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ORIGINAL ARTICLE

Hollow fiber supported liquid membrane microextraction of Cu^{2+} followed by flame atomic absorption spectroscopy determination

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KEYWORDS

Copper ion;
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Abstract Hollow fiber supported liquid membrane microextraction, a relatively new sample preparation technique, has attracted much interest in the field of environmental analysis. In the current study, a novel method based on hollow-fiber liquid-phase microextraction and flame atomic absorption spectrometry (FAAS) for the measurement of copper ion in aqueous samples is described. Hollow-fiber liquid-phase microextraction conditions such as the type of extraction solvent, pH, the stirring rate, and the amounts of chelating agents, sample volume, and the extraction time were investigated. Under the optimized conditions, the linear range was found to be 0.01–15 μg ml^{-1} for copper ion, and the limit of detection to be 0.004 μg ml^{-1}. Tap water and surface water samples collected from Mashhad, Iran and Dorongar river; Khorasan, Iran, respectively, were successfully analyzed using the proposed method. The recoveries from the spiked water samples were 72.4% and 105%, respectively; and the relative standard deviation (RSD) at the 2 μg ml^{-1} level was 6%.

1. Introduction

The determination of trace heavy metal contents of environmental materials including natural water and food samples have been continuously performed to put forward the level of pollution levels of the environment by trace metals (Sabaliunas et al., 2003; Lindström et al., 2002; Blanca, 2008; Faruque and Hiroaki, 2006). For the direct determination of heavy metals in environmental samples, a number of sensitive instrumental methods including atomic spectroscopic methods are available, which, however, can suffer from interferences by the matrix of the samples. Also, another important problem is the lower concentration of the analytes than the limit of detection of the instruments. Due to these points of view, a separation and preconcentration step for heavy metals is often necessary before the determination of the analytes (Suarez et al., 2009; Tuzen and Soylak, 2009; Ghaedi et al., 2009).

Sample preparation is a bottle neck in the environmental analysis. Conventional solid-phase extraction (SPE) and

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liquid–liquid extraction (LLE) have been widely used for the extraction of metal ions from water samples (Chen et al., 2009b; Dadfarnia et al., 2009). It is well known, however, that these methods are time consuming, tedious, often require large amounts of organic solvent, and can be relatively expensive. Simplification and miniaturization of sample preparation is a recent trend in analytical chemistry (Arthur and Pawliszyn, 1990; Barri and Jönsson, 2008). Solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) are of most recently developed sample preparation techniques. Both techniques are typical representative of this novel trend. They eliminate the disadvantages of conventional extraction methods, such as being time consuming operation, the need for large amounts of organic solvent, and so on.

Recently, liquid-phase microextraction or solvent microextraction was developed as a fast, simple and inexpensive solvent-minimized liquid–liquid extraction (LLE) technique Ma and Cantwell, 1999; Charalabaki et al., 2005. Subsequently, hollow-fiber liquid-phase microextraction (based on the application of a supported liquid membrane) was introduced using a porous hollow-fiber membrane (Dadfarnia and Haji-Shabani, 2010; Rasmussen and Pedersen-Bjergaard, 2004; Basheer and Lee, 2004) in order to improve solvent stability. In liquid-phase microextraction using a hollow-fiber membrane, the organic solvent is injected into and contained within the lumen of the porous hollow fiber as an interface between the sample solution and the extracting phase (the phase into which the analyte is extracted). Since very little solvent is used, exposure of the operator to toxic organic solvents is minimized. At the same time, the technique combines extraction, concentration and sample introduction into one step. It has been successfully used for the determination of chemical warfare agents (Millerioux et al., 2009), dichlorophenol isomers (Ziagova et al., 2009), primary amines (Desouky et al., 2009), polycyclic aromatic hydrocarbons (De La Torre-Roche et al., 2009), insecticides (Chen et al., 2009a), endocrine-disrupting alkylphenols, chlorophenols and bisphenol-A (Soares et al., 2008).

The aim of this present study is to develop a simple, sensitive and cheap analytical method for the fast measurement of copper ion in environmental water samples. To date, and to the best of our knowledge, no report has been published on the measurement of copper ion in water samples using hollow-fiber liquid-phase microextraction by FAAS. 8-Hydroxy quinoline forms soluble derivatives with several inorganic species. By proper control of the pH of the solution or the concentration of 8-hydroxy quinoline or by using masking agents, a greater degree of selectivity may be achieved. Consequently, 8-hydroxy quinoline and its derivatives have been widely used as chelating and/or preconcentration agents in analytical chemistry. Martínez et al. (2008) reviewed the role of 8-hydroxy quinoline and its derivatives as reagents in analytical chemistry with the main emphasis on liquid extraction.

In this study, copper ion in aqueous samples was first complexed with 8-hydroxy quinoline and then extracted with hollow-fiber liquid-phase microextraction, and finally determined by atomic absorption spectrometry. The method developed was applied to real environmental samples with satisfactory results.

2. Experimental

2.1. Reagents and materials

Acetone, 1-octanol and methanol (HPLC grade), HCl, NaOH all were obtained from Merck (Darmstadth, Germany). 8-Hydroxy quinoline was purchased from Fluka (Buchs, Switzerland). 8-Hydroxy quinoline solution was prepared in 1-octanol. Working solutions of copper were prepared daily by proper dilution of the stock solution with double-distilled water. All solutions were stored at 4 °C in dark. The metal salts and other chemicals used were of analytical reagent grade. The stock solutions of metal ions (concentration 100 mg l^{-1}) were prepared from analytical reagent grade. The water samples from Dorongar River collected, filtered and stored in corning glass bottles. All other chemicals were of analytical grade.

The Accurel Q 3/2 polypropylene hollow-fiber membrane was purchased from Membrana (Wuppertal, Germany). The inner diameter was 600 μm, the thickness of the wall was 200 μm, and pore size was 0.2 μm. Before use, the hollow-fiber membrane was sonicated in acetone for several minutes to remove any possible contaminants. The fiber was then removed from the acetone and allowed to dry completely.

2.2. Instrumentation

The measurements of metal ions were performed with a Model PU9600X Philips flame atomic absorption spectrometer equipped with a single element hollow-cathode lamp and 5.0 cm of an air/acetylene burner head. The instrumental parameters were those recommended by the manufacturer. The selected wavelength (nm) for analyte is 324.8 nm. A digital pH meter (Metrohm Instruments Model 744) with a glass electrode was used for all pH measurements.

2.3. Sample preparation

A 10 ml vial with a stir bar was placed on a magnetic stirrer. Seven millilitres of working solution aqueous samples were placed in the vial. Then, 0.1 M sodium hydroxide solution was added for pH adjustment. HF-LPME experiments were performed as previously described (Barri and Jönsson, 2008; Rasmussen and Pedersen-Bjergaard, 2004; Basheer and Lee, 2004). Briefly, HF-LPME was performed with a commercially available 50 μl Hamilton microsyringe. Before each extraction, the syringe was rinsed with at least 10 times with the solvent. The hollow fiber was immersed into the solvent for impregnation of its wall. Then the hollow fiber was removed from the solvent and its outside was washed with 1 ml of ethanol. A 20 μl aliquot of organic solvent was withdrawn into the microsyringe and was injected in the lumen of the fiber, so that the channel of the fiber was filled with the extracting solvent. It was immersed into the donor aqueous solution containing analytes. During the extraction, the solution was stirred at a reasonable stirring rate. When the extraction was finished (after 30 min), the extraction solvent was retracted into the syringe, which was removed from the sample vial. The hollow-fiber membrane was then discarded. The extracted analyte was introduced to the FAAS, and analysis was carried out.

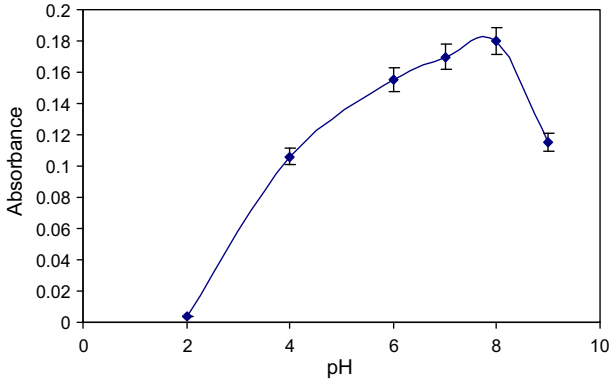

Figure 1 Effect of pH on the extraction efficiency.

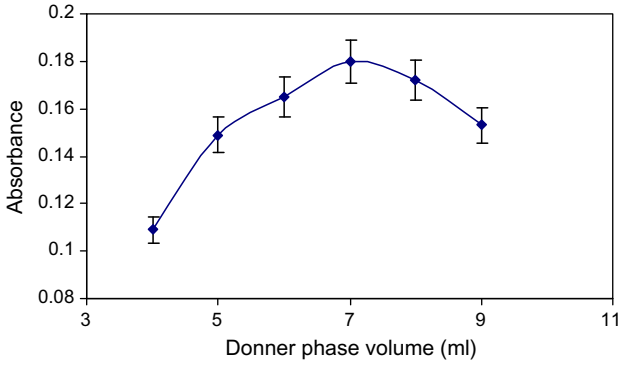

Figure 2 The effect of donor phase volume on the extraction efficiency.

3. Results and discussion

3.1. Effect of pH on the extraction

The pH study was carried out to investigate its effect on the extraction of copper ions with the proposed procedure at the range 2–9. The results are depicted in Fig. 1. According to the results the optimum pH was selected as 8.0 for the donor solution.

3.2. The effect of sample volume on the extraction

Because of low concentrations of copper ion in real samples, large sample volume is generally required for effective preconcentration and determination of trace metals. According to the last researches (Barri and Jönsson, 2008; Ma and Cantwell, 1999; Rasmussen and Pedersen-Bjergaard, 2004; Basheer and Lee, 2004) recovery % (R %) was calculated according to the following equation for each analyte:

$$R = n_{\mathrm{a}},\ \mathrm{final}/n_{\mathrm{s}},\ \mathrm{initial} \times 100\% = (V_{\mathrm{a}}/V_{\mathrm{s}}) \times (C_{\mathrm{a}}, \mathrm{final})/(C_{\mathrm{s}}, \mathrm{initial}) \times 100\%, \quad (1)$$

where n_s, initial and n_{a}, final are the number of moles of analyte present in the initial sample and the number of moles of analyte finally collected in the acceptor solution, respectively. V_{a} is the volume of acceptor solution, V_{s} the volume of sample, C_{a}, final, the final concentration of analyte in the acceptor solution, and C_{s}, initial, is the initial analyte concentration within the sample.

The concentration enrichment (EF) was calculated by the following formula:

$$EF = (C_{\mathrm{a}}, \mathrm{final})/(C_{\mathrm{s}}, \mathrm{initial}) = (V_{\mathrm{s}}/V_{\mathrm{a}}) \times R/100. \quad (2)$$

To achieve a good enrichment usually large sample volume has to be used. Therefore, to maximize the sample/acceptor volume ratio instead of increasing the sample volume, acceptor volume could be minimized. It can be easily done using a hollow fiber as a support for liquid membrane.

On the other hand, the volume of donor phase depending on the size of the vial. Thus for achieving the best volume phase ratio condition, we fixed the acceptor phase volume (or the length of the fiber used was fixed on 8.0 cm) and the donor phase volume was changed till achieving the optimal phase volume ratio. Therefore, the effects of sample volume on the recoveries of the analytes were investigated by using model solutions containing the same amount of trace metals in the volume range of 4–9 ml. The results are given in Fig. 2.

3.3. Extraction time

Like SPME, static LPME is a process that is dependent on equilibrium rather than on exhaustive extraction (Arthur and Pawliszyn, 1990; Barri and Jönsson, 2008; Ma and Cantwell, 1999; Charalabaki et al., 2005). The principle behind LPME is the equilibrium partition of the analyte between the extraction solvent and aqueous solution. In LPME, as discussed for SPME by Pawliszyn (Barri and Jönsson, 2008), once the partition equilibrium is reached, the amount of analyte extracted has a linear relationship with the initial concentration of the analyte in the sample matrix. The effect of extraction time was examined in the range of 20–60 min at room temperature with the sample stirred at constant speed using a 7 ml sample of working solution.

The results, as shown in Fig. 3, demonstrate that the absorption signal generally increased with extraction time. After 40 min, with additional extraction time, the LPME system began to decrease. These results indicated that the organic solvent is being lost. However, it seems a time to take 30 min is appropriate.

3.4. Selection of extraction solvent and stirring rates

It is essential to select a proper organic solvent for the HF-LPME method, which is dependent on the chemical nature of the target analytes (Barri and Jönsson, 2008). Three solvents including chloroform, 1-octanol and mixture of them were compared. Chloroform evaporated during the experiment and it was also lost during the extraction process. Therefore, in subsequent experiments 1-octanol, was chosen as the extraction solvent (Fig. 4).

Stirring the water samples can enhance the diffusion of the analytes towards the hollow fiber containing the extraction solvent, reducing the extraction equilibrium time. In these experiments low, medium and high stirring rates were tested. The stirring rate was optimized. The experimental results obtained are shown in Fig. 5. Although higher stirring rates resulted in greater extraction efficiencies, they also gave rise to bubbles on the surface of the hollow fiber, which affect the repeatability of

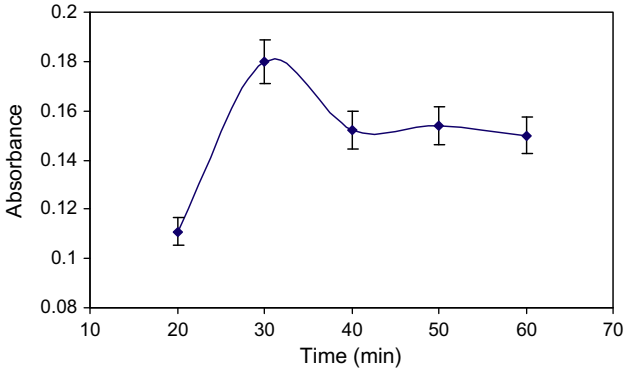

Figure 3 The effect of extraction time on the process.

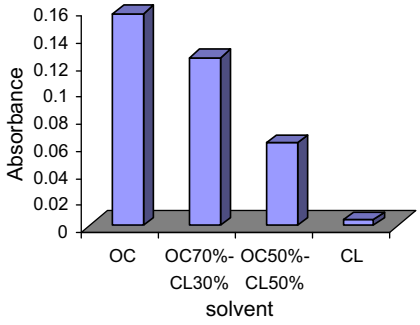

Figure 4 The organic solvent effect on the extraction efficiency; OC, octanol and CL, chloroform.

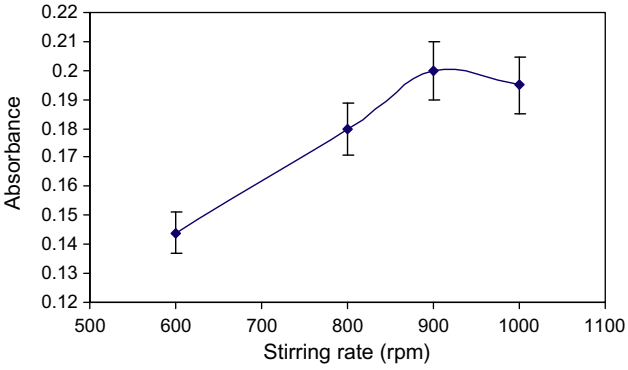

Figure 5 The effect of stirring rate on the extraction efficiency.

the extraction. Therefore 900 rpm stirring rate was used in subsequent experiments.

3.5. Ionic strength

The addition of salt improves the extraction efficiency in many conventional extraction techniques, and sodium chloride (NaCl) is commonly added to analytical samples (Rasmussen and Pedersen-Bjergaard, 2004). Therefore, the effect of salt concentration on extraction efficiency was tested by adding NaCl at 0.5–10% (w/v), respectively. The results obtained showed that the salt almost had positive effect on the extraction efficiency of the copper ion. The optimal concentration of NaCl was obtained at 1.0% w/v. Thus, the LPME was done

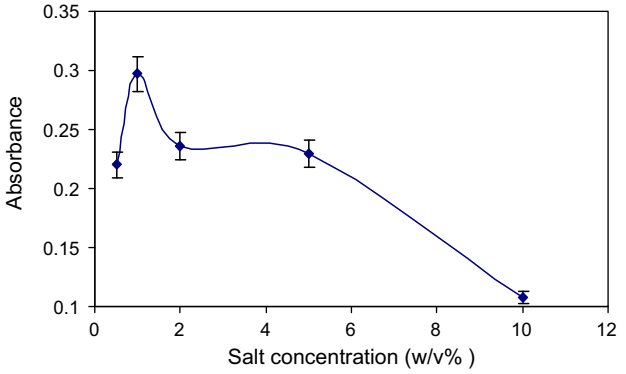

Figure 6 The effect of NaCl concentration on the extraction of Cu^{2+}.

with the addition of NaCl with a concentration of 1.0% w/v (see Fig. 6).

3.6. Surfactant effect

Surfactants, or surface active agents, are amphiphilic molecules which are added to donor phase. The head of the surfactants are polar, or hydrophilic, and the tail of then are hydrophobic. The tail is generally a hydrocarbon chain with different number of carbon atoms and may be linear or branched, and also contains aromatic rings. One of the most important properties of these compounds is their good capacity to solubilize solutes of different character and nature.

In this work, the effect of nonionic surfactants, Brij54, and Span 80 were tested. But these compounds have not shown the positive effect on the Cu^{2+} extraction. Its may be due to the high viscosity of surfactants and thus these molecules closed the pores of polypropylene hollow fiber.

Table 1 Effect of ionic interferences on the copper ion microextraction procedure.

Interfering ions	Interfering ions concentration (μg ml^{-1})	A^b (Au)	A^a (Au)
Mg^{2+}	20	0.297	0.289
Mg^{2+}	200	0.297	0.269
Mg^{2+}	2000	0.297	0.266
Ca^{2+}	20	0.297	0.278
Ca^{2+}	200	0.297	0.221
Ca^{2+}	2000	0.297	0.291
K^+	20	0.297	0.250
K^+	200	0.297	0.276
K^+	2000	0.297	0.210
SO_4^{2-}	20	0.297	0.298
SO_4^{2-}	200	0.297	0.292
SO_4^{2-}	2000	0.297	0.283
CO_3^{2-}	20	0.297	0.214
CO_3^{2-}	200	0.297	0.295
CO_3^{2-}	2000	0.297	0.293
$C_2O_4^{2-}$	20	0.297	0.281
$C_2O_4^{2-}$	200	0.297	0.270
$C_2O_4^{2-}$	2000	0.297	0.180

[a] Analyte absorption before addition of interfering ions.
[b] Analyte absorption after addition of interfering ions.

3.7. Interferences study

The influence of increased concentration of some cations and anions on the interfering effects of Cu(II) is shown in Table 1. In the third concentration stage individual influence of each interfering ion on copper preconcentration at the optimal conditions was examined.

Selectivity of the copper ion was investigated and possibility of different metal ions extraction was evaluated for three concentration levels of each interfering ion.

There was no significant change in copper ion absorption in the presence of the ionic species. Result shows that metal ions at the concentrations much higher than those likely to be encountered in an environmental water sample did not interfere with the quantitative analysis of Cu(II). It should be noted that some metal cations in particular which has the same electronic configuration as Cu(II), showed no interference with the formation of the Cu and 8-hydroxy quinoline complex. These data confirm to the specificity of the microextraction method and reagent for copper determination.

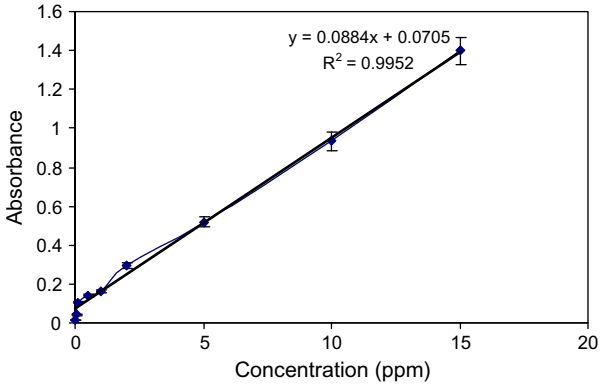

Figure 7 Calibration curve and equation parameters of the method under the optimal conditions.

Table 2 Relative recovery % (RR %) and RSD % for environmental water samples.

Water sample	RR (%)	RSD (%)
Tap water	72.4	4.3
River water	105.0	7.5

4. Analytical performance and application to environmental water samples

Under the above optimum conditions, some characteristics of the present method were investigated and the calibration curve was drawn (see Fig. 7).

The linear range and the limit of detection were calculated. Linearity was observed over the range 10–15,000 $\mu g\,l^{-1}$ for copper ion, with a correlation coefficient of $r = 0.9952$. The limit of detection (LOD), based on a signal-to-noise ratio (S/N) of 3, was 4.00 $\mu g\,l^{-1}$. The enrichment factor of the method was 551.00 (see Table 2). The proposed method was then applied to the determination of copper ion in water samples. Tap water was collected from Mashhad, Iran. The other samples were collected from the Drongar River. Analytical results show that they were free of copper ion contamination.

In order to test the present method, the relative recoveries of copper ion were calculated and reported as 72.4% and 105% for the tap water and Drongar river water samples, respectively. To assess the precision of the measurement, the repeatability of the method was determined by performing it four times using tap water samples spiked with 0.5 $\mu g\,ml^{-1}$ copper ion. The relative standard deviation of the method (RSD %) was 5.7%.

5. Conclusion

Hollow fiber supported liquid membrane microextraction is fast, effective, inexpensive, virtually solvent free method which provides a high degree of selectivity and enrichment. The disposable nature of the hollow fiber totally eliminates the possibility of sample carry over and ensures high reproducibility. In addition, the small pore size prevents large molecules in matrix and un-solved particles in the donor solution from entering the acceptor phase, thus yielding very clean extract. All this, combined with the fact that HF-LPME should be relatively easy to automate, suggest that hollow fiber-based LPME may become an important technique for preconcentration and extraction of metal ions.

This technique is compatible with a broad range of analytes, including biological and environmental samples and in connection with wide range of analytical instruments, such as spectroscopic and chromatographic methods like AAE, HPLC, GC and CE. This compatibility may provide a strong platform for future analytical extractions. The review of some methods which were used for determination of Cu^{2+} in the environmental water samples is shown in Table 3.

Table 3 Comparison of HF-LPME with some other extraction methods for determination of Cu^{2+} in the environmental water samples.

Method	EF	LOD ($\mu g\,l^{-1}$)	Linear range ($\mu g\,l^{-1}$)	RSD (%)
HLLE-FAAS Farajzadeh et al., 2009	–	6.0	10–2000	7.6
DLLME-AAS Farajzadeh et al., 2008	–	3.0	50–2000	5.1
MSE-ICP-OES Suleiman et al., 2009	96	–	–	4.6
SPE-FAAS Kiran et al., 2007	–	75	–	–
HF-LPME-FAAS (this work)	551.00	4.0	10–5000	5.7

HLLE: homogeneous liquid–liquid extraction, DLLME: dispersive liquid–liquid microextraction, MSE: internal standard liquid–liquid microextraction, SPE: solid-phase extraction.

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