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A spiral flowing supported liquid membrane based on DEHPA carrier for the separation of lead from seawater

M. Ben Omar[a,b,*], C. Mendiguchía[b], M. García-Vargas[b], C. Moreno[b]

[a]*Tangier-M'diq Regional Centre, National Institute of Halieutic Research, BP 5268 Dradeb, Tangier, Morocco, Tel. +212 539946586/87; Fax: +212-539325139; email: mostapha.benomar@uca.es (M. Ben Omar)*
[b]*Faculty of Marine and Environmental Sciences, Department of Analytical Chemistry, University of Cádiz, Puerto Real, 11510 Cádiz, Spain, Tel. +34 956 016165; email: carolina.mendiguchía@uca.es (C. Mendiguchía), Tel. +34 956 016358; email: manuel.garciavargas@uca.es (M. García-Vargas), Tel. +34 956 016433; email: carlos.moreno@uca.es (C. Moreno)*

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ABSTRACT

This work aims to study the use of a spiral supported liquid membrane (SLM) to extract lead (Pb) from seawater matrix using the di-(2-ethylhexyl) phosphoric acid (DEHPA) dissolved in kerosene as carrier. In this regard, several physical and chemical parameters which could affect Pb extraction (sample pH, sodium acetate buffer, HNO_3 concentration in stripping solution, masking agent effect, flow rate, filter porosity, and configuration of the SLM cell) were studied. In this sense, the permeability parameter was selected to probe the system efficiency. The optimal preconcentration factor was found to be of 14.2, after 2 h under the following conditions: sample pH equal to 4.7 buffered until a 0.08 M of sodium acetate, DEPHA concentration fixed at 0.21 M and HNO_3 concentration of 0.23 M in stripping solution. Besides, SLM filters were analyzed by electron microscopy after each period of 2 h and several microparticles and other deposits in form of a thin layer were observed in the polymeric support.

Keywords: Spiral supported liquid membrane; Lead; Seawater; Pre-concentration; Extraction

1. Introduction

The determination of trace elements in seawater by direct analytical techniques is still a challenging task despite the availability of very sensitive analytical tools, such as the inductively coupled plasma mass spectrometry (ICP–MS), mainly due to seawater matrix interference and low concentration of trace elements [1,2].

To overcome these difficulties, separation and preconcentration of the analytes are necessary prior to the instrumental determination. These steps avoid seawater interference matrix and increase the concentration of the analytes making them detectable by direct analytical techniques. To do this, several alternatives are available such as the ion exchange [3], liquid–liquid extraction [4], coprecipitation methods [5,6], and liquid membranes. According to their physical configuration, liquid membranes can be classified as bulk liquid membranes (BLM), supported liquid membranes (SLM), and emulsion liquid membranes [7].

The use of liquid membranes as a separation and preconcentration technique is presented as a good alternative to solvent extraction, the traditional

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*Corresponding author.

method used in oceanographic studies, mainly due to extraction and re-extraction processes can be performed simultaneously. In the last decades, it have been applied in several areas, such as agricultural and alimentary [8], industrial wastes [9], hydrometallurgy [10], and environmental analysis [11–13].

The SLM has been widely used in several analytical applications because of the low solvent volume required and the high extraction percentages achieved [14]. However, its application to separate trace metals from seawater is currently scarce.

On the other hand, the determination of lead levels in different environmental matrices, including seawater, is of great importance to humanity because it is one of the most toxic elements for the biota [15,16].

In this work, a spiral SLM was applied to separate and preconcentrate lead from seawater samples. The system has been previously described and applied by Jönsson and Mathiasson to determine aliphatic and aromatic amines in urine and blood samples, as well as to study herbicides in water samples [17]. Besides, this type of membrane was used by Papantoni et al. for the preconcentration of several metals (Cu, Cd, Co, Ni, and Zn) [18], and by Soko et al. for the extraction and the preconcentration of Mn(II) in water, milk, and blood samples [19]. This type of system was also applied by Kertész et al. to study phenylalanine [20], whereas Ndungu et al. used it to study the speciation of Cu in estuarine water [21]. Moreover, it was applied by Belkhouche et al. to study the extraction of metals (M (II) and M (III)) by means of new organophosphorus derivatives like extracting agents [22].

This work is based on the previous studies carried out by Benomar et al. for the Pb preconcentration in marine waters using BLM [23]. In this sense, the SLM system attempts to solve some drawbacks found when the BLM system was applied reducing the solvent volumes required for BLM and increasing the extraction percentage simultaneously to the reduction of the extraction time.

2. Materials and methods

2.1. Reagents and solvents

Nitric acid (65%, reagent grade), hydrochloric acid (37%, reagent grade), sodium acetate (p.a.), calcium chloride dehydrate (p.a.), magnesium chloride hexahydrate (p.a.), and sodium chloride (p.a.) were used. All of them were provided from Merck (Darmstadt, Germany). Kerosene from Fluka (Buchs, Switzerland) and di-(2-ethylhexyl) phosphoric acid DEHPA from Sigma–Aldrich (Steinheim, Germany) were used after purification. Lead, calcium and magnesium solutions were prepared from a 1,000 mg L^{-1} standard solution obtained from Merck (Darmstadt, Germany).

Ammonium acetate (25%, p.a., Scharlab, Spain), ammonium hydroxide (p.a., Merck, Germany), chloroform (p.a, Merck, Germany), diethylammonium diethyldithiocarbamate (DDDC) (Scharlab, Spain), and ammonium pyrrolidine dithiocarbamate (APDC) (Fluka, Switzerland) were used in solvent extraction.

Ethylenediaminetetraacetic acid (Scharlab, Spain), sodium tartrate (p.a., Panreac, Spain), sodium citrate dihydrate (p.a, Panreac, Spain), and hydrofluoric acid (40%, reagent grade) were used such as masking agents.

A model 2001 pH-meter equipped with a model 52-02 combined glass-Ag/AgCl electrode (Crison, Spain) was used to measure pH.

Scanning electronic microscope QUANTA 200, FEI (Estados Unidos) was used to analysis a SLM filters, while an inductively coupled mass spectrometer (ICP-MS) Series X-7 (Thermo Elemental, UK) and an atomic absorption spectrometer (AAS), SolaarM Series (ThermoElement, USA) were used for metal determinations.

2.2. SLM system

The homemade SLM modules consisted of two circular plates made of either PolyEthylene Terephthalate (Ertalyte^{R}) or Teflon material. Each plate is equipped with machined grooves like an Archimedes spiral which allows the circulation of aqueous solutions by means of a peristaltic pump, in a way that the sample (feed phase) is placed on one plate and the receiving phase on the other (Fig. 1 and Table 1). Between the two blocks a polyvinylidenedifluoride (PVDF) filter is located after its impregnation with the organic solution (DEHPA dissolved in kerosene). Metal transport takes place through the organic phase located into the fiber's pores from the sample to the receiving solution. Finally, the system was maintained by two other aluminum blocks and clamped with screws. Table 2 shows the characteristics of the two types of PVDF filters used in this work.

The plates were cleaned with 2 M HNO_3 between different experiments in order to avoid sample contamination.

2.3. Experimental procedure

The water sample (500 ml) and the acidic receiving solution (10 ml) were located into plastic bottles and they were continuously homogenized by means of magnetic stirrers. These solutions were pumped to the SLM system by means of a peristaltic pump through polypropylene tubes with an internal diameter of

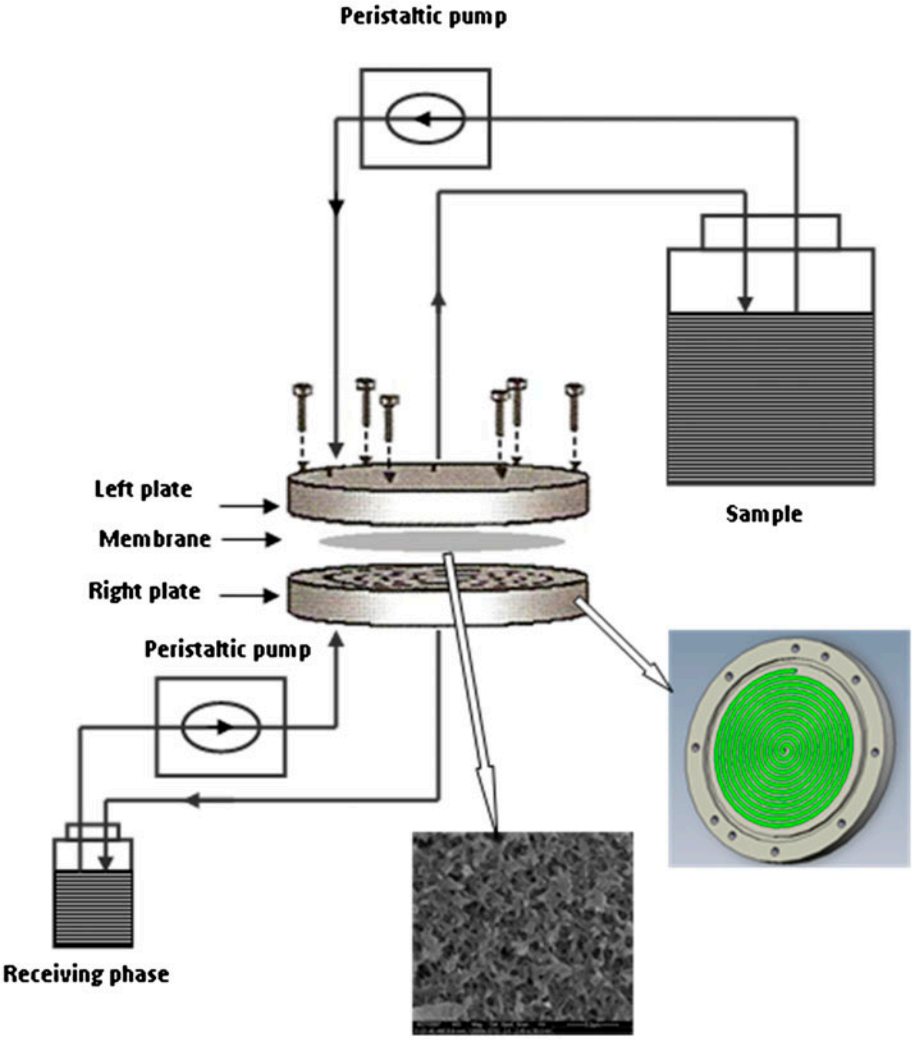

Fig. 1. Scheme of the SLM system.

Table 1
Characteristics of spiral excavated in each plate

Parameters	System I	Modified system
Material	Ertalyte^R	Teflon
Spiral length (mm)	2,705	2,705
Spiral depth (mm)	2	0.3
Spiral width (mm)	3	3
Area (cm^2)	81.15	81.15
Volume (ml)	16.23	2.43

1.14 mm. Once the solutions filled the spirals in the SLM module they were returned to the bottles in order to maintain a continuous recirculation.

During transport experiments, aliquots of 1.6 ml were taken periodically from receiving solution to measure lead concentration, and other aliquot of 1.6 ml with the same concentration of nitric acid was added to keep its volume constant. After measurements, the obtained concentration values were properly corrected taking into account the dilution factors. The metals' concentration in the receiving solution was measured by AAS or ICP-MS.

The parameter used to determine the efficiency of the preconcentration system was the permeability coefficient (P) calculated from the slope of the curve Eq. (1) [24]:

$$-\ln\left[\mathrm{Pb}^{2+}\right]_{\mathrm{t}} = \frac{S}{V_{\mathrm{s}}}\mathrm{Pt} - \ln\left[\mathrm{Pb}^{2+}\right]_{0} \tag{1}$$

where A is the effective membrane area, V_s is the volume of the sample, and $[\mathrm{Pb}^{2+}]_0$ and $[\mathrm{Pb}^{2+}]_t$ are

Table 2
Characteristics of the two filters used in the study

	Filter I	Filter II
Material	PVDF	PVDF
Color	White	White
Diameter (mm)	142	142
Pore size (μm)	0.22	0.45
Porosity (%)	75	70–75
Thickness (μm)	125	165
Fabricant	Durapore membrane, millipore (GVHP 14250)	Pall filters (Biotrace)

the sample lead concentrations at time 0 and *t*, respectively.

The first experiments were carried out using the optimized conditions obtained for the previous BLM system [23]. Then, a sample solution of 35 g L^{-1} NaCl with a pH value of 4.7 (adjusted with NaOH when it was necessary) buffered with sodium acetate until a final concentration of 0.08 M and a receiving solution of 0.23 M HNO_3 were used. In the case of DEHPA concentration in the organic solution, a new optimization study was performed due to the volume of organic phase is drastically reduced in the SLM system. These reduction suppose a decrease in the quantity of DEHPA available to perform the extraction from 2.52×10^{-3} moles in BLM to 3.15×10^{-4} moles in SLM for the same DEHPA concentration. In addition, optimization of hydrodynamic conditions was also necessary due to the different hydrodynamic characteristics of the SLM in comparison with BLM.

To perform the optimization experiments the polyethylene terephthalate cell (system I) was applied (Table 1).

3. Results and discussion

3.1. Optimization

First, the influence of DEHPA concentration on the permeability coefficient was studied using a SLM filter with a pore size of 0.22 μm and a flow rate of 0.5 ml min^{-1}. Four different concentrations of DEHPA (0.07, 0.14, 0.21, and 0.28 M) were studied and the maximum permeability coefficient ($3.80 \times 10^{-3} \pm 0.27 \times 10^{-3}$ cm min^{-1}) was observed for a DEHPA concentration of 0.21 M. Although an increase in the permeability coefficient could be expected for higher DEHPA concentrations, the higher viscosity of organic solution for concentrations above 0.21 M reduce the Pb transport and an increase in the *P* value is not observed. Also, high concentrations of extracting agent cause a microemulsion that could block organic/aqueous interphases and produce a low diffusion of the elements through the liquid membrane. This effect has been previously observed by Schlosser et al. [25].

Then, hydrodynamic conditions were studied. In the case of BLM a magnetic stirred was used to reduce the diffusion layer between organic and aqueous phases; however, in the case of SLM this effect is achieved by means of the peristaltic pump. Then, in the SLM system, the magnetic stirrer is only used to homogenize the aqueous solutions. Fig. 2(a) shows the effect of the flow rate on the permeability coefficient. The higher *P* value ($10.71 \times 10^{-3} \pm 1.73 \times 10^{-3}$ cm min^{-1}) was found at 1.6 ml min^{-1} and a decrease was observed for higher flow rates. This decrease could be related to the instability of the membrane when high flow rates are used due to the loss of organic phase into the aqueous phases forming microemulsions.

Finally, these new optimized values were applied to study the Pb transport through the SLM.

3.2. Pre-concentration yield

The percentage of lead transported through the membrane was studied at different times to establish the time necessary to perform the extraction. First, a sample solution of NaCl (35 g L^{-1}) was used and then

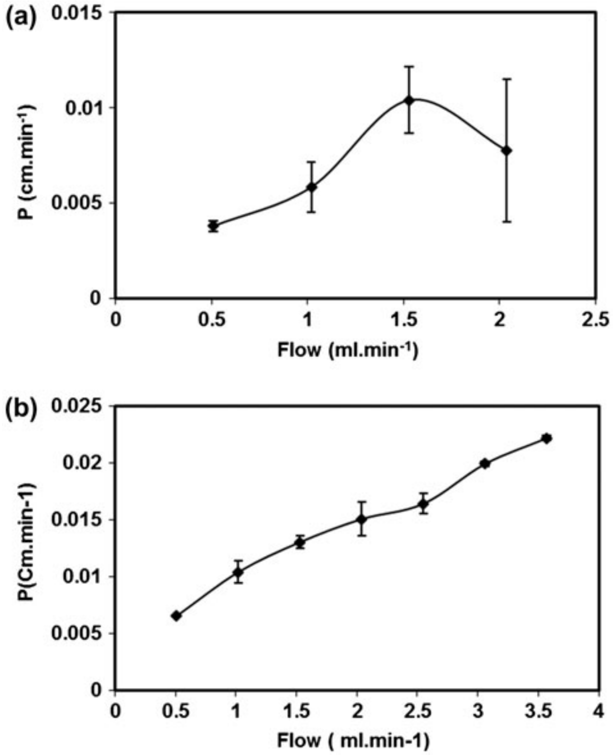

Fig. 2. Effect of flow rate on the permeability coefficient. (a) system I; (b) system II).

the effect of other major cations was studied using a sample solution with NaCl (23.939 g L^{-1}), $MgCl_2{\cdot}6H_2O$ (10.825 g L^{-1}), and $CaCl_2{\cdot}H_2O$ (1.3 g L^{-1}). Each case was studied separately and aliquots of 1.6 ml were taken each hour from the receiving solution to determine the Pb concentration. The obtained results are shown in Fig. 3(a) and (b), respectively.

In the first case, with a sample matrix of NaCl, the 100% of lead was transported after 19 h. This slow Pb transport could be related to the formation of diverse Pb complexes in the sample that are transported through the liquid membrane more slowly than the free ion.

However, when a sample matrix of $MgCl_2$, $CaCl_2$, and NaCl was used, the maximum transport of Pb was achieved after 11 h although the percentage was considerably lower (46%). Moreover, in order to verify if cotransport of Ca and Mg occurs, these elements were analyzed in addition to Pb in the same aliquots of receiving phase. The results showed that both major ions (Ca and Mg) were in high concentrations in the receiving phase and these concentrations increased as extraction time increase, reaching 3.250 g L^{-1} for Ca and 1.750 g L^{-1} for Mg at 10 h.

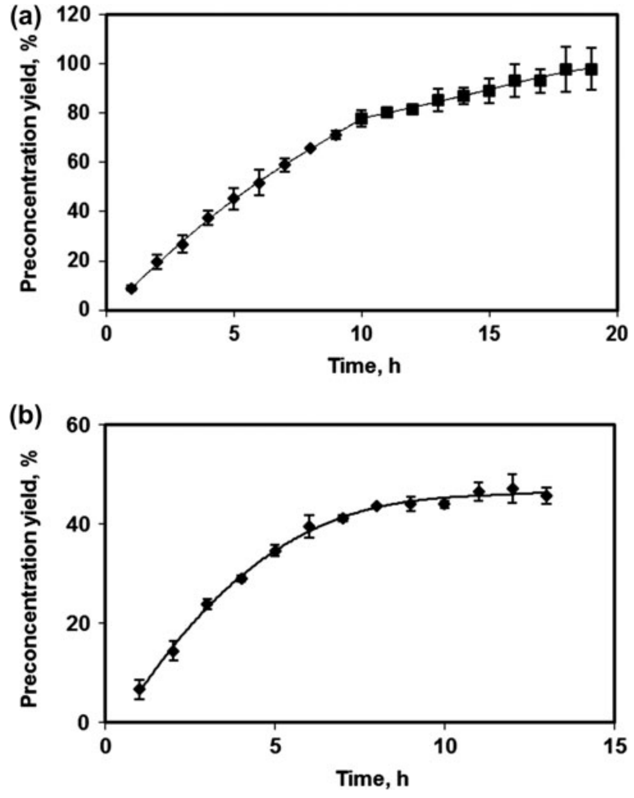

Fig. 3. Temporal variation of preconcentration yield for different samples. (a) NaCl; (b) NaCl, $MgCl_2$, $CaCl_2$.

The decrease in the percentage of lead transported through the membrane when Ca and Mg are present in the sample could be related to different reasons. On the one hand, a competition for DEHPA could be occurring between major ions (Ca and Mg) and Pb. To solve this problem, different masking agents (EDTA, HF, sodium tartrate, and sodium citrate) were tested to inhibit the transport of Ca and Mg through the membrane. Nevertheless, an improvement in the lead transport was not observed in the presence of these masking agents.

On the other hand, precipitation of some Pb compounds in the filters could be occurred and they could be working as a barrier for Pb transport. In this case, a loss of Pb could be observed in both aqueous phases. The same phenomenon was observed by Ashrafizadeh et al. [26]. Thus, to confirm this hypothesis, the filters were analyzed at the end of each experiment by electron microscopy. As it can be seen in Fig. 4(a) and (b), several microparticles and other kind of deposits in form of a thin layer were observed in the polymeric support.

To avoid these issues, some characteristics of the SLM cell were modified.

3.3. *Modified modular system*

The changes in the SLM cell were focusing on the dimensions of the spirals (length, width, area, and volume) by which the two aqueous solutions circulate. These modifications allowed the use of a small volume of receiving phase and, at the same time, enable the increase in the contact area between the receiving and the organic phases (Table 1).

Then, the dependence of P on the flow rate was studied again using the new cell. Fig. 2(b) shows that P increases with the flow rate increases, reaching its maximum ($22.18 \times 10^{-3} \pm 0.\ 23 \times 10^{-3}$ cm min^{-1}) at 3.57 ml min^{-1}. For higher flow rates, a mixture of the two aqueous phases was observed.

3.4. *Application to real samples*

First, the preconcentration yield was studied again with a real seawater sample taken in the Bay of Cádiz. Two filters with different pore size (0.22 and 0.45 μm) were tested in order to reduce the effect caused by the precipitates. The results were similar for both filters as it is reported in Fig. 5. The maximum extraction percentage was observed after 2 h with a value of 28 ± 1%. The decrease observed after 2 h could be related to precipitation of lead compounds over the filters, as it has been explained before. For the next experiments, a filter with a pore size of 0.45 μm was used.

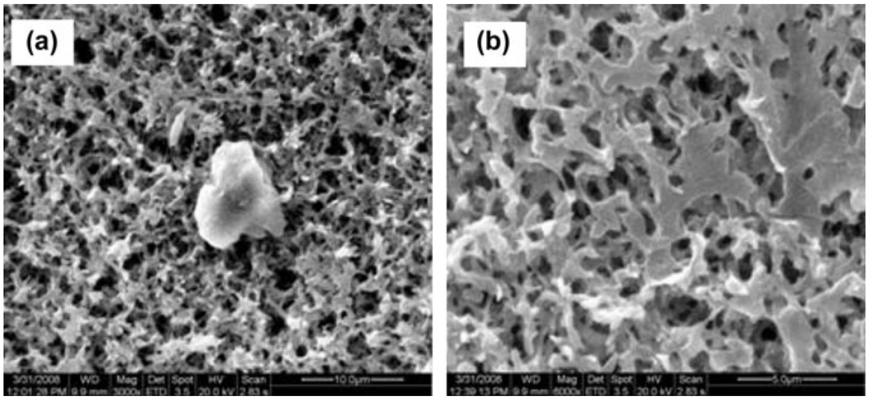

Fig. 4. Observation of the filter by the electronic microscope. (a): particle; (b) microlayer.

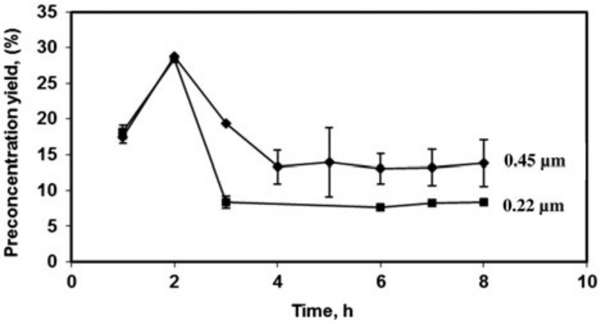

Fig. 5. Preconcentration yield for a seawater sample using two filters with different pore size.

Then, several methodological blanks with a NaCl (35 g L^{-1}) matrix were studied ($n = 8$). They were acidified with Suprapur nitric acid and buffered with sodium acetate as real seawater samples. An average value of Pb concentration was determined to be (0.041 ± 0.018 μg L^{-1}). This value was in the same order to that obtained when solvent extraction was used (0.020 ± 0.007 μg L^{-1}). Using these blanks real samples containing lead at the low ppb-level may be determined. If required blank levels could be easily decreased using clean methodologies.

Finally, the optimized conditions were applied to analyze a coastal seawater sample taken in the Bay of Cádiz spiked with different lead concentrations in the range of 2.5–100 μg L^{-1}. After 2 h, Pb concentrations were determined in the receiving phase. The percentage of lead transported was calculated and an average value of 28 ± 3% was obtained. The result for each experiment can be observed in Fig. 6. These results indicate a very good reproducibility and also the independence of lead transported on the initial lead concentration.

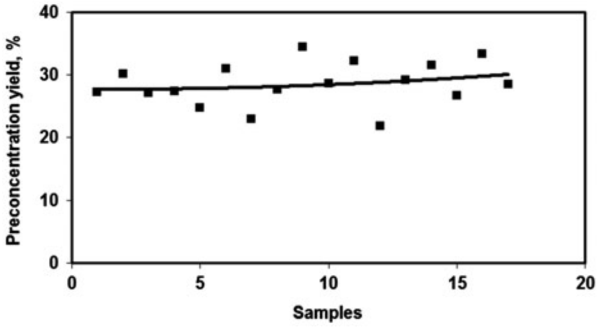

Fig. 6. Variation of the preconcentration yield at 2 h.

Finally, a preconcentration factor of 14.2 was calculated taking into account the volume of the aqueous solutions and the extraction percentage. This preconcentration factor was used to determine lead concentration in the spiked seawater samples. The recoveries were in the range of 88–106%, as it can be observed in Table 3. These results confirm the applicability of the optimized method to determine lead concentrations in seawater, mainly coastal seawater.

3.5. Comparison of SLM system with a well-established methodology (solvent extraction)

The validity of the proposed SLM system to analyze lead in seawater was confirmed by comparison with a well-established methodology for metal analyses in seawater based on solvent extraction [4]. Although other methodologies as coprecipitation and solid phase extraction methods have been developed to analyze lead in seawater, solvent extraction is the most extensively used as routine analyses in oceanographic studies.

Table 3
Relative error between the calculate and added lead

Sample	$[Pb]_{added}$ (μg L^{-1})	$[Pb]_{measured}$ (μg L^{-1})	Recovery (%)	Relative error (%)
1	2.5	2.2	88.0	−12
2	5	5.10	102.0	+2.0
3	8	7.40	92.5	−7.5
4	10	9.70	97.0	−3.0
5	20	19.1 ± 3.7	95.5	−4.5
6	20			
7	30	29.5 ± 6.7	98.3	−1.7
8	30			
9	30			
10	50	53.2 ± 4.5	106.4	+6.4
11	50			
12	60	58.3 ± 12.8	97.2	−2.8
13	60			
14	60			
15	70	73.8 ± 11.5	105.4	+9.5
16	70			
17	100	93.00	93.0	−7.0

Table 4
Lead concentration obtained by SLM and liquid–liquid extraction (LLE)

$[Pb]_{added}$ (μg L^{-1})	$[Pb]_{LLE}$ ± SD (μg L^{-1})	$[Pb]_{SLM}$ ± SD (μg L^{-1})	Relative error (%)
50	49.86 ± 2.25	53.27 ± 4.47	6.8
60	59.39 ± 0.34	58.30 ± 12.78	−1.8
70	69.88 ± 1.06	73.72 ± 11.52	5.5
100	94.00 ± 2.83	93.04	−1.1

Then, different spiked seawater samples were analyzed by solvent extraction and SLM methods and the results are shown in Table 4. As it can be observed in the table, the results were very similar for both methodologies, with an average relative error of 2.3%. These results confirm the applicability of the developed methodology to analyze lead in seawater samples, with the advantages of smaller volume of organic dissolvent and shorter times than the traditional method.

In addition, the SLM system could be automatized easier than coprecipitation methods and avoid the highly concentrated buffer solution (2 M) used in ion-exchange procedures which can be a source of sample contamination and also interference for some instrumental determinations (ICP-MS) [27].

4. Conclusions

The SLM system proposed to extract and preconcentrate Pb from seawater showed a better preconcentration factor (14.2) than the previous BLM system (4.7) reducing the volume of organic solution used, and being more environmental-friendly. In addition, the quantity of lead transported was independent on initial lead concentration. Then, the method has been applied to analyze different lead concentration in real seawater.

Also, a good reproducibility was observed when real samples were analyzed and the results were similar to those obtained by a well-established methodology based on solvent extraction. This confirms the applicability of the proposed method to determine lead concentration in seawater samples.

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