# Selective ionic liquid solvent bar micro-extraction for estimation of ultra-trace silver fractions in marine waters
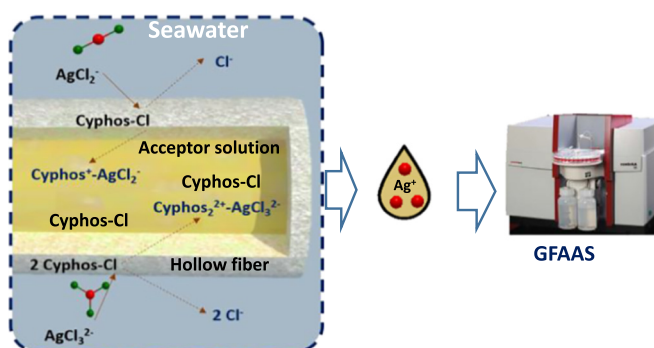
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## HIGHLIGHTS

- $AgCl_n^{(n-1)-}$ can be selectively pre-concentrated in seawater by Cyphos® 101 IL.
- Cyphos® 101 SBME was used to analyze Ag in seawater and to estimate its speciation.
- Ag complexation by dissolved organic matter is predicted by Cyphos® 101 SBME.
- Efficient SBME permitted the determination of environmental levels of Ag in seawater at the natural pH values.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## ABSTRACT

Ag can be found in the ocean at the ultra-trace level, mainly as $AgCl_n^{(n-1)-}$ and complexed by dissolved organic matter (Ag-DOM). However, methods for studying Ag speciation in marine waters are limited by the lack of extractants capable to separate organic and inorganic silver species in natural conditions of seawater samples.
In this work, a two-phase solvent bar micro-extraction method using the ionic liquid trihexyltetradecylphosphonium chloride (Cyphos® 101) was applied for selective micro-extraction of $AgCl_n^{(n-1)-}$ from organic silver in marine waters, working at seawater pH,. The application to real samples was performed under the following conditions: 2.5% Cyphos® 101 in kerosene solution with 10% dodecan-1-ol inside the fiber, and 30 min of sample extraction at a stirring rate of 800 rpm. The proposed SBME was successfully used for estimation of Ag fractions in waters from the Bay of Cádiz (South-west Spain) showing its applicability for a simple, fast and environmentally friendly speciation of silver in marine water samples. The method presented a linear response up to 500 ng L$^{-1}$ and a detection limit of 0.4 ng L$^{-1}$, using GF-AAS for instrumental determination.

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## 1. Introduction

Studying metals distribution in seawater is essential due to their potential negative effects on the marine environment and human health (Baby et al., 2010; Crompton, 1997). Silver can be found in the nature as part of ores such as argentite ($Ag_2S$) and horn silver (AgCl) (Doherty and Williams, 1994). However, in the last decade silver use has been increased in a wide variety of applications as medicine, pharmacy, personal care products, cloud seeding, textile, photography, electronics, and disinfection of drinking waters, which have resulted in an increase of anthropogenic Ag inputs to marine ecosystems (Ballarin et al., 2015; Ćurić and Janc, 2013; Peng et al., 2012; Purcell and Peters, 1998). Most of these applications are based on the silver

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bacteriostatic and fungicide properties (Hadrup and Lam, 2014). In this sense, silver toxicity to bacteria, phytoplankton and invertebrates even at trace levels is only exceeded by mercury (Bryan, 1984; Ratte, 1999). Silver accumulation by organisms is controlled by its speciation, with $Ag^+$ considered as the most toxic silver species in aquatic environments (Katarina et al., 2006; Luoma et al., 1995; Tappin et al., 2010). In particular, in estuarine and marine waters, salinity and dissolved organic matter are the main factors affecting Ag speciation. In these cases, most of silver is found as $AgCl_2^-$ and $AgCl_3^{2-}$ (Savenko and Tagirov, 1996; Tappin et al., 2010). While complexation by chloride ion has been previously studied, interaction of Ag with dissolved organic matter in marine systems has been scarcely treated (Ndung'u et al., 2006).

The analysis of Ag at ultra-trace level in seawater requires a previous step for sample preparation, due to its low concentration and to the influence of a highly saline matrix (Bruland et al., 1979; Djerahov et al., 2016; He et al., 2017; López-López et al., 2010; Malcus et al., 1996). Up-to–date the most extended methodologies for sample treatment in metals monitoring in the ocean –including silver- are based on liquid and solid phase extraction. However, they present several drawbacks associated to excessive amounts of solvents and reagents, samples handling as well as the need of highly sensitive instrumental techniques such as ICP-MS (Flegal et al., 1995; Ndung'u et al., 2006; Yang et al., 2017). In addition, estimation of inorganic and organic silver fractions, is limited and requires the use of multi-step methods such as UV-digestion of organometallic Ag complexes (Ndung'u et al., 2006).

Hence, during the last years efforts have been focused to develop new methodologies based on liquid phase micro-extraction (LPME), in order to achieve a more efficient and selective pre-concentration of metallic species with a better environmental profile (Dadfarnia and Haji Shabani, 2010; Pedersen-Bjergaard and Rasmussen, 1999). Amongst LPME methods, hollow fiber liquid phase micro-extraction (HFLPME) has gained popularity due to the use of a support for the extractant system, improving its stability, increasing the simplicity of the process and enhancing the reproducibility of the results (Han and Row, 2012).

HFLPME has been applied mainly in a three phases configuration (as a supported liquid membrane) for pre-concentration of different metal species. Thus, Ni ions were pre-concentrated by di-2-ethylhexylphosphoric acid (DEHPA), 1,10 didecyl diazo 18 crown 4-ether (Kriptofix-22DD) was used for separation and determination of Cd,Cu, Ni, Pd and Zn, and silver determination was carried out by using tri-isobutyl phosphine sulfide (Cyanex 471X) (Pinto et al., 2015) (López-López et al., 2014; Slaveykova et al., 2009). However, some extractants such as DEHPA and Kriptofix-22DD can only be used after sample acidification, limiting the possibility of speciation studies; and micro-extraction of Ag with Cyanex 471X is deployed for saline samples because Ag is mainly found as $AgCl_2^-$ and $AgCl_3^{2-}$, which are not transported through the organic solution into the fiber (López-López et al., 2015). Moreover, there are some limitations of HFLPME for routine analysis because operation time is often excessive, instability of the liquid membrane, and the need of additional equipment to hang the fiber during extraction.

In this work the ionic liquid trihexyltetradecylphosphonium chloride (Cyphos® 101) has been used for selective micro-extraction of $AgCl_n^{(n-1)-}$ complexes at the natural pH of seawater samples, by means of anionic exchange of $Cl^-$ from the ionic liquid (Cui et al., 2015). Therefore, inorganic silver can be separated from Ag associated to organic matter. This can be a potential tool for determination of inorganic and organic silver fractions working in natural conditions without sample manipulation prior to sample processing. The ionic liquid played a double role as extractant as well as a stabilizer of the organic solution due to its high viscosity and thermal stability (Abulhassani et al., 2010; Aguilera-Herrador et al., 2010; Herce-Sesa et al., 2018a).

The HFLPME system was setup in the configuration of two-phase solvent bar micro-extraction (SBME). In SBME, both ends of the fiber segment are thermally sealed and the fiber can be left free into the sample during extraction (López-López et al., 2016). The process is simplified, as the same organic solution is impregnating the fiber pores and lumen, and the need of a support to hang the fiber during extractions is avoided (Stanisz et al., 2014).

The aim of this work is to develop a simple, affordable, direct and environmentally friendly methodology for determination Ag fractions in marine samples, based on the application of an ionic liquid supported in a micro-extraction solvent bar.

## 2. Material and methods

### 2.1. Reagents and solutions

Unless otherwise stated, analytical grade reagents were used in this work. NaOH (98%) and NaCl (99.5%) were purchased from Panreac (Barcelona, Spain) and $HNO_3$ PlasmaPURE (67%–69%) was obtained from SCP Science (Quebec, Canada). Sodium salt of humic acids and trihexyltetradecylphosphonium chloride (Cyphos® 101) were provided by Aldrich (Steinheim, Germany). Kerosene (97.5%) and dodecan-1-ol (97%), obtained from Fluka (Buchs, Switzerland), were used as solvents to prepare acceptor solutions of Cyphos. 1-pyrrolidine-dithiocarbamate (APDC) and diethylammonium-diethyldithiocarbamate (DDDC) were supplied by Merck (Darmstadt, Germany). Atomic absorption
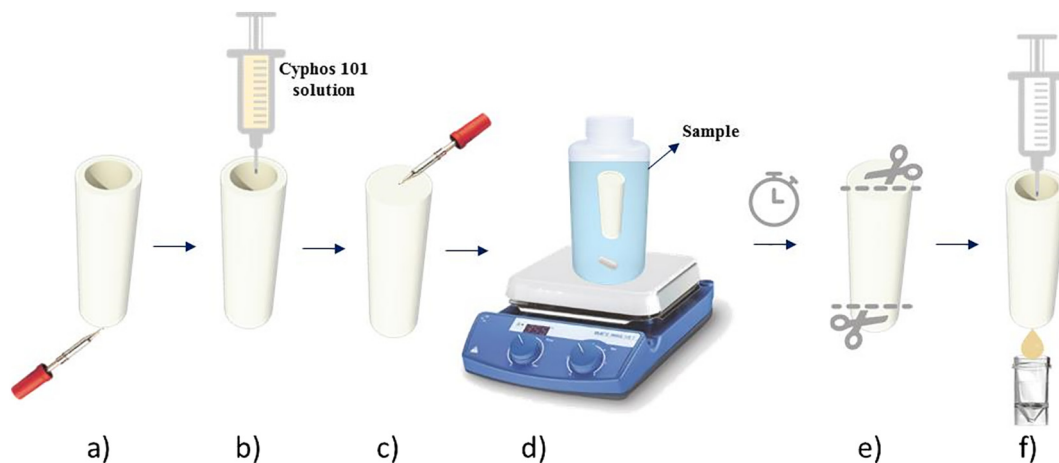


**Fig. 1.** Setup of the solvent bar micro-extraction used in this work: a) sealing one fiber end, b) filling and impregnation with the ionic liquid solution, c) sealing the second fiber end, d) exposition of the SBME to the sample, d) opening the SBME, e) recovery of the acceptor solution.