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A new analytical method for selective pre-concentration of free silver in estuarine waters using liquid membranes

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ABSTRACT

Silver is recognized as an important pollutant of natural waters. This element is a selective tracer of anthropogenic pollution related to sewage. Studying its bio-availability requires the application of specific separation of the free ion. A liquid membrane is proposed for separating Ag^+ from estuarine water samples.

A bulk liquid membrane (BLM) has been selected. Free silver is transported from the sample to a receiving solution through an organic membrane containing tri-isobutylphosphine sulfide (TIBPS). Effects of formation of chlorinated and organic complexes on silver pertraction have been evaluated. The extent of formation of the aforementioned complexes has been based on the decrease of silver transport to the receiving phase, measured as enrichment factor (EF), because only Ag^+ is assumed to be transported. Finally, after quantifying the effects of the employed ligands on EF, total concentration of silver can be estimated from the experimental data of Ag^+ analyzed by the proposed BLM system.

1. Introduction

Heavy metals pollution presents environmental, health and economical implications which have made them a main subject for water protection [1]. In particular, silver is considered as a risk pollutant of natural waters in EU legislation [2]. Moreover, the presence of the both organic and inorganic ligands in waters results in the formation of different species of silver, affecting its toxicity [3–5]. As recently reviewed, the study of silver concentration in natural waters is scarce [6]. Thus, the development and optimization of procedures for estimating the bio-available fraction of silver are required.

Silver total concentration has been used as a tracer for urban activities because its employment in photography and film industry [7]. Although these uses have decreased with the use of digital technologies, new applications such as biocide for medical, textile, and self-care products have appeared [8,9]. Thus, determining the different forms in which Ag can appear is of main importance due to their different toxicity. On the one hand, Ag^+ is not toxic for humans, but it is dangerous to aquatic life in the level of $2\ \mu g\ l^{-1}$ [3]. On the other hand, silver forms chloro-complexes $AgCl_n^{(n-1)-}$ with increasing Cl^- concentration [10], which present different toxicity [4] and Ag accumulation is dependent in the presence of organic matter [11]. Therefore, evaluating its bio-availability in the different parts of an estuary, where salinity increases linearly in the direction of the river mouth, is of main importance.

Due to the low silver levels in estuarine water samples and matrix effects, pretreatment procedures as traditionally liquid–liquid extraction (LLE) have been used for its determination [6,12]. However, some drawbacks as a high wastes generation and samples handling, must be taken into account. Therefore, liquid membranes (LM) appear as a free-of-handling technique [13,14] which needs fewer amounts of organic solvents and reagents than LLE [15]. Previous studies have proved the suitability of LMs for silver transport using different ligands [16–19]. In particular, tri-isobutylphosphine sulfide (TIBPS) has been used for the determination of total silver concentration in freshwaters by a bulk liquid membrane (BLM) system [20].

In general, heavy metals bio-availability is related with the uptake of different fractions by organism [21]. Those fractions are considered labile because they can be transported through biological membranes [22]. It is assumed that the bio-available fraction of a metal corresponds to its free form and those species that are soluble in lipidic membranes [23]. When liquid membranes are used, the labile fraction is the one to be transported through the organic solution, while the inert one is retained in the sample [24].

The selective transport of the free form of metals through liquid membranes in the presence of organic matter or inorganic ligands has been previously conducted [25]. Bayen et al. (2009) [22] studied the influence of Cl^- and CO_3^{2-} on Cd, Cu and Pb transport through liquid membranes. Moreover, hollow fibers

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have been employed in heavy metals speciation [26,27]; for instance, LMs were applied for Cu speciation in natural waters, studying the influence of humic acids on Cu^{2+} transport and estimating, this way, the Cu labile fraction [28].

The analysis of silver fractions has been conducted by LLE [29], solid phase extraction [30], and ion exchange chromatography combined with UV digestion [31]. However, liquid membranes have never been applied for its speciation. In this work, a BLM system is proposed for the selective transport of free silver in estuarine waters, where Cl^- and dissolved organic matter (DOM) appear as main ligands for Ag complexation [10,29].

2. Experimental

2.1. Reagents and solutions

Unless otherwise noted, all reagents were analytical-reagent grade. Nitric acid (65%, for trace analysis), Hydrogen peroxide (30%), toluene (99.5%, extra pure), and sodium chloride (100%) were obtained from Scharlab (Barcelona, Spain). Potassium nitrate (99.0%) and sodium sulfite (98%), were obtained from Merck (Darmstadt, Germany). Tri-isobutylphosphine sulfide (Cyanex 471X®) was kindly provided by Cytec Industries Inc. (NJ, USA). Humic acids from Acros (Belgium). Aqueous solutions of silver were prepared from a AAS 1000 mg l^{-1} standard solution obtained from Merck (Darmstadt, Germany).

2.2. Apparatus

Liquid membrane experiments were conducted using a home-made glass beaker-in-a-beaker type cell which consisted in two concentric beakers, description of the cell can be found elsewhere [32], containing the sample (external beaker, 75 mm inner diameter, 160 ml volume) and the receiving solution (internal beaker, 25 mm inner diameter, 24 ml volume). The organic solution containing the carrier constitutes a thin layer making the contact between the sample and the acceptor phase [20]. Aqueous solutions were stirred with an Ikamag-RH magnetic stirrer (Janke & Kunkel, Germany). Concentrations of silver in aqueous solutions were measured by a SolaarM Atomic Absorption Spectrometer (Thermo Scientific, USA). Organic matter concentration was measured by a total organic carbon analyzer Analytik Jena multi N/C 3100 (Analytik Jena, Germany). UV digestion was used for organic matter degradation using a Metrohm 705 Mod. (Metrohm, Switzerland).

2.3. Procedure

Feed solutions containing 1.83 μmol l^{-1} of silver and the corresponding concentration of organic matter and Cl^-, were used as a sample, in order to evaluate the effect of the ligands on silver transport. Experiments were conducted under previously optimized conditions for total silver concentration analysis [20]: 0.1 mol l^{-1} KNO_3 in the donor phase, 4.8 mmol l^{-1} TIBPS dissolved in toluene in the membrane, 10 mmol l^{-1} Na_2SO_3 in the acceptor phase, and 900 rpm stirring speed.

Studying the influence of ligands, dissolved organic matter (DOM) was added as humic acids salt and measured as dissolved organic carbon (DOC), while NaCl was used as a source of Cl^- ions. When required, DOM was digested during 90 minutes by UV and H_2O_2 (0.3%).

In this study, the enrichment factor (*EF*) was employed as a tool for quantifying the efficiency of the system in silver transport, because it reflects silver pre-concentration from the donor to the receiving phase and its value is stable when the equilibrium is reached. It is defined as the ratio between the concentration of analyte, at a particular time *t*, in the receiving solution ($[Ag^+]_t$) and the initial concentration in the donor phase ($[Ag^+]_0$) (Eq. (1)). For this reason, these experiments were conducted during 240 min [20].

$$EF = \frac{[Ag^+]_{t\ \mathrm{Receiving\ phase}}}{[Ag^+]_{0\ \mathrm{Donor\ phase}}} \tag{1}$$

Finally, the influence of DOM and Cl^- concentration on pre-concentration efficiency was employed to estimate the different free and inert silver fractions.

Characterizing Ag^+ transport, 1.6 ml aliquots of stripping solution were taken every 30 min to measure silver concentration, while the same amount of clean solution was added to keep the volume constant. After FAAS measurements, silver concentrations were corrected taking into account the metal amount into the aliquots of receiving phase solution previously removed.

3. Results and discussion

3.1. Effect of Cl^- and humic acids on silver transport

In a previous work, the BLM system here applied was optimized for, silver pre-concentration, before determination its total concentration in natural waters, with an average enrichment factor of 3.96 times in acidified samples and an average concentration for 10 replicates of blank samples of 33 ng l^{-1} [20]. In the present work, the system has been used as a tool selective pre-concentration of Ag^+ from the sample in the presence of chloride and humic acids in estuarine waters at natural pH. Humic acids were selected to evaluate the extent of the influence of organic matter in silver complexation due to its influence in heavy metals uptake [29]. Chloride was used because silver is mainly found in the form of chloro-complexes in saline waters; as an example, it is essentially as $AgCl_2^-$ (46.9%) and $AgCl_3^{2-}$ (47.7%) in seawater [10]. Attending to the formation of complexes with humic acids and Cl^-, the mechanism of silver transport with TIBPS [33], could be expressed as follows (Fig. 1). As it can be seen, TIBPS selectively transports Ag^+, while silver bonded to humic acids and Cl^- remains in the donor phase.

Estimating the influence of salinity, different concentrations of Cl^- were added in the range 0.069–0.603 mol l^{-1}. As a consequence, a decrease of the enrichment factor for silver was appreciated with the increasing concentration of Cl^-. Moreover, a linear relationship was established between the variation of *EF* for silver and the logarithm of the added concentration of chloride ($R^2=0.988$), by the formation of the corresponding chloro-complexes (Fig. 2).

In the case of organic matter, humic acids salt was added as a source of organic carbon, in concentrations from 0.083 to 8.3 mmol l^{-1} of DOC. As for the presence of Cl^-, *EF* decreases with the addition of humic acids, and a linear resaltionship

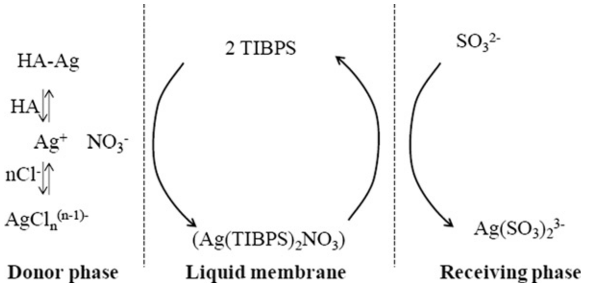

Fig. 1. Mechanism of silver transport by TIBPS in the presence of humic acids and Cl^- [33].

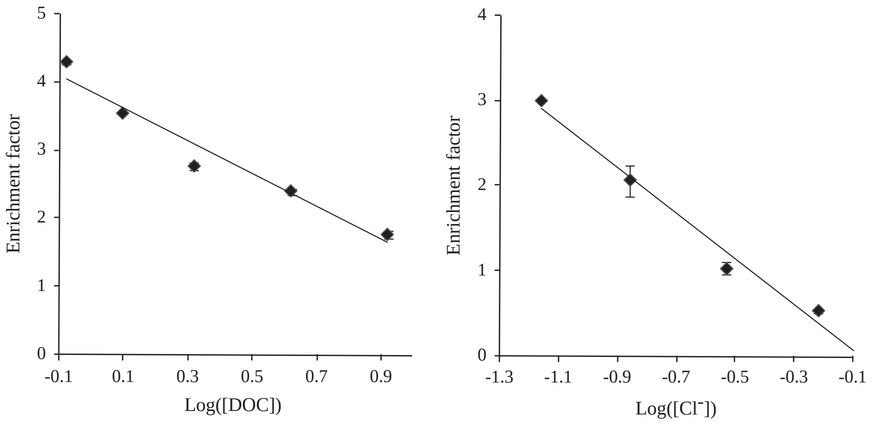

Fig. 2. Evolution of the enrichment factor for silver with the addition of humic acids (mmol l^{-1}) and Cl^- (mol l^{-1}). Experiments were conducted during 240 min.

between *EF* and the logarithm of added dissolved organic carbon is appreciated (R^2=0.995) (Fig. 2). In order to confirm that the observed decrease of *EF* is a response to the presence of humic acids, samples containing them were analyzed by the LM before and after digestion by UV, resulting in a recovery of *EF* for silver if compared with the results obtained for humic acids- free samples (EF_{ref}).

From the results, it could be extracted that adding Cl^- and HA in silver containing solutions leads to the formation of $AgCl_n^{(n-1)-}$ and Ag-HA respectively. Besides, these complexes are not transported through the membrane because tri-isobutylphosphine sulfide is not capable to dissociate them, and they could be considered as inert against the action of the carrier. As a consequence, only Ag^+ is transported so it could be assumed as the labile fraction.

3.2. Estimation of labile and inert silver fractions

In real samples, HA and Cl^- appear together. Thus, the combined effect of both ligands on silver transport was studied. To complete this study, the evolution of *EF* for a fixed concentration of Cl^- and different additions of humic acids was measured. In particular, Cl^- concentrations used were 0, 0.069, 0.138, and 0.293 mol l^{-1}. In each case dissolved organic carbon concentration was added from 0 to 5 mmol l^{-1} to the donor phase.

As a result, a decrease of transport efficiency was appreciated in all cases. A linear relationship was observed for the enrichment factor evolution with the logarithm of the addition of HA for each Cl^- concentration (Fig. 3). Fit curves for this relationship were obtained, and their equations were applied for predicting the enrichment factor for silver in samples of known concentrations of Cl^- and DOC. Eq. (2) shows the relationship of enrichment factor evolution for a particular concentration of Cl^- (EF_{Cl-}) with the logarithm of additions of dissolved organic carbon in the donor phase [34], where *a* is the slope of the curve and *b* the intercept. Values of *a* and *b* for every fit curve equations are shown in Table 1.

$$EF_{Cl^-} = a\,Log([DOC]) + b \tag{2}$$

As previously stated, using the proposed liquid membrane, Ag^+ has been defined as the labile fraction of silver, while the inert fraction is constituted by Ag-HA and $AgCl_n^{(n-1)-}$. From this point, total silver concentration could be expressed by the following mass balance (Eqs. (3) and (4)):

$$Ag_0 = Ag^+ + AgAH + AgCl_n{}^{(n-1)-} \tag{3}$$

$$Ag_0 = Ag^+ + Ag_i \tag{4}$$

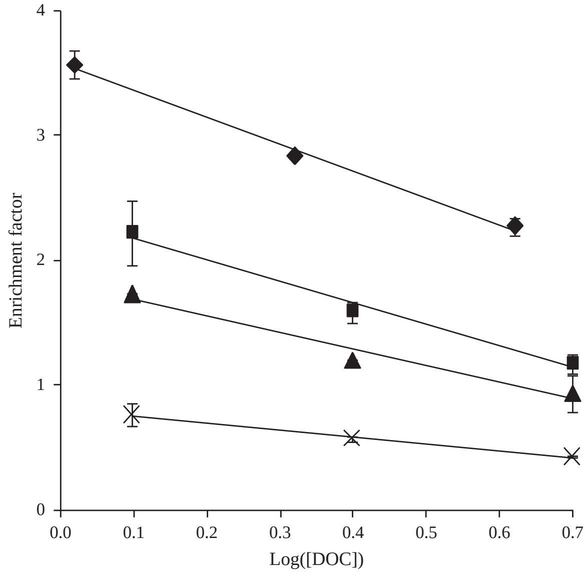

Fig. 3. Time evolution of silver transport for samples containing different concentrations of Cl^- when different amounts of humic acids are added (mmol l^{-1}). Chloride concentration: ◆ 0 mol l^{-1} ■ 0.075 mol l^{-1}, ▲ 0.150 mol l^{-1}, and x 0.300 mol l^{-1}. Experiments were conducted during 240 min.

Table 1
Equations of the fit curves obtained for EF evolution against the logarithm of dissolved organic carbon concentration for each fixed concentration of Cl^-.$EF_{Cl^-} = aLog([DOC]) + b$, where *a* is the slope, *b* is the intercept and R^2 is the coefficient of regression of the fit curve.

Cl^- (mol l^{-1})	*a*	*b*	R^2
0	−2.160	3.583	0.993
0.069	−1.734	2.353	0.986
0.138	−1.318	1.816	0.966
0.293	−0.557	0.870	0.992

where Ag_0 is the total concentration of silver and Ag_i is its inert fraction.

Applying the LM, Ag^+ in the acceptor phase ($Ag^+_{acceptor}$) can be determined. As previously mentioned, enrichment factor for Ag^+ (EF_{ref}) is 3.96 times. Thus, Ag^+ in the sample can be calculated by Eq. (5), assuming that only Ag^+ is transported through the membrane. In the case of Ag_0 calculation, enrichment factor includes formation of Ag-HA and $AgCl_n^{(n-1)-}$ complexes (EF_{Cl-}), and can be calculated by Eq. (2). Therefore, Ag_0 can be estimated

Table 2
Estimation of the Ag fractions by the proposed BLM.

DOC (mmol l^{-1})	Cl^- (mol l^{-1})	Ag_{FAAS} ($\mu\text{mol l}^{-1}$)[a]	EF[b]	$Ag_{0\ \text{BLM}}$ ($\mu\text{mol l}^{-1}$)	Ag^+ ($\mu\text{mol l}^{-1}$)	Recovery (%)[c]
1.66	0	1.80	3.58	1.59	1.23	88
2.50	0.15	2.01	1.59	2.22	0.72	110
5.00	0.29	2.06	0.57	1.93	0.21	93
5.00	0.07	1.83	1.18	1.73	0.50	94
1.25	0.15	2.00	1.73	1.93	0.82	97
1.25	0.29	0.93	0.77	0.97	0.19	104
5.00	0.15	0.92	0.94	0.83	0.19	91

[a] Corresponds to the total concentration of silver, measured by flame atomic absorption spectroscopy as a reference method.
[b] EF calculated for the corresponding concentration for DOC and Cl^-.
[c] Recovery is referred to the total concentration of silver.

by Eq. (6).

$$Ag^+ = \frac{Ag^+_{\text{acceptor}}}{EF_{\text{ref}}} \tag{5}$$

$$Ag_0 = \frac{Ag^+_{\text{acceptor}}}{EF_{Cl^-}} \tag{6}$$

Finally, the inert fraction of silver could be estimated by subtraction of Ag^+ from Ag_0 (Eq. (4)). The applicability of the system was evaluated using different estuarine samples of known concentration of dissolved organic carbon and Cl^- (Table 2). Concentrations of total silver analyzed by the proposed method were compared with those obtained using flame atomic absorption spectroscopy (FAAS) as a reference method. As can be appreciated, using a bulk liquid membrane, Ag_0 and Ag_i concentrations can be estimated using a single experiment from the determination of transported Ag^+ in estuarine water samples.

4. Conclusions

Separation of Ag^+ from samples containing $AgCl_n^{(n-1)-}$ and Ag-HA complexes can be conducted using a liquid membrane containing TIBPS as carrier. The effect of salinity and organic matter concentration in silver transport efficiency can be quantified and used to estimate the total concentration of silver. Therefore, applying this method, the transportable or labile fraction of silver can be distinguished from non-transportable complexes as an approach to its bio-availability.

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