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SEPARATION OF HEAVY METALS IN SEAWATER BY LIQUID MEMBRANES: PRECONCENTRATION OF COPPER

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ABSTRACT

A bulk liquid membrane system has been used to preconcentrate and separate the copper ions present in a seawater sample prior to its analysis by flame atomic absorption spectroscopy. The liquid membrane comprised an organic solution containing di-(2-ethylhexyl) phosphoric acid (DEHPA) in kerosene. The preconcentration system was optimized by studying the influence of the acidity of the sample and the receiving solution, the DEHPA concentration in the organic membrane, and the stirring rate. Under optimum conditions, the preconcentration yield for real samples was 87.0%. The average relative error of the determination was 3.6%, while relative standard deviation averaged 7.8%. The reliability of the new method was confirmed by analyzing several real samples of seawater, analyzed previously by a well-established technique.

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Key Words: Liquid membrane; Seawater; Preconcentration; Copper determination; Flame atomic absorption spectroscopy

INTRODUCTION

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 in 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 the 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 BLM and the high preconcentration factors obtained in SLM (3). Besides, when BLM and SLM are compared, the former presented some advantages in optimization studies due to their simplicity, and the latter exhibited typical instability (8).

As mentioned before, the use of liquid membranes in the extraction and enrichment of environmental samples has been described previously. They have been applied to sample preparation in the determination of levels of organic compounds, such as herbicides and pesticides, in natural waters (9,10). The application of liquid membranes to the separation and preconcentration of heavy metals from various complex matrices—mainly industrial wastes and river waters—is also important in environmental analysis. 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 (11,12) studied the application of liquid membranes to the transport of Cu(II) through an SLM containing a combination of diaza-crown ether and fatty acids, and across a BLM containing Lix-984N, respectively. Although in some analyses the main objective is to determine levels of a single metal, the possibility of reducing the time necessary to perform multi-elemental 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 an 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 (13). Li et al. (14) 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.

In this study, a reliable new method was developed to separate and preconcentrate copper ions from seawater based on a BLM containing DEHPA in kerosene. After separation, the concentration of copper in the receiving solution was determined by flame atomic absorption spectroscopy (FAAS). The effects of several variables such as pH of the sample and receiving solutions, carrier concentration in the organic membrane, and stirring rate were studied, in order to establish the optimum performance of the system. This is the first application of liquid membrane methodology to the analysis of seawater samples.

EXPERIMENTAL

Reagents and Solutions

Nitric acid (65%, reagent grade) and hydrochloric acid (37%, reagent grade) were 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 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 mg L^{-1} Cu(II) and a matrix of 35 g L^{-1} NaCl.

Apparatus

Liquid membrane experiments were performed using a homemade glass cell (see description below). Aqueous solutions were stirred with a model

Agimatic-S magnetic stirrer (Selecta, Abrera, Spain). The concentration of copper in the receiving solution was measured by an Atomic Absorption Spectrometer, Solaar M Series (Unicam, Cambridge, UK). A model 2001 pH meter equipped with a model 52-02 combined glass–Ag/AgCl electrode (Crison, Alella, Spain) was used to measure acidity.

Procedure

A BLM was used for matrix separation and Cu(II) preconcentration in seawater samples prior to determination of copper concentrations by FAAS. The preconcentration system was based on the reaction

$$Cu^{2+} + 2(AH)_2 \rightleftharpoons Cu[(AH)A]_2 + 2H^+ \tag{1}$$

where the AH represents the acidic extractant DEHPA. In this case, the driving force that made the transport of copper ions possible is the pH gradient between the sample and the aqueous receiving solution. The mechanism of membrane transport is a coupled counter-transport. The 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.

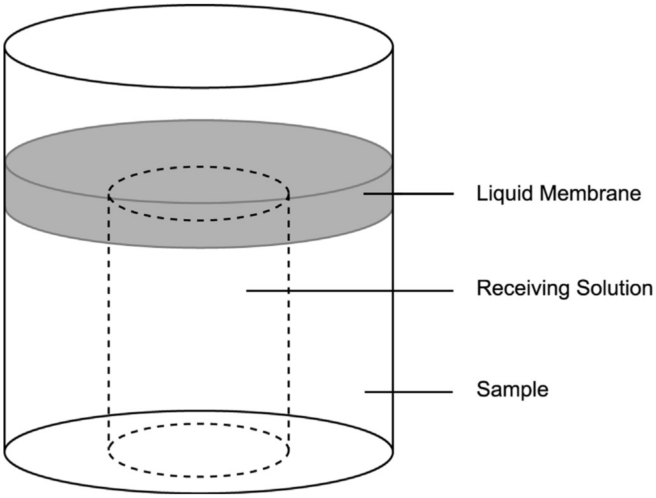

Figure 1. Preconcentration cell.

A beaker-in-a-beaker type cell, shown in Fig. 1, was used to perform the preconcentration experiments. It consisted of two concentric beakers, containing the sample solution (external beaker) and the acidic receiving solution (internal beaker). The volumes of the sample and the receiving solution were 40 and 24.7 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 was 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 was added to the receiving solution to keep its volume constant. After FAAS measurements, the concentration values obtained were modified taking into account the correction of the volume.

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 vs. time using the following linear relationship (15)

$$-\ln[\mathrm{Cu}^{2+}] = \frac{S}{V_{\mathrm{S}}}Pt - \ln[\mathrm{Cu}^{2+}]_0 \tag{2}$$

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

Optimization of the System

To optimize the efficiency of the liquid membrane separation process, the influence of the chemical variables affecting the permeability coefficient was studied. Thus, the pH of source solution and the concentration of buffer solution used to control it (within the ranges 2.5–6.5 and 0–0.5 mol L^{-1} acetate, respectively), the concentration of nitric acid in receiving solution (0.001–3.0 mol L^{-1}), and the concentration of DEHPA in the organic phase (0.05–0.75 mol L^{-1}) were studied. The hydrodynamic conditions were also studied in terms of the dependence of permeability coefficient on the stirring rate of both aqueous solutions within the range 300–700 rpm.

Applicability

Once the conditions controlling the behavior of the system were optimized, its applicability to the analysis of real samples of seawater was studied. Thus, on one hand, the variation of preconcentration yield vs. 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 the methodologies.

RESULTS AND DISCUSSION

Optimization of the System

The first variable studied was the influence of the acidity of the source solution. Figure 2 shows the variation in the permeability coefficient (calculated for the first hour of experiment) obtained when the initial pH of the source solution was varied from 2.5 to 6.5, without the addition of buffer solution. At pH 2.5, the permeation of copper was negligible; then, the permeability coefficient increased, and the transport rate reached maximum values between pH 4.5 and 6.5. This behavior may probably be explained in terms of optimum pH gradient between both aqueous phases and by the different diffusion of the copper species formed in the sample–membrane interface, which will be maxima between pH 4.5 and 6.5. This pH range was, therefore, selected for preconcentration experiments. In order to study the influence of the addition of a buffer solution to control the acidity of the sample, new experiments were carried out. Figure 3 shows the variation of P when the concentration of the acetate buffer solution was varied within the range $0–0.5\,\mathrm{mol\,L^{-1}}$. In all cases, the initial pH of the solution, after buffer addition, was 5.5, to ensure that the small increment in the acidity of the solution caused by the transport mechanism did not affect the performance of the system. The control of the pH with the buffer solution improved the values of the permeability coefficients obtained. Optimum transport was reached for a buffer concentration of $0.1\,\mathrm{mol\,L^{-1}}$. However, further increment in acetate concentration caused a decrease in the transport rate, the permeability coefficient obtained for a buffer concentration of $0.5\,\mathrm{mol\,L^{-1}}$ being similar to that corresponding to the experiment without buffer. This may probably be explained by the formation of ternary complexes (Cu–Acetate–DEHPA) in the organic membrane, which present diffusion coefficients substantially lower. The formation of this kind of ternary complexes has been described previously

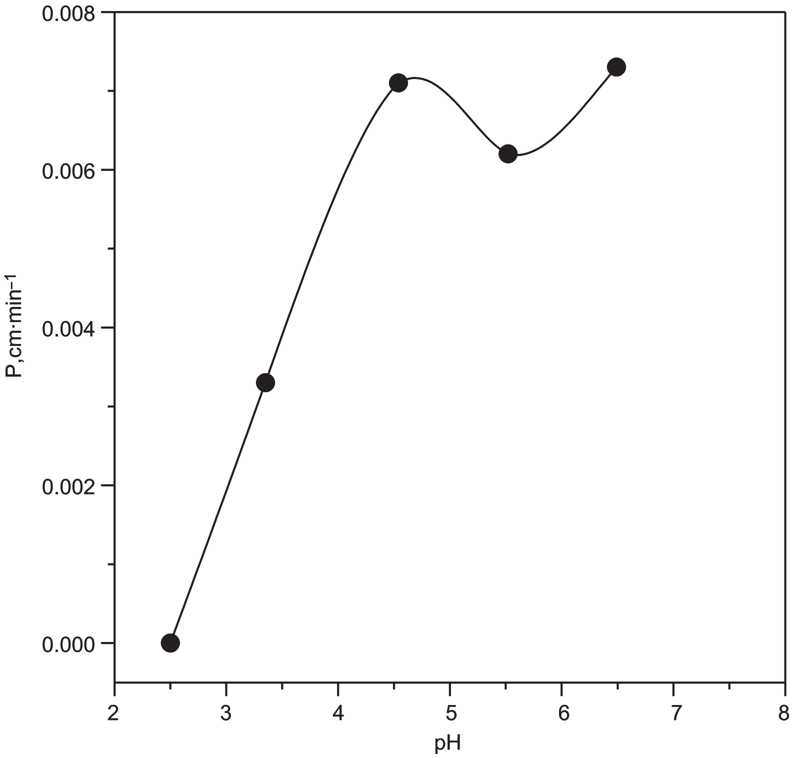

Figure 2. Dependence of permeability coefficient on pH of feed solution. Source solution: 0.5 mg L^{-1} Cu(II), 35 g L^{-1} NaCl; receiving solution: 0.5 mol L^{-1} HNO_3; BLM: 50 mmol L^{-1} DEHPA in kerosene; stirring rate: 500 rpm.

in liquid membranes (16). Thus, a 0.1 mol L^{-1} acetate buffer solution was used henceforth.

The study of the dependence of *P* on pH of source solution was repeated in the presence of 0.1 *M* acetate buffer solution. The shape of the curve was very similar to that obtained in the absence of buffer solution, and maximum permeability was obtained for pH 5.5.

The next variable studied was the concentration of the nitric acid solution used as receiving phase. The results obtained are shown in Fig. 4. For low acidity, the transport of copper through the membrane was very slow. When the acid concentration increased, an initial increase in permeability coefficient was observed till optimum pH gradient was reached between the sample and stripping solutions at 0.5 mol L^{-1} HNO_3, and then the permeability coefficient decreased. A

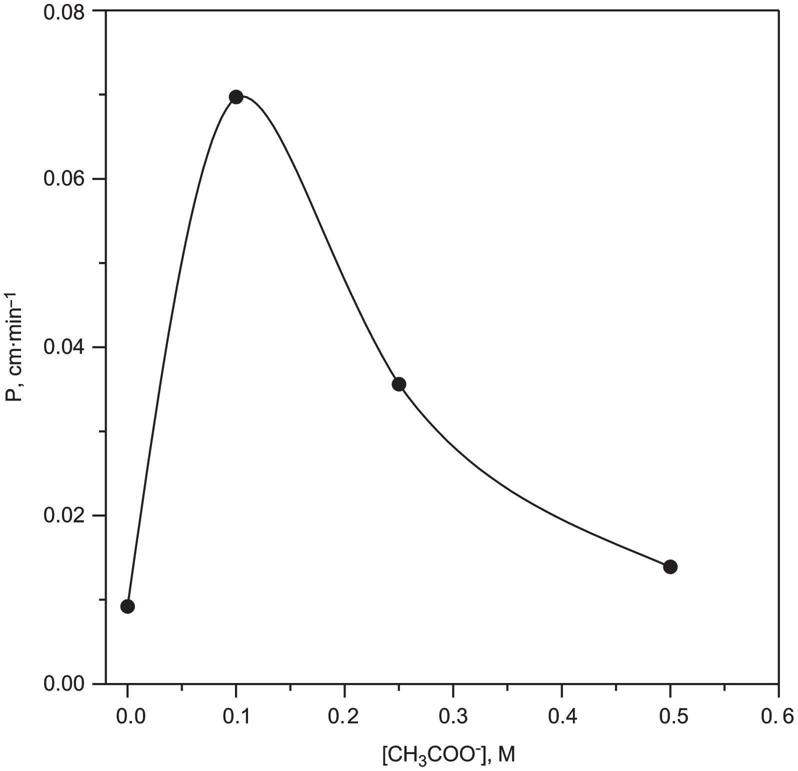

Figure 3. Dependence of permeability coefficient on concentration of buffer solution. Source solution: $0.5\,\mathrm{mg\,L^{-1}}$ Cu(II), $35\,\mathrm{g\,L^{-1}}$ NaCl, pH 5.5; receiving solution: $0.5\,\mathrm{mol\,L^{-1}}$ HNO_3; BLM: $50\,\mathrm{mmol\,L^{-1}}$ DEHPA in kerosene; stirring rate: 500 rpm.

concentration of $0.5\,\mathrm{mol\,L^{-1}}$ HNO_3 in receiving solution gives the best acidity gradient between both aqueous solutions, allowing to obtain optimum permeation through the membrane.

The last chemical variable studied was the influence of the concentration of DEHPA present in the organic solution. Figure 5 shows the variation of *P* due to this variable. An initial increase in *P* was observed with increasing carrier concentration, but for higher DEHPA concentrations, *P* decreased due to the slowing down of transport because of the high viscosity of the organic membrane. Permeability remained stable between 0.25 and $0.5\,\mathrm{mol\,L^{-1}}$; an optimum value of $0.250\,\mathrm{mol\,L^{-1}}$ DEHPA was selected.

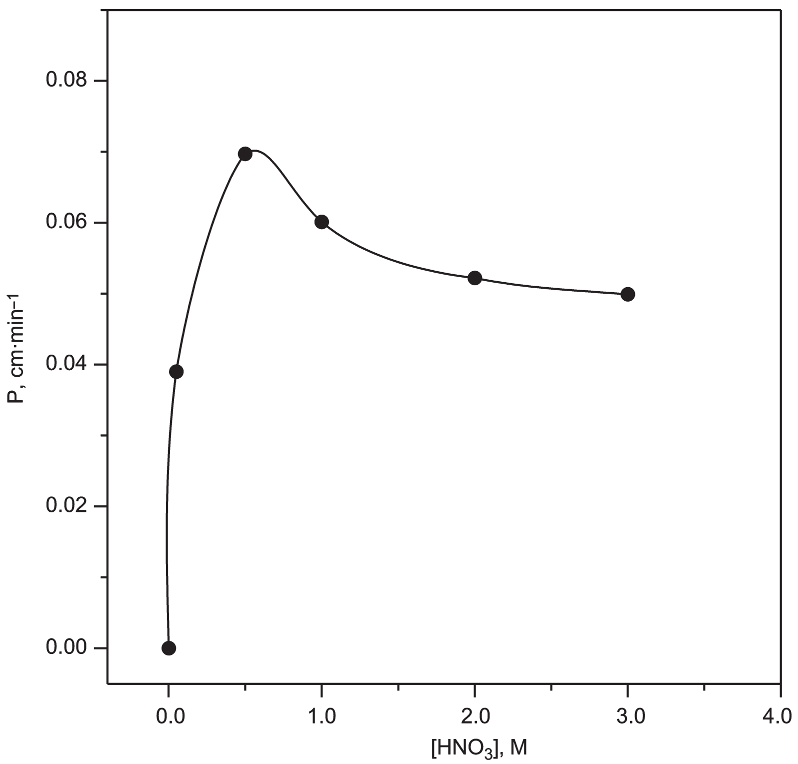

Figure 4. Dependence of permeability coefficient on nitric acid concentration in the receiving phase. Source solution: 0.5 mg L^{-1} Cu(II), 35 g L^{-1} NaCl, pH 5.5, 0.1 mol L^{-1} acetate; BLM: 50 mmol L^{-1} DEHPA in kerosene; stirring rate: 500 rpm.

Once the chemical variables were optimized, the study of hydrodynamic conditions was carried out. As shown in Fig. 6, a better mixing of aqueous–organic interfaces made that the permeability coefficient increased with the stirring rate of the aqueous solutions up to 700 rpm, which was selected as the optimum stirring rate. For higher rates, mixing of different phases occurred.

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, the

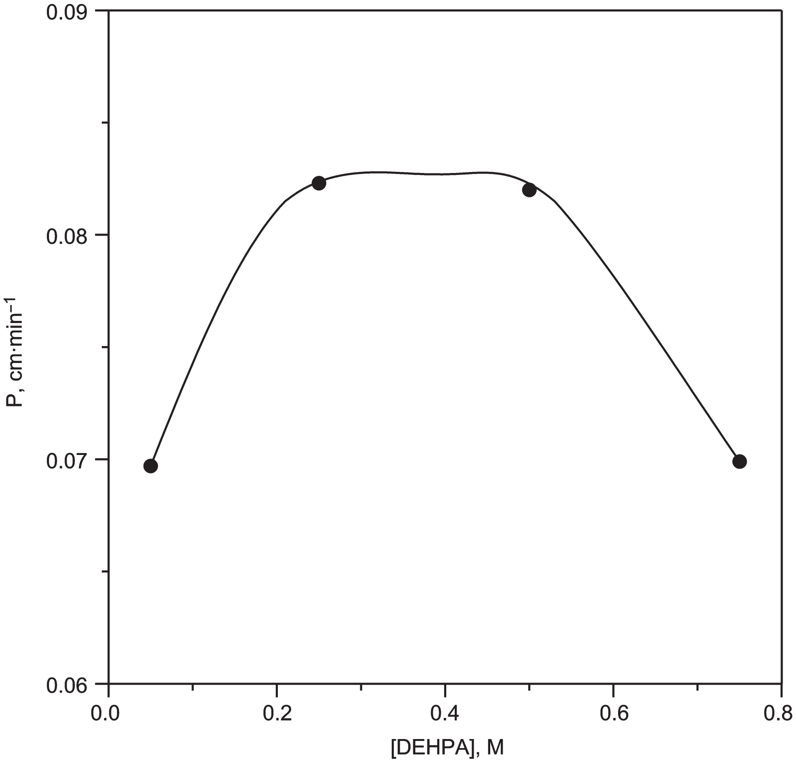

Figure 5. Dependence of permeability coefficient on DEHPA concentration in the BLM. Source solution: 0.5 mg L^{-1} Cu(II), 35 g L^{-1} NaCl, pH 5.5, 0.1 mol L^{-1} acetate; receiving solution: 0.5 mol L^{-1} nitric acid; stirring rate: 500 rpm.

temporal variation of copper concentration in the receiving solution for six different real samples of coastal seawater was studied. The concentration of each sample was measured previously by anodic stripping voltammetry and used as a reference 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 10 and 80 μg L^{-1}. The results are shown in Fig. 7. The copper transport was independent of its initial concentration in the sample, and was completed during the first 2–3 hr of experiment. The average preconcentration yield was 87.0% with a confidence interval of ± 1.9, calculated as $ts/n^{1/2}$ with $n = 37$ and $p = 0.05$. The subsequent analysis of copper concentration in real samples was performed after 3 hr of preconcentration, and taking into account the preconcentration yield.

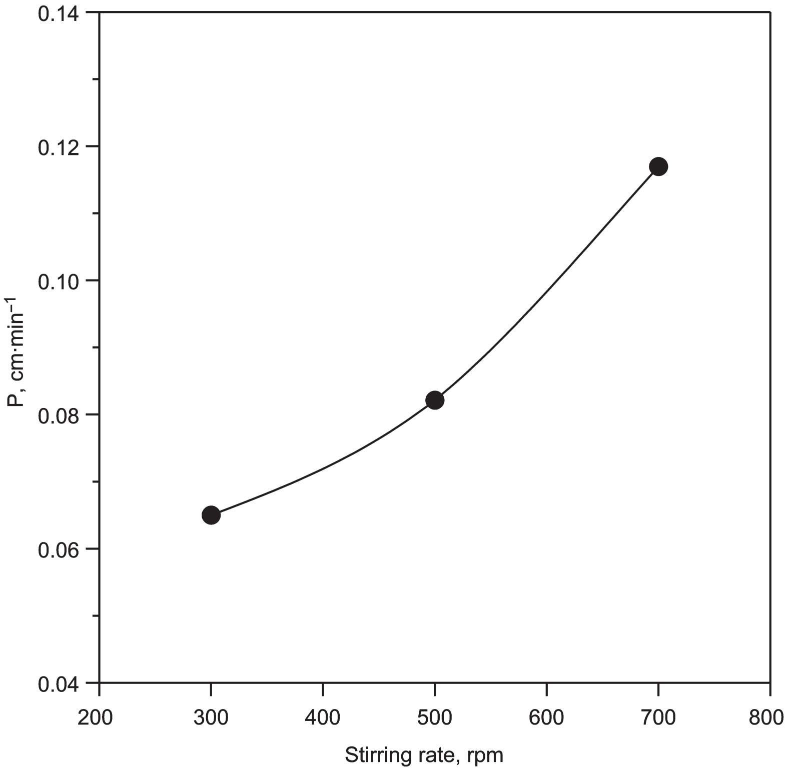

Figure 6. Dependence of permeability coefficient on stirring rate. Source solution: 0.5 mg L^{-1} Cu(II), 35 g L^{-1} NaCl, pH 5.5, 0.1 mol L^{-1} acetate; receiving solution: 0.5 mol L^{-1} nitric acid; BLM: 250 mmol L^{-1} DEHPA in kerosene.

Application

To validate the new preconcentration method, it was applied to the analysis of five real samples of coastal seawater from the Gulf of Cádiz (SW Spain). After metal enrichment using the optimized criteria during 3 hr, the receiving solution was analyzed by FAAS. Simultaneously, the samples were analyzed by a well-established methodology using anodic stripping voltammetry (17). Each sample was analyzed in duplicate. The results obtained are shown in Table 1. The average relative standard deviation was 7.8%; the relative error averaged 3.6%. The accuracy of the results was tested by applying the paired *t*-test, which confirmed that the results obtained by the two methods do not differ significantly at the 0.05 level.

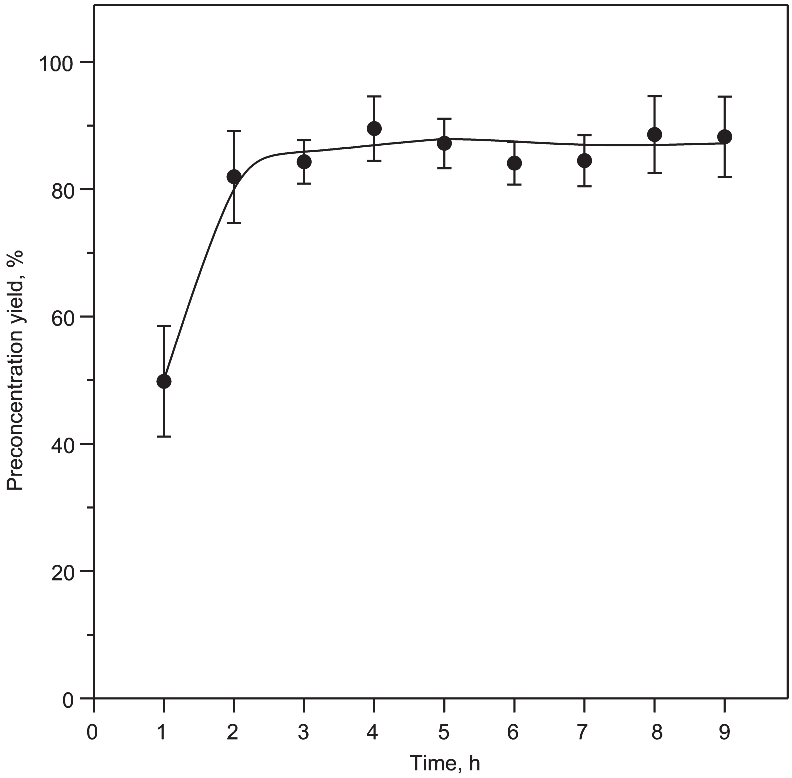

Figure 7. Temporal variation of preconcentration yield. Source solution: real seawater; receiving solution: $0.5\,\mathrm{mol\,L^{-1}}$ nitric acid; BLM: $250\,\mathrm{mmol\,L^{-1}}$ DEHPA in kerosene; stirring rate: 700 rpm. Errors bars indicate standard deviation of six experiments.

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 had a preconcentration efficiency of 87.0%, which is higher than the efficiency obtained by other authors for natural waters (7). Although the co-transport of some other metals could take place during the preconcentration of copper, they did not interfere with the determination of copper because of their low levels and the use of a selective analytical technique such as FAAS. Besides, as shown in Fig. 7, they did not affect the preconcentration yield of the system. The method was demonstrated to

Table 1. Results of the Analysis of Copper in Five Samples of Coastal Seawater

	Known[a]		Measured[b]		
Sample	$[Cu^{2+}]$ (μg L^{-1})	RSD[c] (%)	$[Cu^{2+}]$ (μg L^{-1})	RSD (%)	ε_r[d]
1	71.0	1.6	73.1	10.2	3.0
2	44.6	3.6	47.6	7.3	6.7
3	22.1	1.8	21.2	2.4	−4.1
4	54.3	2.4	54.3	6.8	0
5	18.7	4.1	19.5	12.3	4.3

[a] Measured by anodic-stripping voltammetry.
[b] This method.
[c] Relative standard deviation.
[d] Relative error.

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. Lower concentrations of copper could be analyzed by modifying the volume ratio of the membrane cell.

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REFERENCES

1. Donat, J.R.; Bruland, K.W. *Trace Elements in Natural Waters*; Salbu, B., Steinnes, E., Eds.; CRC Press: Boca Raton, FL, 1995.
2. Bond, A.H.; Dietz, M.L.; Rogers, R.D. *Metal-Ion Separation and Preconcentration*; ACS Symposium Series 716, American Chemical Society: Washington, DC, 1999.
3. Bartsch, R.A.; Way, J.D. *Chemical Separation with Liquid Membranes*; ACS Symposium Series 642, American Chemical Society: Washington, DC, 1996.
4. Doležal, J.; Moreno, C.; Hrdlička, A.; Valiente, M. Selective Transport of Lanthanides Through Supported Liquid Membranes Containing

Non-selective Extractant, Di-(2-Ethylhexyl) Phosphoric Acid, as a Carrier. J. Membr. Sci. **2000**, *168*, 175–181.

5. Florido, A.; Bachas, L.G.; Valiente, M.; Villaescusa, I. Anion-Selective Electrodes Based on a Gold(III) Triisobutylphosphine Sulfide Complex. Analyst **1994**, *119*, 2421–2425.
6. Jönsson, J.A.; Mathiasson, L. Supported Liquid Membrane Techniques for Sample Preparation and Enrichment in Environmental and Biological Analysis. TRAC Trends Anal. Chem. **1992**, *11*, 106–114.
7. Djane, N.K.; Ndungu, K.; Malcus, F.; Johansson, G.; Mathiasson, L. Supported Liquid Membrane Enrichment Using an Organophosphorus Extractant for Analytical Trace-Metal Determinations in River Waters. Fresenius' J. Anal. Chem. **1997**, *358*, 822–827.
8. Moreno, C.; Valiente, M. Characterization of a Solid Supported Liquid Membrane for Lanthanide Transport by Impedance Spectroscopy. J. Electroanal. Chem. **1997**, *422*, 191–195.
9. Knutsson, M.; Nilve, G.; Mathiasson, L.; Jönsson, J.A. Supported Liquid Membrane Technique for Time-Integrating Field Sampling of Acidic Herbicides at Sub Parts-Per-Billion Level in Natural-Waters. J. Agric. Food Chem. **1992**, *40*, 2413–2417.
10. Knutsson, M.; Nilve, G.; Mathiasson, L.; Jönsson, J.A. Supported Liquid Membranes for Sampling and Sample Preparation of Pesticides in Water. J. Chromatogr. A **1996**, *54*, 197–205.
11. Guyón, F.; Parthasaraty, N.; Buffle, J. Mechanism and Kinetics of Copper(II) Transport Through Diaza-Crown Ether Fatty Acid-Supported Liquid Membrane. Anal. Chem. **1999**, *71*, 819–826.
12. Yang, X.J.; Fane, A.G. Facilitated Transport of Copper in Bulk Liquid Membranes Containing Lix-984N. Sep. Sci. Technol. **1999**, *34*, 1873–1890.
13. Malcus, F.; Djane, N.K.; Mathiasson, L.; Johansson, G. Automated Trace Enrichment and Determination of Metals Using a Combination of Supported Liquid Membrane for Sample Pretreatment and Graphite-Furnace Atomic-Absorption Spectrometry for the Determination. Anal. Chim. Acta **1996**, *327*, 295–300.
14. Li, Y.T.; Van Loon, J.C.; Barefoot, R.R. Preconcentration of Trace-Elements in Potable Liquids by Means of a Liquid Membrane Emulsion for Flame Atomic-Absorption Determination. Fresenius' J. Anal. Chem. **1993**, *345*, 467–470.
15. Danesi, P.R. Separation of Metal Species by Supported Liquid Membranes. Sep. Sci. Technol. **1984–1985**, *19*, 857–894.
16. Moreno, C.; Valiente, M. Studies on the Mechanism of Transport of Lanthanide Ions Through Supported Liquid Membranes Containing Di-(2-

Ethylhexyl) Phosphoric Acid (D2EHPA) as a Carrier. J. Membr. Sci. **1999**, *155*, 155–162.
17. German Standard Method DIN 38406-16, 1990.

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