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Determination of copper in seawater based on a liquid membrane preconcentration system

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Abstract

A new method to determine the concentration of copper in seawater has been developed. It was based on the use of a bulk liquid membrane (BLM) system to separate and preconcentrate the copper ions, allowing the use of a very simple and common analytical technique as flame atomic absorption spectroscopy (FAAS). The liquid membrane consisted of an organic solution containing di-(2-ethylhexyl)phosphoric acid (DEHPA) in kerosene. The chemical optimization of the preconcentration system was performed by using the modified simplex method. Under optimum conditions, the preconcentration yield for real samples was 76.21%, copper preconcentration factor being 4.30. The reliability of the new method was confirmed by analyzing several real seawater samples, with copper concentrations ranging between 2.5 and 5 $\mu g\,l^{-1}$, previously analyzed by a well-established technique. For these real samples, the average relative error of the determination was 9.96%, while relative standard deviation averaged 0.33%. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Liquid membrane; Preconcentration; Copper determination; Seawater; FAAS

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1. Introduction

In many cases, the analysis of heavy metals in environmental samples presents a notable difficulty due to both the low levels of metals in the samples and the high complexity of the matrices. This is especially true of seawater analysis, and it is usually necessary to carry out a separation step prior to analysis, to preconcentrate the metal to be analyzed and to separate it from the matrix [1].

At present, several techniques are available to perform this separation step, solvent extraction and ionic exchange being the most frequently used [2]. The use of liquid membranes is a relatively new alternative that allows the extraction and back-extraction processes to be performed simultaneously [3]. These membranes have been used as a separation tool for many chemical species, mainly in hydrometallurgy [4], and the development of selective electrodes [5]. Examples of their application as an analytical tool in the study of biological and environmental samples are more scarce [6,7]. To date, liquid membrane methodology has not been applied to the analysis of chemical species in seawater, probably due to the high matrix complexity.

In a typical liquid membrane system, the donor and acceptor aqueous phases are separated by an organic phase containing an extracting agent (the liquid membrane). Among the several liquid membrane configurations, bulk liquid membranes (BLMs) and supported liquid membranes (SLMs) are the most appropriate to be applied as analytical tools, because of the simplicity and easy accessibility of the aqueous phases in

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BLM and the high preconcentration factors reached in SLM [3].

As mentioned before, the use of liquid membranes in the extraction and enrichment of environmental samples has been previously described. They have been applied to sample preparation in the determination of levels of organic compounds, such as herbicides and pesticides, in natural waters [8,9]. Also important in environmental analysis is the application of liquid membranes to the separation and preconcentration of heavy metals from various complex matrices, mainly industrial wastes and river waters. In most cases, the studies were not applied to real samples, but rather were focused on establishing the optimal conditions to improve the efficiency of the extraction and to reduce the time necessary to concentrate the metal ions. Thus, Guyón et al. and Yang and Fane studied the application of liquid membranes to the transport of Cu(II) through a SLM containing a combination of diaza-crown ether and fatty acids; and across a BLM containing Lix-984N, respectively [10,11]. Although in some analyses the main objective is to determine levels of a single metal, the possibility of reducing the time necessary to perform multielemental analysis by simultaneous preconcentration of various metal ions using the appropriate liquid membrane system would be generally useful as well. Thus, Djane et al. used a SLM system with di-(2-ethylhexyl)phosphoric acid (DEHPA) to preconcentrate Cu, Cd and Pb from river waters, although when tested, the results obtained for copper analysis presented a significant difference at 95% confidence limit [7]. Al, Cd and Cu have been determined in synthetic samples by graphite furnace atomic absorption spectrometry after preconcentration with the same carrier [12]. Li et al. developed an emulsion liquid membrane system for the simultaneous extraction of up to eight metal ions (Cd, Co, Cu, Fe, Mn, Pb, Ni and Zn) from potable liquids, with relative errors ranging from 6 to 10% for copper determination [13].

In this study, a BLM containing DEHPA in kerosene was used to separate and preconcentrate copper in seawater samples. A modified simplex method has been applied to optimize the chemical variables involved in the transport of copper through the liquid membrane. After the separation step, the concentration of copper in the receiving solution was determined by flame atomic absorption spectroscopy (FAAS).

2. Experimental

2.1. Reagents and solutions

Nitric acid (65%, reagent grade) was obtained from Scharlab (Barcelona, Spain). Acetic acid (100%, p.a.), ammonium hydroxide (25%, p.a.), sodium chloride (p.a.) and ammonium acetate (p.a.) were obtained from Merck (Darmstadt, Germany). Kerosene (Fluka, Buchs, Switzerland) and DEHPA (Sigma–Aldrich, Steinheim, Germany) were used as received. Aqueous copper solutions were prepared from 1000 $\mathrm{mg\,l^{-1}}$ standard solution obtained from Merck (Darmstadt, Germany). All the synthetic solutions used as source phases during the optimization of the preconcentration system were prepared with 0.5 $\mathrm{mg\,l^{-1}}$ Cu(II) and a matrix of 35 $\mathrm{g\,l^{-1}}$ NaCl.

2.2. Apparatus

Liquid membrane experiments were performed using a homemade glass beaker-in-a-beaker type cell. It consisted of two concentric beakers, containing the sample solution (external beaker) and the acidic receiving solution (internal beaker). Aqueous solutions were stirred with a model Agimatic-S magnetic stirrer (Selecta, Spain). The concentration of copper in receiving solution was measured by an Atomic Absorption Spectrometer, Solaar M Series (Unicam, UK). A model 2001 pH-meter equipped with a model 52-02 combined glass-Ag/AgCl electrode (Crison, Spain) was used to measure pH.

2.3. Procedure

For preconcentration experiment, the volumes of sample and receiving solution were 48 and 8.5 ml, respectively. The transport of copper ions took place through a liquid membrane formed by the carrier (DEHPA) dissolved in kerosene. This organic solution was placed over both aqueous solutions, which were stirred magnetically during the process. To maximize the transport rate, the volume of organic solution must be as small as possible. In this case, 7 ml were used.

During transport experiments, different 1.6 ml aliquots of the receiving solution were taken periodically to measure copper concentration, while 1.6 ml of nitric acid with the same concentration were added to the receiving solution to keep its volume constant. After FAAS measurement, the concentration values obtained were corrected taking into account the metal amount contained into the aliquots of receiving solution previously removed.

The parameter used to determine the efficacy of the preconcentration system was the permeability coefficient (*P*). These values were determined from data sets in the form of copper concentration versus time by using the following linear relationship [14]:

$$-\ln[\mathrm{Cu}^{2+}] = \frac{S}{V_\mathrm{s}}Pt - \ln[\mathrm{Cu}^{2+}]_0 \qquad (1)$$

where S is the effective membrane area, V_s the volume of the sample, and $[\mathrm{Cu}^{2+}]_0$ and $[\mathrm{Cu}^{2+}]$ are the sample copper concentration at time 0 and t, respectively.

2.3.1. Optimization of the system

To optimize the efficiency of the liquid membrane separation process we studied the influence of the chemical variables affecting the permeability coefficient. These variables were the pH of source solution and the concentration of buffer solution used to control it, the concentration of nitric acid in receiving solution and the concentration of DEHPA in the organic phase. Due to the high correlations between the chemical variables studied, they must be optimized simultaneously. In this case, a modified simplex method was applied [15], by using the software Multisimplex 2.0 [16].

At optimum chemical conditions, the hydrodynamics were also studied, in terms of the dependence of permeability coefficient on the stirring rate of both aqueous solutions within the range 600–1000 rpm.

2.3.2. Applicability

Once the conditions controlling the behaviour of the system were optimized, we studied its applicability to real samples of seawater. Thus, on the one hand the variation of preconcentration yield versus time was studied in real samples with known copper concentration, and then an optimum preconcentration time was selected. Finally, the method was validated by analyzing several real samples of seawater in duplicate, and the results obtained were compared with those obtained using a standard methodology based on anodic stripping voltammetry. A statistical analysis of the results was carried out to determine whether there were significant differences between the concentrations of copper determined by both methodologies.

3. Results and discussion

The preconcentration system was based on the following reaction:

$$\mathrm{Cu}^{2+} + 2(\mathrm{AH})_2 \rightleftharpoons \mathrm{Cu}[(\mathrm{AH})\mathrm{A}]_2 + 2\mathrm{H}^+ \qquad (2)$$

where AH represents the acidic extractant DEHPA. In this case, the driving force for the transport of copper ions is the pH gradient between the sample and the aqueous receiving solution. The mechanism of membrane transport is a coupled counter-transport; Cu^{2+} present in source solution (sample) reacts with the carrier present in the organic solution, and the complex is transported across the membrane. On the membrane-receiving solution interface, the reverse reaction proceeds. Energy for the copper transport is gained from the counter-transport of protons from the receiving solution to the source solution, with lower acidity.

3.1. Optimization of the system

Table 1 shows the conditions and results of the simplex optimization. The selection of the initial simplex (vertices 1–5) was software-performed by assignment of a reference value and a step size for each variable. Then, each new vertex was calculated by evaluating the permeability coefficients obtained for the previous simplex. After 13 experiments, the simplex was stopped. The criterion used to stop the simplex was the comparison of the variance of each simplex with the variance of the determination method, which was 3.44×10^{-5} (evaluated from five replicates of one experiment) [15].

Optimum conditions corresponded to experiment number nine: pH 5.0 and buffer concentration of $0.43\,\mathrm{mol\,l^{-1}}$ acetate in the feed solution, a nitric acid concentration of $2.13\,\mathrm{mol\,l^{-1}}$ in receiving solution, and a DEHPA concentration of $0.144\,\mathrm{mol\,l^{-1}}$ in the organic membrane.

Once the chemical variables were optimized, the influence of hydrodynamic conditions was studied (previous studies were done at 700 rpm). As can be seen in Fig. 1, the permeability coefficient increased with the

Table 1
Simplex optimization of chemical variables

Vertex	Type	pH_{sample}	$[CH_3COO^-]$ (M)	$[HNO_3]$ (M)	[DEHPA] (mM)	$P \times 10^3$ (cm min^{-1})
1	I	2.5	0.45	3.50	75	0.0
2	I	3.5	0.55	3.50	75	2.9
3	I	3.5	0.45	3.50	125	4.1
4	I	2.5	0.55	2.50	125	0.5
5	I	3.5	0.45	2.50	75	3.9
6	R	4.0	0.55	2.50	125	18.2
7	E	4.8	0.60	2.00	150	20.6
8	R	5.2	0.47	3.25	88	16.8
9	R	5.0	0.43	2.13	144	26.1
10	E	5.8	0.38	1.44	179	19.8
11	R	5.8	0.52	2.94	179	12.5
12	R	6.9	0.56	1.66	156	12.0
13	C+	6.1	0.53	2.12	148	15.1

I: initial simplex; R: reflexion; E: expansion; C+: positive contraction; P: permeability coefficient.

stirring rate of the aqueous solutions up to 1000 rpm, which was selected as optimum value. For higher rates, mixing of different aqueous phases occurred.

3.2. Preconcentration yield

Once optimized, and before its application to the analysis of copper in seawater, the preconcentration yield of the system was studied. With this aim, we studied the temporal variation of copper concentration in the receiving solution for seven different real samples of seawater. The concentration of copper in these samples was previously determined by anodic stripping voltammetry, and this value was used to calculate the temporal variation of the metal transported from the sample to the receiving solution. The concentration of copper was different for each sample, ranging between 2 and 50 μg l^{-1}. Fig. 2 shows the temporal variation of copper concentration in the receiving solution. Error bars indicate the precision of the experiments, expressed as standard deviation, which varied between ±(3.99–9.47)%. The copper transport was independent of the initial concentration and was completed after 9 h of experiment. The average preconcentration yield was 76.21%, giving a copper preconcentration factor of 4.30. The subsequent analysis of copper concentration in real samples was done after 9 h of preconcentration, and taking into account the preconcentration yield.

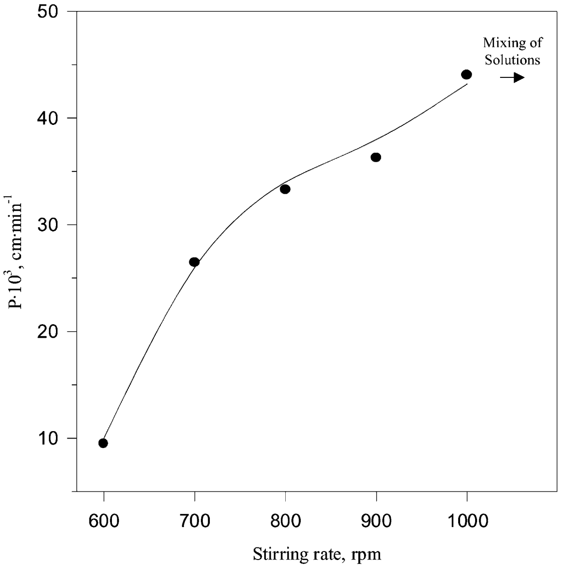

Fig. 1. Dependence of permeability coefficient on stirring rate. Source solution: 0.5 mg l^{-1} Cu(II), 35 g l^{-1} NaCl, pH 5.0, 0.43 mol l^{-1} acetate. Receiving solution: 2.13 mol l^{-1} nitric acid. BLM: 144 mmol l^{-1} DEHPA in kerosene.

3.3. Application

To validate the new method, the analysis of five real samples of seawater from the Gulf of Cadiz (SW Spain) was done. Samples were filtered on-line through 0.45 μm pore-size acid-washed polypropylene Calyx Capsule, stored in acid-precleaned low-density polyethylene bottles and acidified with

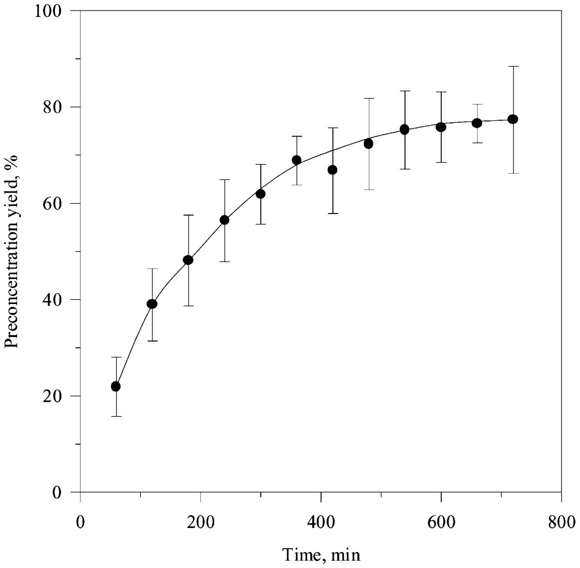

Fig. 2. Temporal variation of preconcentration yield. Source solution: 0.5 mg l^{-1} Cu(II), 35 g l^{-1} NaC1, pH 5.0, 0.43 mo1 l^{-1} acetate. Receiving solution: 2.13 mo1 l^{-1} nitric acid. BLM: 144 mmo1 l^{-1} DEHPA in kerosene. Stirring rate: 1000 rpm. Error bars indicate standard deviation of seven experiments.

nitric acid until analysis. Simultaneously the samples were analyzed by a well-established methodology, using anodic stripping voltammetry [17]. The results obtained are shown in Table 2. The average relative standard deviation was 0.33%, and the relative error averaged 9.96%. The accuracy of the results was tested by applying the paired *t*-test, which confirmed that the result obtained by the two methods do not differ significantly at the 0.05 level.

Table 2
Results of the analysis of copper in five samples of seawater

Sample	Reference method		This method	
	$[Cu^{2+}]$ ($\mu g\,l^{-1}$)	R.S.D. (%)	$[Cu^{2+}]$ ($\mu g\,l^{-1}$)	R.S.D. (%)
1	4.63	0.11	4.86	0.23
2	3.47	0.03	3.77	0.52
3	2.51	0.25	2.84	0.03
4	3.01	0.37	2.46	0.49
5	5.02	0.39	5.26	0.37

4. Conclusions

A simple analytical technique (FAAS) has been used to determine copper concentration in seawater, after a preconcentration step based on the use of a simple liquid membrane system. The method enables eliminating matrix interferences and has a preconcentration efficiency of 76.21%, and a copper preconcentration factor of 4.30. The method was demonstrated to be both precise and accurate and was successfully applied to the analysis of copper in real samples of seawater containing copper at the ppb level.

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