk. The solution was allowed to penetrate inside the membrane completely. Thereafter, the modified disk was placed into an oven and the solvent was evaporated at 70 °C. The general procedure for the extraction of

R= H or Bu^t

Synthesis consists of two steps. At the first step, a solution of 4-tert-butylphenol (5.000 g, 33.3 mmol) for synthesis **L$_1$** and 2,4-di-tert-butylphenol (5.000 g, 24.2 mmol) for synthesis **L$_2$** in EtOH (15 ml) was refluxed with NaOH (10,000 g, 250 mmol) dissolved in

copper ions on the modified membrane was as follows: the sample solution containing Cu^{2+} ions was passed through the disk. After extraction, the adsorbed metal complex was stripped by
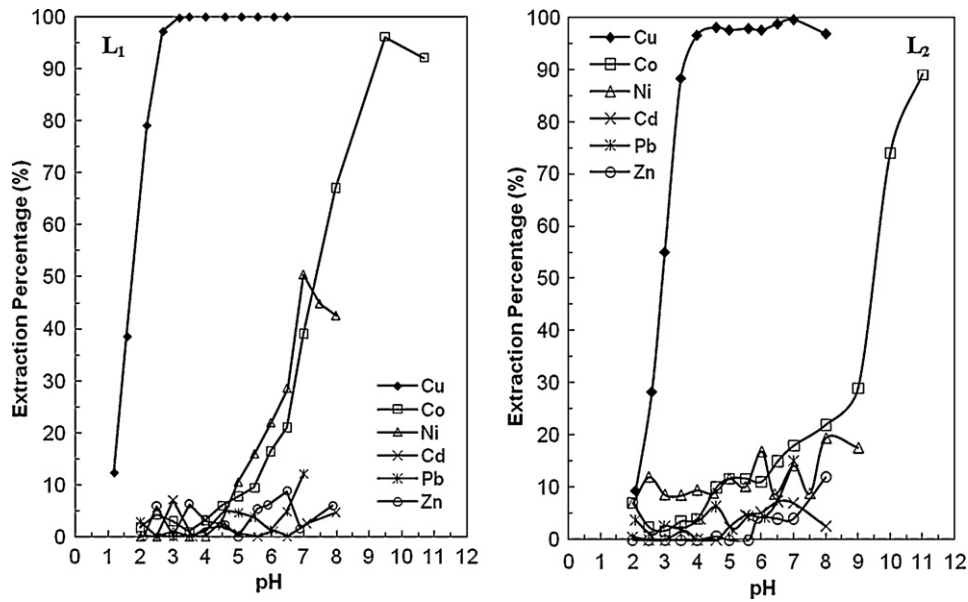
Fig. 2. Extraction percentages of different ions (initial concentration 1×10^{-4} M) from aqueous solution into dichloromethane solutions of L_1 and L_2 (0.005 M) as a function of pH.

using 5 ml acid solution as eluent (0.3 M sulfuric acid for L_1 and 0.03 M nitric acid for L_2) for copper determination by AAS method.

3. Results and discussion

The selectivity of the studied oximes was checked by performing a competitive extraction experiments of Cu^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} ions (each 1×10^{-4} M) from aqueous solution in different pH into dichloromethane solution of the ligands (0.005 M). The results (Fig. 2) shown that the extraction percentage of the Cu^{2+} ions by L_1 and L_2 in pH 4 is about 100% wherever extraction percentage about other ions is under 10%. The observed results show a high selectivity of the ligands towards copper ions. This outcome provokes us to examine the effi-

ciency of L_1 and L_2 as a suitable reagent for selective separation and pre-concentration of Cu^{2+} ions by using those as a modifier of octadecyl-bonded silica membrane disks in solid phase extraction.

3.1. Effect of pH

The influence of the pH of test solutions on the recovery of 5 μg Cu^{2+} from 100 ml solutions by the modified disk with 6 mg of L_1 or L_2 was studied at the range of 2.0–8.0. The pH was adjusted by using mixture of phosphoric, formic or acetic acids and sodium hydroxide. The results (Fig. 3) indicate that the amount of copper can be retained quantitatively on the disk at pH range 6–8 for L_1 and 5–7 for L_2. Therefore pH 7 (phosphate buffer) and pH 6 (acetate buffer) were selected as optimum pH
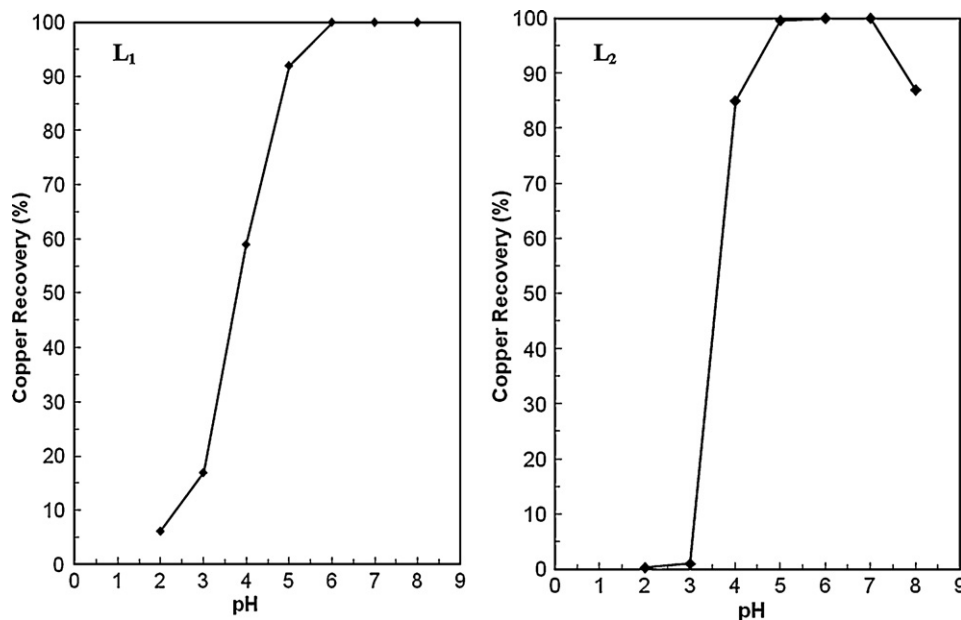

Fig. 3. Effect of the sample pH on the extraction of copper. Experimental conditions: 5 μg Cu^{2+} in 100 ml solutions at different pH; octadecyl silica disk modified by 6 mg of ligands; sample solution and strippant flow rate, 12 ml/min and 5 ml/min, respectively. $\sigma_{N-1} \leq 1.1\%$.

Table 1
Effect of different stripping acid solutions (5 ml) on the recovery of copper complexed on the modified octadecyl silica disks by 6 mg of L_1[a] or L_2.[b]

L_1				L_2			
Concentration (M)	Copper recovery (%)[b]			Concentration (M)	Copper recovery (%)[c]		
	HNO_3	HCl	H_2SO_4		HNO_3	HCl	H_2SO_4
0.10	84	95	99	0.01	99	98	96
0.20	86	97	100	0.02	102	100	102
0.30	87	97	100	0.03	102	101	102
0.40	95	99	100	0.04	101	100	100
0.50	99	100	100	0.05	93	100	100
1.00	100	100	100	0.06	96	102	101

[a] The sample solutions were buffered at pH 7 (phosphate buffer).
[b] The sample solutions were buffered at pH 6 (acetate buffer).
[c] $\sigma_{N-1} \leq 1.7\%$, strippant flow rate was 5 ml/min.

for L_1 and L_2, respectively. Higher pH values (>8) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.

3.2. Selection of stripping reagent

In order to choose the most effective eluent for the quantitative stripping of copper retained by the modified disk with 6 mg of ligands, the copper ions were stripped with 5 ml of various acids (HNO_3, HCl and H_2SO_4) with different concentrations. The results are summarized in Table 1. It is obvious that, among different stripping acids, H_2SO_4 for L_1 and HNO_3 for L_2 is the most promising one. Therefore 5 ml of 0.30 M sulfuric acid and 5 ml of 0.03 M nitric acid were used for further works with L_1 and L_2 respectively.

3.3. Effect of amount of the ligand

In order to investigate the optimum amount of ligand an experiment for a quantitative extraction of 5 μg copper ions from 100 ml aqueous solutions at the optimum pH the modified C18 disks with the oximes (0–8 mg), was performed (Fig. 4). The minimum quantity of L_1 and L_2 required for quantitative extraction of copper was

4 mg and 2 mg. Hence, for subsequent studies 6 mg of L_1 and 4 mg of L_2 was used.

3.4. Influence of flow rate on the extraction efficiency

The dependency of uptake of metal ions on the flow rate was studied. The flow rates of sample and stripping solution were investigated from 3.3 to 100 ml/min and from 1 to 10 ml/min, respectively. The obtained results were shown that the extraction and recovery efficiency of the method is not influenced by the flow rates of sample and stripping solution in the investigated interval. Hence, flow rates of 12 ml/min and 5 ml/min for the sample and stripping solution, respectively, were used.

3.5. Analytical performance

When solutions of 5 μg copper in 25 ml, 50 ml, 100 ml, 250 ml, 500 ml, 1000 ml and 2000 ml solutions under optimal experimental conditions for each ligand were passed through the modified disks, the copper was quantitatively recovered in all cases. Thus, the breakthrough volume for the both methods must be greater than 2000 ml, providing a concentration factor of >400.
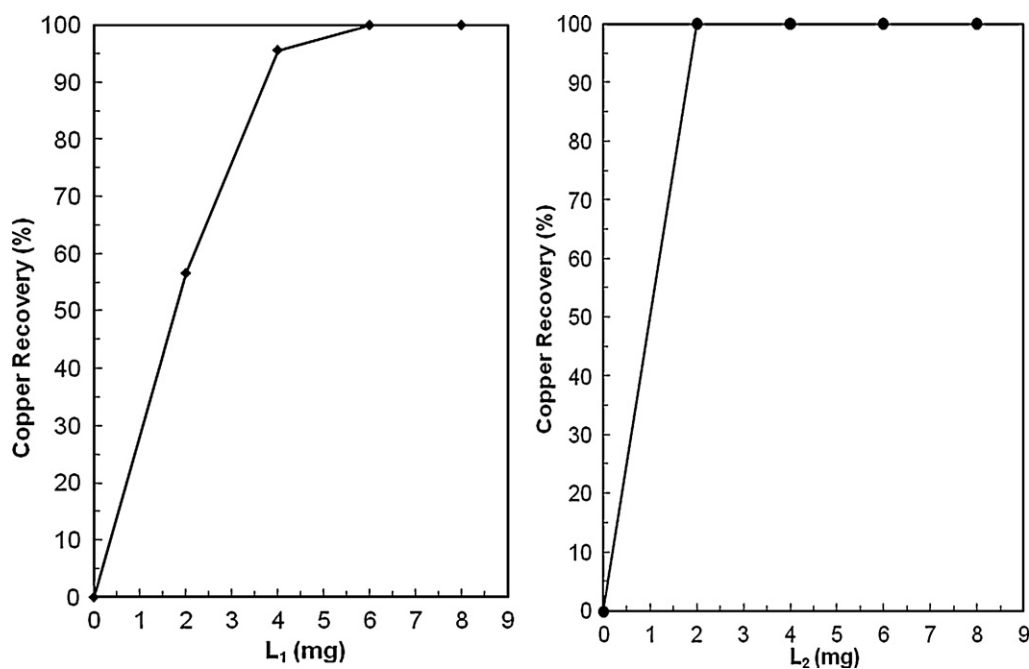

Fig. 4. Variation of copper recovery as a function of amount of the oximes on the disks. Extraction experiment: 5 μg of copper in aqueous solution (100 ml, pH 7 for L_1 and 6 for L_2); sample flow rate 12 ml/min, stripping agent 5 ml H_2SO_4 0.3 M for L_1 5 ml HNO_3 0.03 M for L_2. $\sigma_{N-1} \leq 1.6\%$.

Table 2
Separation of copper ions from binary mixtures.[a].

Added cation	Amount taken (each ion, mg)	L_1		L_2	
		Copper recovery (%)	Added cation recovery (%)	Copper recovery (%)	Added cation recovery (%)
Na^+	100.0	101.0 ($\pm$1.4)	–	102.0 ($\pm$0.8)	–
K^+	100.0	100.5 ($\pm$0.7)	–	101.0 ($\pm$1.1)	–
Ca^{2+}	100.0	99.0 ($\pm$1.4)	–	102.0 ($\pm$0.9)	–
Mg^{2+}	100.0	99.5 ($\pm$1.9)	–	103.0 ($\pm$0.7)	–
Sr^{2+}	100.0	99.0 ($\pm$1.7)	–	99.0 ($\pm$1.5)	–
Co^{2+}	100.0	101.5 ($\pm$0.7)	1.2 ($\pm$0.1)	100.0 ($\pm$1.1)	6.0 ($\pm$0.3)
Zn^{2+}	100.0.0	99.0 ($\pm$1.2)	1.0 ($\pm$0.3)	101.0 ($\pm$0.4)	0.5 ($\pm$0.1)
Pb^{2+}	100.0	100.0 ($\pm$1.6)	0.4 ($\pm$0.1)	100.1 ($\pm$0.5)	5.0 ($\pm$0.2)
Cd^{2+}	100.0	99.8 ($\pm$0.8)	1.1 ($\pm$0.2)	100.0 ($\pm$0.7)	0.4 ($\pm$0.1)
Ni^{2+}	100.0	100.0 ($\pm$1.4)	1.4 ($\pm$0.1)	98.2 ($\pm$0.3)	0.6 ($\pm$0.1)

[a] Initial samples contained 5 µg Cu^{2+} and different amounts of various ions in 100 ml aqueous solution buffered at pH 7 for L_1 and pH 6 for L_2.

Table 3
Recovery of copper from real samples by modified disks.

Sample	Added copper (µg)	L_1	L_2
		Copper recovery (µg/l)	Copper recovery (µg/l)
Sea water	0	0.50 ($\pm$0.02)	0.48 ($\pm$0.02)
	5	5.61 ($\pm$0.02)	5.58 ($\pm$0.03)
	10	10.73 ($\pm$0.01)	10.68 ($\pm$0.02)
Spring water	0	0.47 ($\pm$0.01)	0.46 ($\pm$0.01)
	5	5.56 ($\pm$0.17)	5.51 ($\pm$0.01)
	10	10.62 ($\pm$0.01)	10.56 ($\pm$0.005)
Tap water	0	0.50 ($\pm$0.04)	0.49 ($\pm$0.01)
	5	5.69 ($\pm$0.07)	5.60 ($\pm$0.07)
	10	10.81 ($\pm$0.31)	10.73 ($\pm$0.06)

The limit of detection (LOD) of the methods for the determination of copper was studied under the optimal experimental conditions. The LODs based on 3σ of the blank are 0.29 ng ml^{-1} for L_1 and 0.25 ng ml^{-1} for L_2. The linear dynamic range of the proposed methods for copper ions was found in a wide concentration range of 0.25 ($\pm$0.08)–284.72 ($\pm$2.80) µg for L_1 and 0.25 ($\pm$0.06)–382.5 ($\pm$3.1) in 100 ml solution.

The maximum capacity of the membrane disk modified by 6 mg of L_1 or 4 mg of L_2 was determined by passing 100 ml of an aqueous solution containing 500 µg copper through the disk, followed by determination of the retained metal ions by FAAS. The maximum capacity of modified disks was found 284.7 ($\pm$2.8) µg of copper and 382.5 ($\pm$3.1) µg of copper for L_1 and L_2 respectively.

In order to study the selective separation and determination of copper ions from its binary mixtures with diverse metal ions, an aliquot of aqueous solutions (100 ml) containing 5 µg Cu(II) and mg amounts of other cations was taken and the proposed procedure was followed. The results are summarized in Table 2. The results show that the modified membrane disks with L_1 or L_2, even in the presence of up to about 100 mg of diverse ions retains the Cu(II) ions in the binary mixtures completely.

To assess the applicability of the method to real samples, it was applied to the extraction and determination of copper from different water samples as tap water (Zanjan city, 2008), spring water (Sarein, 2008) and sea water (taken from the Caspian sea-Hasan rood area, 2008). The results (Table 3) show that, in all cases the copper recovery is almost quantitative.

4. Conclusion

Results presented in this work demonstrate the applicability of the solid phase extraction for separation and pre-concentration of trace amounts of Cu^{2+} in water samples using octadecyl bonded silica membrane disks modified by two oximes, 5-tert-butyl-2-hydroxy-benzaldehyde oxime (L_1) and 3,5- di-tert-butyl-2-hydroxy-benzaldehyde oxime (L_2) and its determination by flame atomic absorption spectrometry. The developed method is a simple, rapid, highly selective, precise and accurate alternative to conventional procedures for determining copper in water samples. The method can be successfully applied to the separation and determination of copper in real samples.

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