Three-phase solvent bar micro-extraction as an approach to silver ultra-traces speciation in estuarine water samples

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ABSTRACT

Silver ion inputs into the environment due to human activities have been increased in the last years because it has been used as a bactericide with application in medical, homecare and self-care products. In addition, it is toxic at low concentration for aquatic organisms. In estuarine waters, salinity and dissolved organic matter (DOM) regulate Ag^+ concentration by the formation of complexes as $AgCl_n^{(n-1)-}$ and Ag-DOM.

Difficulties of Ag^+ analysis in estuaries are associated to its low concentration level and interferences of sample matrix. Liquid and solid phase extraction methods have been used for speciation of silver in waters; however, miniaturized methods that offer a better environmental profile are desirable. Hollow fiber liquid phase micro-extraction (HFLPME) allows obtaining higher pre-concentration factors with a reduction of waste generation. Notwithstanding, some operational improvements are needed to permit their use as a routine method that can be afforded using a configuration of three-phase solvent bar micro-extraction (3PSBME).

In this work, tri-isobutylphosphine sulphide (TIBPS) has been used as an extractant for Ag^+ pre-concentration in estuarine waters by 3PSBME. Under optimized conditions, Ag^+ has been pre-concentrated 60 times and the method presents a limit of detection of 1.53 ng L^{-1}. To evaluate which Ag species is transported by TIBPS, Cl^- and DOM have been added to synthetic samples. As a result, a decrease in Ag pre-concentration efficiency after additions has been observed and quantified. Results showed that Ag^+ is selectively transported by TIBPS from estuarine water samples after comparison of the results with those obtained by the reference method of liquid extraction with APDC/DDDC.

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1. Introduction

During the last years, silver inputs into natural water resources have been increased and diversified due to the use of silver and silver compounds in several applications and everyday-used products, such as home and self-care products, fabrics recovery, additives for paints, etc [1–4]. All of them are based on silver capability as a bactericide and fungicide [5]. In particular Ag^+ has been identified as the main reason for its toxicity for aquatic organisms [6]. Ag^+ analysis normally requires pre-concentration and/or separation of the metal from the sample due to its low concentrations and matrix effects on analytical methods [7,8]. In the case of natural waters and in particular for estuarine waters, Ag speciation is ruled by salinity and dissolved organic matter (DOM) being mainly in the form of $AgCl_2^-$ and $AgCl_3^{2-}$ [9,10].

Complexation of silver by Cl^- and DOM affects Ag^+ concentration in estuaries, modifying availability of the metal for aquatic

organisms [11,12]. For this reason, different alternatives have been proposed for selective analysis of Ag^+ in natural waters that are based on sample pre-treatment using liquid-liquid extraction and solid phase extraction [9,13]. Also bulk liquid membranes (BLM) have been applied for selective transport of Ag^+ in natural water with the objective of simplifying sample preparation [14]. In general, these techniques present drawbacks associated to solvents and reagents consumption and the need of highly sensitive instrumental techniques for quantification of the metal [9,15].

In order to overcome these drawbacks, sample preparation processes can be miniaturized using micro-extraction methods. Among others, hollow fiber liquid phase micro-extraction (HLFPME) has gained increasing attention in the last years for trace metals analysis, due to its pre-concentration capability and stability [16]. It can be used in a three-phase (3HFLPME) configuration in which simultaneous extraction and re-extraction can be carried out [17]. 3HFLPME consists in the transport of the metal ion from the sample to a small volume of aqueous acceptor solution located inside the fiber. Transport takes place through an organic solution of an extractant agent that is placed in the fiber pores [8,16]. This methodology has been applied for selective pre-concentration of

the free ion of Pb, Cd, and Ni in seawater analysis using kriptofix-22DD as extractant [18].

In spite of the advantages it presents, HFLPME has not been established as a routine technique because it normally needs a support for the fiber, special devices are required to set up fiber's modules, and leaks may appear in the connection with the support [17]. These limitations can be overcome using a three-phase solvent micro-extraction bar (3PSBME), in which the ends of the fiber are thermally sealed [19]. This way, the fiber can be left free into the sample without needing any support, making the 3HFLPME portable and easy to handle, without diminishing features related with high pre-concentration factors and chemical selectivity [16,20].

The aim of this work was the application of 3PSBME to selectively pre-concentrate Ag^+ for Ag speciation in estuarine water samples. In this work, tri-isobutylphosphine sulphide (TIBPS) has been selected as an extractant due to its capability, for selective transport of Ag^+ through liquid membranes from estuarine water samples, offering an approach to silver speciation [14].

2. Materials and methods

2.1. Reagents and solutions

All reagents were analytical-reagent grade unless otherwise stated. Potassium nitrate (99%) and sodium chloride (99,5%) were obtained from Scharlau (Barcelona, Spain). Kerosene and ammonia (30%) were obtained from Panreac (Barcelona, Spain). Sodium thiosulphite (100%), 1-pyrrolidine-dithiocarbamate (APDC) and diethylammonium-diethyldithiocarbamate (DDDC) were purchased from Merck (Darmstadt, Germany). Tri-isobutylphosphine sulphide (TIBPS) was provided by Cytec Industries Inc. (NJ, USA) and humic acids were obtained from Aldrich (Steinheim, Germany). Aqueous solutions of silver were prepared from a 1000 mg L^{-1} standard solution obtained from Merck (Darmstadt, Germany) and samples for optimization studies contained 0.1 mg L^{-1} of silver. Deionized water of resistivity lower than 18.2 MΩ cm was obtained by a Millipore Quantum Ultrapure water supplier (Millipore, USA). Acetylene, air, and argon for atomic spectrometry were obtained from Air Liquid (Madrid, Spain).

2.2. Apparatus

Polypropylene Accurel PP S6/2 hollow fibers of 0.2 μm pore size and 1800 μm internal diameter were used in this study (Membrana, Germany). Samples were stirred using an IKA-Big Squid magnetic stirrer (Ika-Werke, Germany). Silver concentration in the aqueous solutions was quantified using a continuum source atomic absorption spectrometer model ContrAA (Analytikjena, Germany), using a flame atomizer (FAAS) for optimization studies and graphite furnace atomizer for application to real samples (GFAAS). Graphite furnaces used were made in pyrolitic graphite (Analytikjena, Germany). Humic acids were measured as dissolved organic carbon (DOC) in a total carbon analyzer Analytik Jena multi N/C 3100 (Analytikjena, Germany).

2.3. Set-up of hollow fiber membranes: three-phases solvent bar micro-extraction (3PSBME)

In order to set up the three phase solvent bars, 5 cm of fiber was cut and one of its ends was thermally sealed using a hot tip and flat ended tweezers. The internal part of the fiber was filled with the acceptor solution containing $S_2O_3^{2-}$ and the other end of the fiber was thermally sealed. This solvent bar was immersed into the organic solution of kerosene containing TIBPS as extractant to impregnate the fiber pores. Finally the excess of organic solution on the fiber was rinsed with deionized water and the fiber was

placed into the sample. After extraction time, the acceptor solution inside the fiber was recovered and measured by atomic absorption spectroscopy. In all cases, three aliquots of each sample were extracted. Additionally, internal replicates were carried out adding three solvent bars to every aliquot of sample [21].

2.4. Optimization

Silver pre-concentration by 3PSBME using TIBPS as extractant agent takes place by coupled cotransport [15]. For this type of mechanism, a cationic complex is formed by Ag and TIBPS. For this reason, the use of a counter-ion (NO_3^-) is needed to form a neutral ion pair {$(AgTIBPS)^+NO_3^-$}, which can be solubilized in the organic solution, to be transported until the organic-acceptor solution interface. Thus, the ion pair reacts with the acceptor agent ($S_2O_3^{2-}$) and the metal is retained in the acceptor solution. Therefore, NO_3^- concentration in the sample, TIBPS concentration in the organic solution impregnating the fiber pores, $S_2O_3^{2-}$ in the acceptor, and stirring rate were optimized. Univariate optimization was conducted, varying one of the parameters each time while the rest were kept constant.

The extent of silver transport from samples into the acceptor solution was measured as enrichment factor (EF) of Ag in the acceptor. This factor is calculated by the ratio between the concentration of silver in the acceptor phase at a certain experiment time (t) ($[Ag^+]_t$) and the initial concentration of silver ion in the sample ($[Ag^+]_0$) (Eq. (1)).

$$EF = \frac{[Ag^+]_t}{[Ag^+]_0} \tag{1}$$

2.5. Instrumental determination of silver

Instrumental analysis of silver concentration in the acceptor solution was carried out by atomic absorption spectroscopy at a wavelength of 328.1 nm and setting up the spectrometer detector between pixels 98 and 102.

For optimization studies, 100 μg L^{-1} Ag was used as initial concentration in the sample. For this reason, analysis of initial Ag^+ concentration in the sample as well as in the acceptor solution was carried out by FAAS using acetylene as fuel and air as oxidizer. To ensure that enough amount of sample was available for measurement in FAAS, the recovered acceptor solution was diluted into 1.5 mL of deionized water. Besides, calibration standards were prepared with the same matrix as the acceptor solution samples by addition of the corresponding amount of $Na_2S_2O_3$.

In the case of silver at natural concentration levels graphite furnace atomic absorption spectroscopy was used for quantification, applying Ar as inert gas. In this case, the acceptor solution was
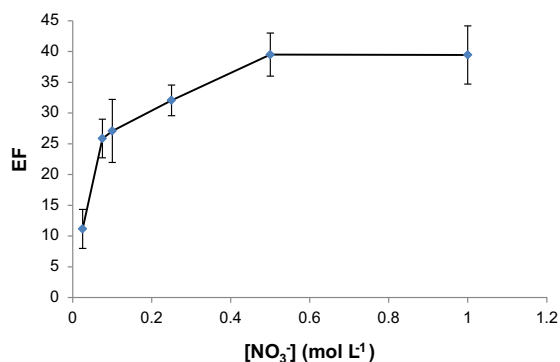

Fig. 1. Optimization of NO_3^- concentration in the sample at 0.1 M TIBPS in the organic phase, 1 M $Na_2S_2O_3$ in the acceptor and 800 rpm stirring speed.