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Application of liquid membranes to sample preconcentration for the spectrometric determination of cadmium in seawater

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Abstract

A bulk liquid membrane system has been used as preconcentration tool for the spectrometric determination of cadmium in seawater. The membrane contained di-(2-ethylhexyl)-phosphoric acid (DEHPA) as mobile carrier dissolved in kerosene. The effects of the composition of both organic and aqueous solutions on the permeation of Cd across the membrane were studied, and optimum conditions were found by the modified simplex method. Maximum preconcentration rates were obtained at a sample pH of 4.7, maintained with a $0.1\,\mathrm{mol\,l^{-1}}$ acetate buffer solution, a $0.3\,\mathrm{mol\,l^{-1}}$ HNO_3 receiving solution, and a carrier concentration of $0.17\,\mathrm{mol\,l^{-1}}$. Under optimum conditions, a preconcentration yield of 100% was obtained for both synthetic and real seawater. The method was successfully applied to the determination of cadmium in real seawater.

Keywords: Liquid membrane; DEHPA; Preconcentration; Heavy metals; Cadmium; Seawater

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1. Introduction

Since their introduction, liquid membranes have been applied to the separation of many chemical species in different fields, such as metallurgy [1,2], biotechnology [3,4], environmental sciences [5,6], material sciences [7,8], etc. One of the applications of liquid membranes that has experienced higher development in last decade is its use in analytical sample preparation, mainly due to the advantages obtained if compared with classical samples preparation techniques [9,10]. In this case, sample is treated before the application of any instrumental analytical method, in order to increase the concentration of analyte and/or to remove matrix compounds. Among others, sample preparation with liquid membrane has been used in bioanalysis [11] or environmental analysis [12]. Particular interest has the later, where very low analyte concentrations together with high matrix effects may be found. A very singular case is the treatment of seawater samples, where the very high salinity implies an extra difficulty for the analysis of the samples [13].

The preconcentration step is almost always required when analysing many trace chemical compounds (as i.e. heavy metals) in natural waters or seawater. The separation procedures mostly used are based on ion exchange or solvent extraction. The later gives more accurate results, but it is tedious and time consuming (about 24 h for the whole procedure) [14]. The use of liquid membranes may decrease the time needed because of the simultaneity of extraction and back extraction processes. Besides, it needs a lower sample manipulation and, as a consequence, implies lower sample contamination risk. In this work, we have used a simple bulk liquid membrane system for matrix separation and preconcentration of cadmium in seawater, which is known to be an environmental pollutant with toxic effects for the living organisms in aquatic ecosystems. It was based on the use of di-(2-ethylhexyl)-phosphoric acid (DEHPA) as a carrier, which was previously used for the extraction of cadmium from different matrices and with different separation system, including liquid membranes [15–17].

2. Experimental

2.1. Reagents and solutions

Aqueous cadmium solutions used as source phases were prepared from a commercial standard solution of $1000\,\mathrm{mg\,l^{-1}}$

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(Merck, Germany) and a matrix of 35 g l^{-1} NaCl. Nitric acid (65%, reagent grade) was obtained from Scharlab (Spain). Acetic acid (100%, pro analysis, p.a.), ammonium hydroxide (25%, p.a.) and sodium chloride (p.a.) were obtained from Merck (Germany). Kerosene (Fluka, Switzerland) and DEHPA (Sigma–Aldrich, Germany) were used as received. Deionised water was prepared using a Milli-Q academic equipment (Millipore, USA).

To prevent the contamination of real samples, they were acidified with nitric acid of Suprapur quality (Merck, Germany), and manipulated into a laminar flow hood.

2.2. Apparatus and procedure

Liquid membrane experiments were performed using a homemade glass beaker-in-a-beaker type cell described elsewhere [18]. It consisted of two concentric beakers, containing 39 ml of the sample solution (external beaker) and 23.5 ml of the acidic receiving solution (internal beaker). Cadmium ions were transported through an organic liquid membrane formed by the carrier (DEHPA) dissolved in kerosene that was placed over both aqueous solutions, which were stirred during the experiments with a model "Big Squid" magnetic stirrer (IKA, Germany). To maximize the transport rate, the volume of organic solution must be as small as possible. In our case, 7.5 ml were used.

The determination of cadmium was done by atomic absorption spectroscopy (AAS) with a Solaar M Series (Thermo Elemental, UK). A model 2001 pH meter equipped with a model 52-02 combined glass–Ag/AgCl electrode (Crison, Spain) was used to measure pH.

The optimisation of the transport system was done by using 1 mg l^{-1} Cd(II) in 35 g l^{-1} NaCl as source phase. During the experiments, 1.6 ml aliquots of the receiving solution were taken periodically to measure cadmium concentration by AAS, and 1.6 ml of nitric acid with the same concentration were added to the receiving solution to keep the volume constant. After measurement, the concentration values were corrected taking into account the metal amount contained into the aliquots of receiving solution previously removed.

The efficacy of the preconcentration system was quantified with the permeability coefficient (P), calculated from the following linear relationship [19]:

$$-\ln[\mathrm{Cd}^{2+}] = \frac{A}{V_{\mathrm{S}}}\mathrm{Pt} - \ln\,[\mathrm{Cd}^{2+}]_0$$

where A is the effective membrane area, V_{s} the sample volume, and $[\mathrm{Cd}^{2+}]_0$ and $[\mathrm{Cd}^{2+}]$ are the sample cadmium concentrations at time 0 and t, respectively.

2.3. Optimization of the system

The liquid membrane system was optimised by studying the influence of the chemical variables influencing the separation process, such as pH of sample (source solution) and receiving solutions, buffer concentration in source solution and the concentration of DEHPA in the liquid membrane. Due to the high interactions between these variables, they must be optimized simultaneously. With this aim, we have applied a modified simplex method, by using the software Multisimplex 2.0 [20].

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 of 200–1200 rpm.

2.4. Application

Once the conditions were optimized, we studied its applicability to real seawater. Thus, the temporal variation of preconcentration yield was studied to select an optimum preconcentration time. Finally, the method was validated by analyzing a real seawater sample, and the results compared with those obtained from the application of a standard methodology based on anodic stripping voltammetry (ASV). The results obtained by both methodologies were statistically compared to determine whether there were significant differences between them.

3. Results and discussion

3.1. Optimization of the system

Table 1 shows the 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. The simplex was stopped after 20 membrane experiments. The criterion selected for stopping the search was based on the comparison of the variance of each simplex with the variance of our method (evaluated from five replicates of one experiment). This comparison was carried out by calculating the corresponding F-values [21]. As may be observed in Table 1, optimum conditions were obtained for trial 18, which corresponds to a source phase with pH 4.7 and 0.1 mol l^{-1} acetate buffer solution, 0.3 mol l^{-1} HNO_3 in the receiving solution, and 0.17 mol l^{-1} DEHPA in the organic membrane.

After the optimisation of chemical variables, the hydrodynamics of the transport system were studied in terms of variation of permeability coefficient versus the stirring rate of aqueous solutions within the range of 200–1200 rpm. As can be seen in

Table 1
Simplex optimisation of chemical variables

Vertex	pH	$[HNO_3]$ (M)	[DEHPA] (M)	$[AcH/Ac^-]$ (M)	P (cm min^{-1})
1	3	0.1	0.02	0.1	0
2	3	0.1	0.08	0.2	0
3	3	0.3	0.08	0.1	0
4	4	0.3	0.02	0	1.38×10^{-3}
5	4	0.1	0.08	0.1	1.72×10^{-3}
⋮	⋮	⋮	⋮	⋮	⋮
18	4.7	0.3	0.17	0.1	1.04×10^{-1}
⋮	⋮	⋮	⋮	⋮	⋮
20	4.3	0.3	0.18	0.1	7.36×10^{-2}

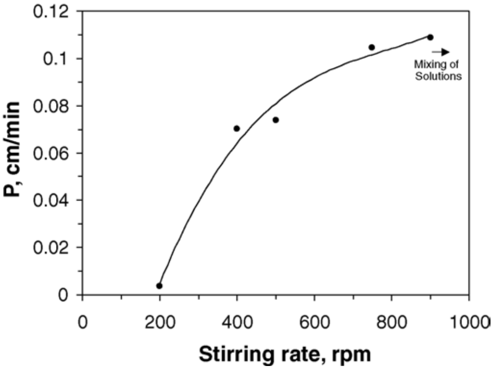

Fig. 1. Variation of permeability coefficient with stirring rate. Source phase: 0.5 mg l^{-1} Cd(II), 35 g l^{-1} NaCl, pH 4.7, 0.1 mol l^{-1} acetate. Receiving solution: 0.3 mol l^{-1} HNO_3. Liquid membrane: 0.17 mol l^{-1} DEHPA in kerosene.

Fig. 1, the value of P increased up to 900 rpm and then, for higher rates, the liquid membrane system was broken (mixing of source and receiving solutions took place). At 900 rpm, the membrane was occasionally broken and so, a stirring rate of 750 rpm was selected as optimum.

3.2. Preconcentration yield

As a first step for its application to the analysis of cadmium in seawater, the preconcentration yield of the system was studied. With this aim, we studied the temporal variation of cadmium concentration in the receiving solution for six different real samples previously spiked with different concentrations of cadmium, ranging between 0.6 and 1 mg l^{-1}. Curve A in Fig. 2 shows the temporal variation of the metal transported from the sample to the receiving solution. Error bars indicate the precision of the experiments, expressed as standard deviation. The temporal variation of preconcentration yield was independent of the initial concentration of cadmium and it was almost stopped after about 8–9 h, reaching a value of 37.3%. This low yield could be due to the co-transport of other cations, such as calcium and magnesium, present at high concentrations in real seawater. The analysis of receiving solutions revealed concentrations of calcium and magnesium over 500 and 2900 mg l^{-1}, respectively, which were transported through the liquid membrane. To prevent the transport of calcium and magnesium, 0.1 g l^{-1} citric acid were added to the samples and the study was repeated. Under these conditions most of the Ca^{2+} and Mg^{2+} ions form complexes with citrate [22]. Although Cd^{2+} may be also complexed, from the results shown in curve B of Fig. 2 it follows that the displacement of the citrate complexes in the sample-membrane interface by DEHPA is strong enough to allow the permeation of Cd^{2+} through the liquid membrane, and then, 100% of the cadmium ions present in the real seawater samples were transported through the liquid membrane after 10–11 h. Under these conditions, the cadmium preconcentration ratio was 1.66. This ratio is controlled only by the volumes of sample and receiving solution and, if required, it could be modified by using a membrane cell with different volumes.

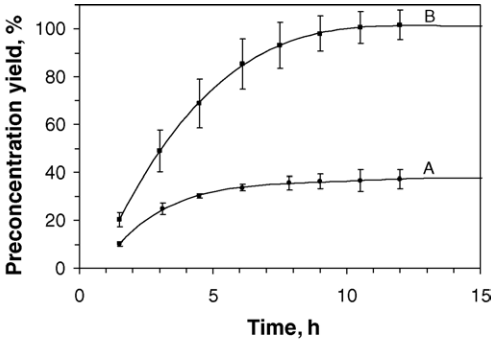

Fig. 2. Temporal variation of preconcentration yield for real seawater. Curve A: source solution: real seawater at pH 4.7, 0.1 mol l^{-1} acetate; receiving solution: 0.3 mol l^{-1} nitric acid; liquid membrane: 0.17 mol l^{-1} DEHPA in kerosene; stirring rate: 750 rpm. Curve B: identical to curve A, but 0.1 g l^{-1} citric acid was added to source solution. Error bars indicate standard deviation of six experiments.

3.3. Application

The new preconcentration system was applied to the analysis of dissolved cadmium in a real seawater sample from the Gulf of Cadiz (SW, Spain). The sample was 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 nitric acid until analysis. The concentration of cadmium in the sample was analysed in duplicate by the proposed methodology (with a result of 1.20 ± 0.24 μg l^{-1}) and by ASV, used as reference technique (with a result of 1.25 ± 0.08 μg l^{-1}). If compared with the reference method, the results obtained by liquid membrane methodology presented a relative error of −4.0%. The accuracy of the obtained result was tested by applying the paired t-test, which confirmed the absence of systematic errors at the 0.05 level

4. Conclusions

Cd^{2+} ions can be effectively separated and preconcentrated from seawater through a bulk liquid membrane containing DEHPA in kerosene, allowing the precise and accurate analysis of this metal in real samples. As DEHPA is a non-selective extractant, other cations are co-transported through the membrane. In this case, the transport of calcium and magnesium decreases the effectiveness of cadmium permeation. This problem may be overcome by masking calcium and magnesium with citric acid. If compared with the standard methodology used in chemical oceanography [14], the new method based on liquid membranes offers advantages such as simplicity, lower sample manipulation (very important in trace analysis to prevent sample contamination) and lower time needed for sample pre-treatment.

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