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Analytical note

Separation and preconcentration of cadmium ions in natural water using a liquid membrane system with 2-acetylpyridine benzoylhydrazone as carrier by flame atomic absorption spectrometry☆

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Abstract

A method for the determination of Cd in natural water by flame atomic absorption spectrometry after separation and preconcentration with a bulk liquid membrane containing 2-acetylpyridine benzoylhydrazone as mobile carrier dissolved in toluene has been developed. Effects of carrier concentration, volume of organic phase and pH of feed and receiving solutions on the flux for Cd across the membrane have been studied, being optimized by the modified simplex method. Optimum values for these variables were: carrier concentration of 0.84 g l^{-1}, 74 ml of toluene, pH 7.8 in the feed solution and 0.06 mol l^{-1} of HNO_3 in the receiving solution, allowing a preconcentration factor of 17.9. The preconcentration step required 7 h to be accomplished. The recovery of Cd at optimum conditions was $101.0 \pm 2.7\%$, even with saline matrix, with good relative standard deviation (2.5%) at 95% confidence level. The detection limit of blank sample was 6 ng l^{-1} of Cd. The method was validated using a certified reference material (TMDA-62) and also applied successfully to the analysis of Cd in four samples of seawater collected from the coast of Huelva (Spain). The relative errors of determinations were −7.6% for certified reference material and ranging between +2.4 and +7.1%, for samples of seawater (obtained between the results of the proposed and differential pulse anodic stripping voltammetry methods).

Keywords: Cd; Natural water; Liquid membrane; Metal preconcentration; 2-acetylpyridine benzoylhydrazone (2-APBH)

1. Introduction

Determination of trace metals in natural waters, in the concentration range 10^{-12}–10^{-8} mol l^{-1} is still a challenging task despite the availability of very sensitive analytical tools. Methods for separation of analytes from interferents in the complex matrices and selective preconcentration are frequently necessary. Many preconcentration techniques have been proposed for the determination of metals in various environmental samples, including solvent extraction, ion exchange, coprecipitation and sorption [1–5]. The liquid membrane technology is an attractive alternative to these sample pretreatment methods for metal ions from complex matrices [6,7]. It is a separation method in which an organic solvent immiscible with water containing an adequate complexing agent (carrier) selective towards the target metal is interposed between two aqueous phases. One of the aqueous phases is the feed solution containing the metal ion to be transported and the other one is the receiving solution. Therefore, the complexed metal diffuses across the organic liquid phase. Usually, the metal ion transport is based on the proton driven mechanism [8]. By using receiving solution volumes much smaller than feed solution volumes, analytes can be concentrated. Thus, target elements can be separated and concentrated at the same time. Among the several liquid membrane configurations, bulk liquid membranes (BLM) and supported liquid membranes (SLM) are

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appropriate to be applied as analytical tools, because of the simplicity and easy accessibility of the aqueous phase and the high preconcentration factors, respectively [6].

There are few reports on the use of liquid membrane for trace metal analysis in natural waters [9–11] and studies referring to their application to metal speciation measurements in natural waters [12–14], although the advantages of these systems are well accepted [8].

Related to metal determination in natural waters, an interesting advantage of liquid membrane is the possibility of avoiding matrix interferences. In freshwater systems humic substances are often present in concentrations of several parts per million whereas in seawater the highly salt content might pose a problem. No significant effects have been observed on the extraction efficiency when using either pure water solution or natural water in some liquid membranes [13].

Cd is known to be a hazardous environmental pollutant with toxic effects for the living organisms in aquatic ecosystems [15]. Adverse effects of Cd are produced not only because of its high toxicity even at trace concentrations, but also due to bioaccumulation processes along the food chain. As water plays an important role in nature as carrier, among others, the anthropogenic inputs of Cd can be easily spread over the aquatic medium. Therefore, Cd can be available to living organisms, including microorganisms and micro algae, which are at first of the food chain and take part in important biological processes [16].

Several methods have been already developed for the determination of Cd in natural water samples. Analytical techniques like stripping voltammetry [17,18], neutron activation analysis (NAA) [19,20], X-ray fluorescence analysis [21,22] are suitable but atomic absorption spectrometry (AAS) and optical emission spectrometry methods are the most widely used for this purpose. Particularly, electrothermal AAS has shown satisfactory detection limits for the determination of Cd at nanogram per litter levels in water samples, but high saline matrix interferes with analysis.

Although the transport of Cd has been examined using liquid membranes, the majority of the studies reported in the literature discuss its use in recovery of target elements from residual solutions or wastewater treatment [23–26]. Thus, few environmental applications of liquid membrane have been reported for the determination of Cd in natural waters [14] and even less in seawater, probably due to the high matrix complexity.

In this work, we present a reliable new method to transport, separate, preconcentrate and determinate Cd ions using a bulk liquid membrane, containing 2-APBH (2-acetylpyridine benzoylhydrazone) in toluene. Previous papers about this ligand, regarding too spectral and metallochromics properties of 2-APBH [27,28] showed its interesting properties as complexing agent of metal ions. This ligand, which belongs to the group of aroylhydrazones, forms uncharged chelates with divalent transition metal ions, which can be extracted into organic solvents [28]. The influence of different variables such as extractant concentration in organic solvent, volume of organic phase and pH of feed and receiving solutions were studied. After separation, the concentration of Cd in the receiving solution was determined by flame AAS (FAAS), a conventional and inexpensive technique available in many laboratories world-wide. This new preconcentration system of Cd was applied to the analysis of several real samples of seawater.

2. Experimental

2.1. Apparatus

The cell of the bulk liquid membrane used in this study is shown in Fig. 1. The system is a glass homemade beaker-in-a-beaker type cell. Solutions in the cell were stirred with two Teflon-coated magnetic bars (12×4 mm diameter) by using a model Agimatic-S magnetic stirrer (Selecta, Spain). The cell and the other laboratory materials were acid cleaned. Typically, the materials were soaked for 3 days in 2 mol l^{-1} HNO_3 and rinsed with Milli-Q deionised water six times. The flame atomic absorption spectrophotometer used for the measurements of metal ion concentration was a Solaar M Series (Unicam, UK), operating under recommended conditions for Cd. A Metrohm model 746 VA Trace Analyzer processor with a Metrohm 747 VA Electrode Stand with automated hanging mercury drop electrode (HMDE) was used for voltammetric measurements. Organic matter was removed from water samples by UV irradiation with a Metrohm model 705 UV Digester in quartz tubes.

The pH measurements were made with a 2001 pH meter using a 52-02 combined glass-Ag/AgCl electrode (Crison, Spain). Transport experiments were carried out with temperature control using a thermostatic bath (TECTRON-100, 3473100, Selecta, Spain).

2.2. Reagents and solutions

All reagents were of analytical-reagent or Suprapur grade and all solutions were prepared using Milli-Q deionised water (Millipore, USA), distilled ethanol or toluene (grade pro analysis from Merck, Darmstadt, Germany). Stock aqueous solutions of Cd (10–100 mg l^{-1}) were prepared from Cd standard solution of 1000 mg l^{-1} (Merck, Darmstadt, Germany). The pyridine-2-acetaldehyde and benzoylhydrazide were obtained from Sigma-Aldrich (Steinhein, Germany). The synthesis of 2-APBH has been described elsewhere [27] and solutions (0.69–1.94 g l^{-1}) of 2-APBH in toluene were

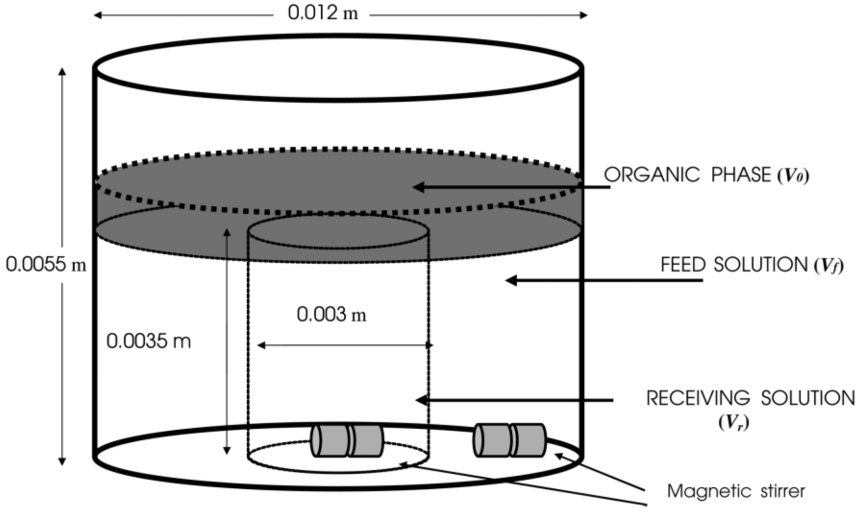

Fig. 1. The cell of bulk liquid membrane containing liquid membrane.

prepared and used as carrier. These solutions were stable for at least 72 h. Britton–Robinson buffer solutions were used to adjust the pH of feed solutions during the optimization process (pH 4–8.5). These solutions were prepared as previously reported [29] using *o*-boric acid, *o*-phosphoric acid, acetic acid and sodium hydroxide of Suprapur grade (Merck, Germany). A constant ionic strength of 1.5 mol l^{-1} was maintained in the buffers by adding KCl Suprapur grade (Merck, Germany). After adjustment of the pH, the final concentration of buffer in the feed solution was 0.25 mol l^{-1}. The real samples were adjusted with NH_3 Suprapur grade (Merck, Germany), being not necessary a significant volume of it and avoiding the dilution of the samples.

2.3. Analytical procedure

The preconcentration experiments were performed with the cell described previously (Fig. 1). It consisted of two concentric beakers, with the feed solution (V_f, external beaker) and the receiving solution (V_r, internal beaker). The pH of the feed solution containing Cd was adjusted with Britton–Robinson buffer solutions or ammonia. The receiving solution was an aqueous solution of nitric acid (0.01–0.4 mol l^{-1}). The volumes of V_f and V_r solutions were 286 ml and 16 ml, respectively; in these conditions the preconcentration factor was 17.9 when the procedure was extended to complete diffusion equilibrium, provided by the ratio of V_f/V_r. The organic solution (V_o), containing 2-APBH as carrier dissolved in toluene, was placed over both aqueous solutions. Aqueous solutions were stirred by Teflon-coated magnetic bars at 700 rev./min. The transport experiments were carried out using a thermostat ($T=30\pm0.5$ °C). UV digestion of natural water with high organic matter content is necessary in order to avoid metal organic complexes with high stability to avoid interference in the metal transport.

During transport experiments, different 2 ml aliquots were taken out from the receiving solution at scheduled time intervals. The same volume of HNO_3 solution saturated in toluene was added to keep the volume of the receiving solution constant. After FAAS measurements, the concentration values obtained were corrected taking into account the metal amount contained into the aliquots of receiving solution previously removed.

The efficiency of the system was evaluated with the permeability coefficient P (cm $\min^{-1}$). The values were determined from sets of primary data in the form of Cd concentration vs. time by using the following linear relationship:

$$-\ln[\mathrm{Cd}]_{\mathrm{f}} = \frac{S}{V_{\mathrm{f}}} \cdot P \cdot t - \ln[\mathrm{Cd}]_{\mathrm{f,0}}$$

where S is the effective membrane area, V_f is the volume of feed solution, and $[\mathrm{Cd}]_{\mathrm{f,0}}$ and $[\mathrm{Cd}]_{\mathrm{f}}$ are the feed metal concentrations at time zero and time t, respectively [10].

To optimize the efficiency of the liquid membrane separation process, the influence of variables affecting the permeability coefficient was studied. A modified simplex method was applied by using the software Multisimplex 2.0 [30].

3. Results and discussion

The transfer and separation of Cd ions across the bulk liquid membrane was based on the reaction of 2-APBH as a polydentate ligand, forming an uncharged chelate in toluene [28]. The neutral complex is destroyed by the acid phase after transportation through the membrane. The driving force for the transport of Cd ions is the pH gradient between feed (sample) and receiving solutions.

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 24 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 9.3×10^{-7} (evaluated from four replicates of one experiment) [31]. The absence of organic reagent did not produce transport of the metal ion.

Optimum conditions corresponded with experiment number 24: pH 7.8 in the feed solution, 0.06 mol l^{-1} of HNO_3 in the receiving solution, 2-APBH concentration of 0.84 g l^{-1} in the organic membrane with 74 ml of toluene. In these conditions, a permeability of 20.9×10^{-3} cm min^{-1} was obtained.

3.2. Influence of feed phase salinity

Before the application of the liquid membrane to natural and seawater samples various experiments were performed to determine the influence of feed solution salinity on the preconcentration of Cd. Therefore, we studied the temporal variation of Cd concentration in the receiving solution for four samples (two replicates) with different salinity values (0, 10, 20 and 35 g l^{-1} of NaCl). Fig. 2 shows preconcentration yield average of these eight experiments as a function of extraction time.

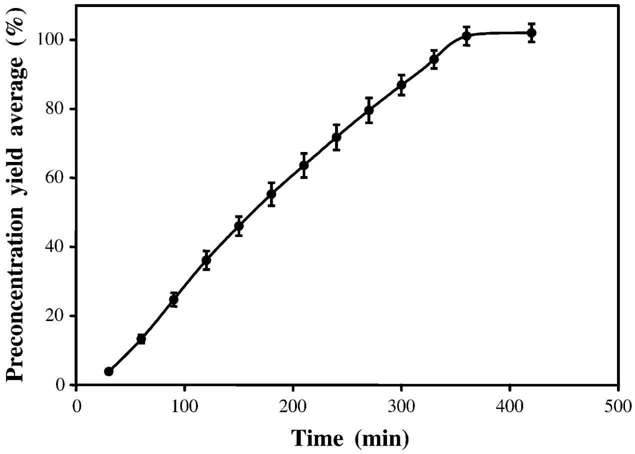

Fig. 2. Temporal variation of preconcentration yield average (bars indicate the standard deviation for $n=8$). Feed solution (V_f): 162.8 μg l^{-1} of Cd; pH 7.8 ; 0, 10, 20 and 35 g l^{-1} NaCl (two replicates). Receiving solution (V_r): 0.06 mol l^{-1} HNO_3. BLM (V_o): 0.84 g l^{-1} of 2-APBH in toluene.

Table 1
Simplex optimization of variables (feed solution: 150 μg l^{-1} of Cd; transport time: 4.5 h)

Vertex	Type	Organic volume V_o (ml)	pH feed solution	[HNO_3] (mol l^{-1})	[2-APBH] (g l^{-1})	Permeability× 10^3 (cm min^{-1})
1	F	75	4	0.2	0.84	0
2	F	75	6	0.4	0.84	5.5
3	F	125	4	0.4	1.55	0.1
4	F	125	6	0.2	0.84	7.8
5	F	75	6	0.2	1.55	9.2
6	R	125	7	0.4	1.55	8.0
7	R	75	8.5	0.2	0.84	7.8
8	R	125	7.8	0.1	1.55	7.3
9	C+	113	7.3	0.17	1.36	12.2
10	R	69	8.4	0.28	1.82	7.1
11	C−	111	6.6	0.22	1.08	14.9
12	R	137	4.9	0.3	1.94	1.8
13	C−	91	7.6	0.22	1.10	18.1
14	R	70	6.8	0.01	1.04	19.3
15	E	43	6.6	−0.19	0.72	*
16	R	118	8.2	0.11	0.72	12.2
17	C+	107	7.6	0.13	0.93	14.5
18	R	77	7	0.12	0.69	17.9
19	R	68	6.4	0.15	1.00	15.4
20	R	42	7.3	0.03	0.81	*
21	C−	94	6.8	0.17	1.00	13.8
22	R	98	7.7	0.11	0.88	19.7
23	E	113	8.3	0.09	0.84	10.6
24	R	74	7.8	0.06	0.84	20.9

F: first simplex; R: reflexion; E: expansion; C+: positive contraction; C−: negative contraction * not possible.

Table 2
Validation of proposed methodology for Cd determination in spiked samples ($n=2$)

Sample	Concentration spiked (μg l^{-1})	Concentration measured (μg l^{-1})	Relative error (%)
Saline matrix[a]	162.8	165.5±2.9 [d]	+1.6
Saline and metal matrix[b]	25.4	23.4±1.9 [d]	−7.8
Synthetic seawater[c]	157.3	161.9±2.2 [d]	+2.9

[a] 35 g l^{-1} of NaCl.
[b] Al (2 μg l^{-1}), Co (0.020 μg l^{-1}), Fe (2 μg l^{-1}), Mo (10 μg l^{-1}), Ni (0.3 μg l^{-1}), Zn (0.6 μg l^{-1}), 35 g l^{-1} NaCl [33].
[c] Ref. [33].
[d] Standard deviation.

Error bars indicate the standard deviation ($n=8$), which varied between ±0.7% and ±3.4 %. The initial Cd concentration on the metal transport was tested (5, 25, 150 and 200 μg l^{-1} of Cd) Efficient preconcentration was achieved after 7 h, even with highly saline samples, with preconcentration yield ranging between 97.6 and 101.5%.

3.3. The new preconcentration proposed method

The blank determination was performed using optimal conditions and Milli-Q deionised water. The blank value was 0.016±0.002 μg l^{-1} of Cd for 4 replicates, the limit of detection (calculated as 3 times the standard deviation) being 0.006 μg l^{-1} of Cd. The blank samples were measured by graphite furnace atomic absorption spectrometry, because of FAAS detection limit was not enough (0.35 μg l^{-1} of Cd).

The relative standard deviation of the proposed method was 2.5%, evaluated for significance level at 95% and $n=5$ with 162.8 μg l^{-1} of Cd, Cd recovery being 101.0±2.7%.

3.4. Application

In order to validate the proposed preconcentration method, the analysis of different synthetic samples and a certified reference material were performed.

Three samples with different matrix were spiked with several known amounts of Cd (two replicates for each sample): 35 g l^{-1} of NaCl, 35 g l^{-1} of NaCl solution with common heavy metals concentrations in seawater, and synthetic seawater [32]. The results are shown in Table 2. Cd was successfully preconcentrated and quantified using the new proposed method.

In the same way, a sample of certified reference water (TMDA-62) for trace elements was analyzed after UV digestion (with H_2O_2). The results are shown in Table 3 and the relative error was +7.6%.

In order to apply the new method to real samples, the analysis of four seawater samples from coast of Huelva (Spain) was carried out. Samples were filtered through 0.45 μm pore-size filters, acidified with HNO_3 and stored until analysis. Dissolved Cd in the samples was measured after UV digestion (with H_2O_2) and neutralization, using the preconcentration method. The results were compared with those obtained by differential pulse anodic stripping voltammetry (DPASV) (Application Bulletin No. 231/1 e; B12916, Metrohm) [33]. The results obtained are shown in Table 3. Relative errors were +3.1%, +3.9%, +7.1% and +2.4%, respectively, and no significant differences at 95% confidence limit were found between the values of Cd after liquid membrane enrichment and the result obtained by DPASV.

4. Conclusions

Cd ions can be effectively separated and preconcentrated through a bulk liquid membrane containing 2-

Table 3
Application of methodology proposed for Cd determination in certified reference material TMDA-62 and seawater samples of Huelva coast (Spain) ($n=3$)

Sample	Cd concentration (μg l^{-1})	Present method (μg l^{-1})	Relative error (%)
TMDA-62	89.9±8.7[a]	83.1±1.2[c]	−7.6
Seawater 1	0.96±0.23[b]	0.99±0.16[c]	+3.1
Seawater 2	2.54±0.35[b]	2.64±0.40[c]	+3.9
Seawater 3	2.67±0.37[b]	2.86±0.46[c]	+7.1
Seawater 4	4.55±0.13[b]	4.66±0.21[c]	+2.4

[a] Certified value.
[b] DPASV value.
[c] Standard deviation.

acetylpyridine benzoylhydrazone in toluene, allowing the precise and accurate analysis of this metal at the mg l^{-1} level using a simple analytical technique (FAAS). The method offers important advantages such as simplicity and economy and enables eliminating matrix interferences, with a Cd preconcentration factor of 17.9. Also, it was successfully applied to the analysis of Cd in real samples of seawater. Therefore, liquid membrane is a potentially attractive technique for trace element separation and preconcentration from complex matrices.

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