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Model experiments to test the use of a liquid membrane for separation and preconcentration of copper from natural water

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Abstract

The transfer and separation of Cu(II) ions across a bulk liquid membrane (BLM) containing pyridine-2-acetaldehyde benzoylhydrazone (2-APBH) as the mobile carrier dissolved in toluene has been investigated and optimised. The system was applied to the preconcentration of copper from natural waters prior to analysis by flame atomic absorption spectroscopy. The flux of copper across the membrane has been studied, and characterised as a function of analytical variables such as the carrier concentration, volume of organic phase, pH of feed and strip receiving solutions, stirring rate and temperature of solutions. The preconcentration yield at optimum conditions was 100.54 ± 0.94%, even with a high saline matrix ($30\,\mathrm{g\,l^{-1}}$ NaCl), with good precision (1.49%). A preconcentration factor of approximately 18 times could be obtained. The detection limit of a blank sample was $0.24\,\mu\mathrm{g\,l^{-1}}$ of Cu.

The method was validated using a certified reference material (TMDA-62) and was applied successfully to the analysis of copper in two samples of seawater collected from the coast of Huelva (Spain). The relative errors were 2.42% for CRM and 0.48 and 3.66%, for seawaters (obtained between the results of the proposed and DPASV methods), respectively.

Keywords: Metal preconcentration; Copper; Natural water; Seawater; Liquid membrane; Pyridine-2-acetaldehyde benzoylhydrazone (2-APBH)

1. Introduction

The vital importance of trace metal analysis in environmental samples is widely recognised. The determinations of heavy metals are usually carried out by flame or graphite furnace atomic absorption spectrophotometry methods. However, due to the low levels of metals in the aquatic samples and the high complexity of the matrixes (i.e. seawater), their separation and also the use of a preconcentration step prior to metal analysis are usually necessary. Separation and preconcentration techniques available include liquid–liquid extraction or solid phase extraction (SPE) using immobilised ligands or chelating resins. The latter has some advantages over liquid–liquid extraction such as higher preconcentration factor, better efficiency and greater reproducibility [1], but one of the drawbacks of SPE is the risk of breakthrough in the presence of interferents at high concentration in the sample [2,3]. Alternative methods that are simple, versatile and adaptable for in situ measurements are therefore required. A one step analytical separation and preconcentration technique that has been used is transport across a liquid membrane, based on liquid–liquid extraction [4,5].

The use of liquid membranes is a novel alternative for the separation and concentration of metal ions. This technology combines solvent extraction and a stripping process in a single step and is especially attractive for the treatment of low metal concentration solutions [6]. In general, a membrane may be regarded as a semipermeable barrier. When placed between two aqueous phases, chemical species can move through the membrane from a region of high solute concentration into the region of low solute concentration by means of a purely diffusional process. Furthermore, the transport process may take place in the presence of an extractant or carrier contained within the membrane (facilitated transport). The separating power of liquid membranes is related to the efficiency of the carrier molecules present in the membrane [7]. The application of liquid membranes appeared to be promising, and researchers are still developing new three-phase (one organic and two aqueous phases). Among the several liquid membrane

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configurations, bulk liquid membrane (BLM) is a simple technique useful in previous studies of behaviour of the carrier in the liquid membrane, but supported liquid membrane (SLM) technology is really an attractive alternative to those two "traditional" sample pre-treatment methods (SPE and liquid–liquid extraction) for metal ions due to its potential of selective enrichment of such ions from complex matrixes [2,8].

Membrane technology is slowly but continuously becoming a very important and promising alternative to the current processing practices normally employed for wastewater treatment, environmental decontamination and metals recovery from residual solutions generated by ores leached or from mine waters [9]. The majority of the studies reported in the literature on liquid membrane technology discuss its use in industrial separation and recovery of target elements. Some examples of the use of SLM can be found in the most recently published works. In this way, simultaneous separation of Fe(III), Cu(II) and Ni(II) from dilute feed [10] have been achieved; it has been possible to separate and concentrate transuranium and lanthanide elements from low-level radioactive waste streams generated in the nuclear industry [11]. The technique has also been applied to the removal of Cr from tannery wastes [12] and a liquid emulsion membrane (ELM) technique for copper recovery from waste mine solutions has been developed [13]. So far, there are few reports on the use of liquid membrane for trace metal analysis in natural waters and biological media [4,14]. There are only a few studies referring to their application to metal speciation measurements in natural waters [15,16], although the advantages of these systems are well accepted [10].

Related to metal analysis in natural waters an interesting advantage of liquid membrane is the possibility of avoiding matrix interference. In freshwater systems humic substances are often present in concentrations of several parts per million, whereas in seawater the high 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 [17].

The aim of this work is to investigate the use of a new bulk liquid membrane containing 2-APBH (pyridine-2-acetaldehyde benzoylhydrazone) as carrier for the separation and preconcentration of copper from aqueous solution. This ligand has been selected because of its complexing properties with Cu (studied in previous papers [18,19]) and the known characteristic of aroylhydrazones of forming uncharged chelates with divalent transition metal ions which can be extracted into organic solvents [19]. The influence of different variables such as extractant concentration in organic solvent, volume of organic phase, stirring rate and temperature of solutions, pH of feed solution and strip receiving solution were analysed. The metal content in the final aqueous phase was analysed by flame atomic absorption spectrophotometry, a very common and simple analytical technique. This procedure permitted the analysis of copper from natural water, such as certified reference water (TMDA-62) and the results obtained showed good concordance with the certified values. Also, it was successfully applied to the analysis of seawater samples (highly saline complex matrix) from the coast of Huelva (Spain), affected by water discharges from the mining activities of the Iberian Pyrite Belt and the important industrial complex developed in the riverine areas of Huelva.

2. Experimental

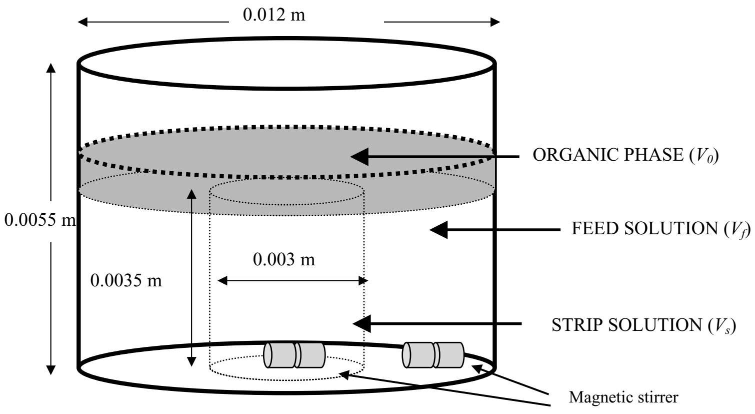
2.1. Reagents and solutions

All reagents were of analytical reagent 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 Cu(II) (10–100 mg l^{-1}) were prepared from copper 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 [18] and solutions (0.02–0.1%) of 2-APBH in toluene were prepared and used as carrier. These solutions were stable for at least 72 h. The potassium hydrogenphosphate/sodium hydroxide (Merck, Darmstadt, Germany) buffer solutions (0.13 mol l^{-1}; pH 6–9) were prepared conventionally [20]. Prior to use liquid–liquid extractions of buffer solutions were performed with 2-APBH in toluene, as a cleaning step, in order to remove the Cu content from buffer reagents.

2.2. 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 (1.2 cm × 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 the recommended conditions for copper. 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 the voltammetric measurements.

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).



Preconcentration factor:17.875

Fig. 1. The cell of bulk liquid membrane (BLM).

2.3. Procedure

The preconcentration experiments were performed with the cell described previously. Two concentric beakers contained the feed solution (V_f, external beaker) and the strip solution (V_s, internal beaker). The pH of feed solutions, containing the sample, was adjusted with KH_2PO_4/NaOH solution. The strip solution was an aqueous solution of nitric acid (0.075–0.3 mol l^{-1}). The volumes of V_f and V_s solutions were 286 and 16 ml, respectively. The organic solution (V_o), containing 2-APBH as the carrier dissolved in toluene, was placed over both aqueous solutions. The system was stirred magnetically and temperature controlled.

The acid solution was measured by flame atomic absorption spectrophotometry during experiments, by taking 2 ml aliquots. The same volume of HNO_3 solution was added to keep the volume of the receiving solution constant. 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 copper concentration versus time by using the following linear relationship:

$$-\ln[M]_f = \frac{Q}{V_f}\cdot P\cdot t - \ln[M]_{f,0}$$

where Q is the effective membrane area, V_f is the volume of feed solution, and $[M]_{f,0}$ and $[M]_f$ are the feed metal concentrations at time zero and time t, respectively [21].

3. Results and discussion

The transfer and separation of Cu(II) ions across the bulk liquid membrane is based on the reaction of 2-APBH as a polydentate ligand, forming an uncharged chelate in toluene [19]. The neutral complex is destroyed by the acid phase after transportation through the membrane. The driving force for the transport of copper ions is the pH gradient between the sample and the acid receiving solution [12].

3.1. Influence of physical and chemical parameters

The efficiency of the liquid membrane separation was first determined in the broad ranges of the chemical and physical variables, such as the volume of organic phase, the stirring rate of solutions, the effect of 2-APBH concentration in liquid membrane and the pH of the feed and strip receiving solutions, the pH of the aqueous solutions being the most important parameters.

The optimum volume of organic phase is that, which being minimal, permits total contact with the two aqueous phases and maximises the transport rate. The influence of the volume of toluene was studied using volumes between 60 and 150 ml. A volume of 60 ml produced a suitable permeability, which decreased very slightly with the increase of toluene volume (Table 1).

Table 1
Variation of permeability coefficient in some previous studies

Organic volume V_o (ml)	2-APBH (mmol)	Stirring rate (rpm)	Temperature (°C)	Permeability ($\times 10^3$ cm min^{-1})
60	0.157	500	30	9.44
75	0.157	500	30	6.68
150	0.157	500	30	5.30
60	0.157	300	30	6.79
60	0.175	700	30	14.49
60	0	700	30	0
60	0.075	700	30	14.46
60	0.293	700	30	14.47
60	0.157	700	25	11.32
60	0.157	700	35	6.44

Source solution: 400 μg l^{-1} of Cu, pH 6 (0.013 mol l^{-1} KH_2PO_4/NaOH); strip solution: 0.15 mol l^{-1} HNO_3, 3 h transport time.

The transport of coppers ions was facilitated with a high stirring rate of the aqueous solutions. So, higher permeability of the LM was obtained with 700 rpm (Table 1). At higher rates, mixing of different phases took place.

The permeability of the LM was constant at a 2-APBH content ranging from 0.075 to 0.293 mmol in toluene. The absence of organic reagent did not produce transport of the metal ion (Table 1).

During these previous experiments, a dependence of permeability on temperature was observed. A range of temperature from 25 to 35 °C was studied and the permeability was found to have increased at 30 °C (Table 1). According to the kinetic theory, molecules move faster with an increase in temperature and so, the diffusion of Cu ions through liquid membrane increases. However, the permeability decreased at 35 °C, probably due to the hydrolysis of 2-APBH [18]. Therefore, the subsequent experiments were performed with the temperature maintained at 30 °C.

For the final optimisation, a chemometrics 3^2 experimental design [22] was applied. The experimental parameters chosen were in the region of the maximum extraction efficiency from the pilot study. The pH of the aqueous feed and receiving phases were varied simultaneously (pH of feed solution: 6, 7 and 8; HNO_3 concentration of receiving solution: 0.075, 0.150 and 0.225 mol l^{-1}). The optimum conditions of pH 8 in the feed solution with 0.15 mol l^{-1} of HNO_3 in the receiving solution gave the highest permeability of 18.35×10^{-3} cm min^{-1}. This optimum pH value is very appropriate for applying the method directly to natural waters such as seawater.

3.2. Influence of feed phase salinity

Before the application of this liquid membrane technique to natural and seawater samples various experiments were performed to determine the influence of feed phase salinity on the preconcentration of copper ion. Fig. 2 shows the results of varying the extraction time of the system. A 100% preconcentration efficiency was possible to achieve even with high saline samples; in which case, the extraction time had to be increased from 6 to 8 h depending on the Cu concentration of the feed phase (Fig. 3).

3.3. The proposed new preconcentration method

Analysis was performed using 270 ml of sample adjusted at pH 8 with 30 ml of 0.13 mol l^{-1} KH_2PO_4/NaOH; 286 ml of this solution was placed as feed phase (V_f) into the cell (Fig. 1); 16 ml of 0.15 mol l^{-1} HNO_3 was placed as strip solution (V_s); and 60 ml of 2.6×10^{-3} mol l^{-1} 2-APBH in toluene was placed over both aqueous solutions. The system was stirred magnetically (700 rpm) during 6–8 h, with the temperature maintained at 30 °C. The strip phase was measured by flame atomic absorption.

The blank determination was performed following the proposed enrichment method using Milli-Q deionised water

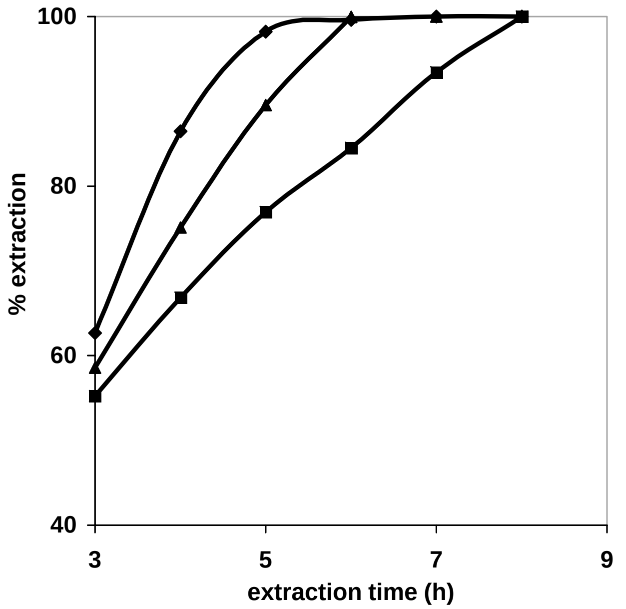


Fig. 2. Influence of feed phase salinity on the preconcentration efficiency, varying extraction time. Feed solution (V_f): 400 μg l^{-1} of Cu, pH 8 (0.013 mol l^{-1} KH_2PO_4/NaOH); 0 g l^{-1} NaCl (◆); 10 g l^{-1} NaCl (▲); 30 g l^{-1} NaCl (■). Strip solution (V_s): 0.15 mol l^{-1} HNO_3. Organic solution (V_o): 0.157 mmol of 2-APBH/60 ml toluene. Stirring rate: 700 rpm. Temperature: 30 °C.

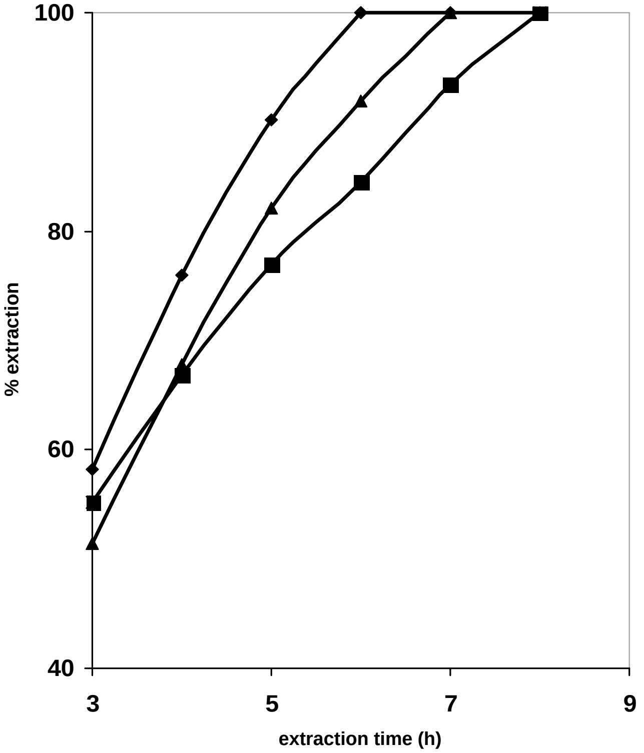


Fig. 3. Preconcentration efficiency (%) vs. extraction time for saline samples. Feed solution (V_f): pH 8 (0.013 mol l^{-1} KH_2PO_4/NaOH); 50 μg l^{-1} of Cu (◆); 200 μg l^{-1} of Cu (▲); 400 μg l^{-1} of Cu (■); 30 g l^{-1} NaCl. Strip solution (V_s): 0.15 mol l^{-1} HNO_3. Organic solution (V_o): 0.157 mmol of 2-APBH/60 ml toluene. Stirring rate: 700 rpm. Temperature: 30 °C.

Table 2
Validation of proposed methodology using spiked samples

Sample	Concentration spiked (Cu, $\mu g\,l^{-1}$)	Concentration measured (Cu, $\mu g\,l^{-1}$)	Relative error (%)
Saline matrix[a]	5.2	5.4 ± 0.1 (8 h)[c]	6.5
Saline matrix[a]	23.7	23 ± 0.2 (8 h)[c]	2.1
Saline matrix[a]	45.5	47 ± 0.4 (7 h)[c]	3.7
Saline matrix[a]	201	202 ± 2.9 (7 h)[c]	0.4
Saline and metal matrix[b]	162	164 ± 1.9 (7 h)[c]	1.5
Synthetic seawater [23]	202	204 ± 2.7 (8 h)[c]	0.8

[a] 30 g l^{-1} of NaCl.

[b] Al (2 $\mu g\,l^{-1}$), Co (0.020 $\mu g\,l^{-1}$), Fe (2 $\mu g\,l^{-1}$), Mo (10 $\mu g\,l^{-1}$), Ni (0.3 $\mu g\,l^{-1}$), Zn (0.6 $\mu g\,l^{-1}$), 30 g l^{-1} NaCl [23].

[c] Preconcentration time.

adjusted to pH 8 with cleaned phosphate buffer. The blank value was $0.29 \pm 0.08\,\mu g\,l^{-1}$ of Cu for four replicates, the limit of detection (calculated as three times the standard deviation) being $0.24\,\mu g\,l^{-1}$ of Cu.

The precision of the proposed method was 1.49%, evaluated for significance level at 95% and $n = 4$ with $200\,\mu g\,l^{-1}$ of Cu.

3.4. Separation and analysis of copper from synthetic and real samples

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

Six samples with different background compositions were spiked with several known amounts of Cu (two replicates for each sample): 30 g l^{-1} of NaCl, 30 g l^{-1} of NaCl and common heavy metals concentrations in seawater and synthetic seawater [23]. The results are shown in Table 2. The copper concentration was successfully quantified using the new proposed method.

In the same way, certified reference water (TMDA-62) for trace elements was analysed. Two samples of the CRM were preconcentrated and analysed (with two replicates) using the optimal conditions, without and with UV digestion. The results are shown in Table 3 and the relative error was 2.42 and 3.74%, respectively, being not necessary UV digestion.

Table 3
Application of methodology proposed to certified reference material TMDA-62 and seawater samples of Huelva coast (Spain)

Sample	Metal concentration (Cu, $\mu g\,l^{-1}$)	Liquid membrane + AAS (Cu, $\mu g\,l^{-1}$)
TMDA-62[a]	106.0 ± 10.7[c]	103.4 ± 1.4
TMDA-62[b]	106.0 ± 10.7[c]	102.0 ± 1.1
Seawater 1	25.2 ± 1.6[d]	25.1 ± 1.1
Seawater 2	34.4 ± 0.9[d]	33.1 ± 1.0

[a] Without UV digestion.

[b] With UV digestion.

[c] Certified value.

[d] DPASV value ($n = 3$).

In order to apply the new method to real samples, the analysis of two 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 copper in the samples was analysed, after UV digestion (with H_2O_2) and neutralisation, 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) [24]. The results obtained are shown in Table 3. The relative error was 0.48 and 3.66%, respectively. Applying the paired *t*-test no significant differences at 95% confidence limit were found between the values for copper after LM enrichment and the results obtained by DPASV.

4. Conclusions

A transport system for copper through a bulk liquid membrane containing pyridine-2-acetaldehyde benzoylhydrazone has been studied for separation and preconcentration of this metal from natural water. A 100% preconcentration efficiency was obtained, with a preconcentration factor of 17.87; by modification of the glass homemade cell (increasing the ratio $V_f{:}V_s$) or using an SLM configuration this factor can be easily improved further. The method offers important advantages such as simplicity, reproducibility and economy, and it enables eliminating matrix interferences. The method has been validated with certified reference samples of freshwater and applied to seawater with satisfactory results.

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