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# Solvent bar micro-extraction with graphite atomic absorption spectrometry for the determination of silver in ocean water

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## Abstract

Main drawbacks for silver determination in seawater are the effects of samples matrix and that Ag appears in the sub ng L<sup>-1</sup>. Available methods for sample preparation in Ag analysis are based on solid and liquid extraction using tedious process that increase the cost of analysis and the risk of sample contamination, producing important waste amounts.

Solvent bar micro-extraction (SBME) allows the pre-concentration of Ag in a micro-volume of the ionic liquid Aliquat 336® in kerosene solution. For this reason, it is considered as a green alternative to standard methods. The method has been optimized using synthetic seawater samples, offering the highest response for samples at pH=2, using 5% Aliquat 336® dissolved in kerosene containing 5% dodecan-1-ol as acceptor solution and after 1 hour stirring at 800 r.p.m.

The method exhibited linearity up to 50 ng L<sup>-1</sup>, with a limit of detection of 0.09 ng L<sup>-1</sup>, covering the concentration range of interest for environmental studies. Finally, it was applied for determination of Ag in real seawater samples, and the results were compared with the reference method of liquid-liquid extraction with 1-pyrrolidine-dithiocarbamate and diethylammonium-diethyldithiocarbamate, showing the applicability of ionic liquid based SBME using Aliquat 336® for the simple monitoring of silver ultra-traces in seawater analysis.

**Keywords:** silver, ultra-trace analysis, seawater, ionic liquid, solvent bar micro-extraction

## 1. Introduction

Despite the growing interest on silver concentration in natural waters during the last years, knowledge on its distribution in marine waters is limited. Research on Ag distribution in the ocean is limited by the low concentration it presents and by the effect of the saline matrix on the instrumental determination [1-3]. For these reasons, silver determination in seawater normally requires a sample preparation step prior instrumental determination [4,5]. This is the case of, liquid-liquid extraction (LLE) with 1-pyrrolidine-dithiocarbamate (APDC) and diethylammonium-diethyldithiocarbamate (DDDC), which is the most commonly used method for analysis of Ag in seawater; however, it is tedious and presents high risk of contamination

[6]. Alternative on-line solid phase extraction (SPE) with Chelex-100 has been developed towards automation of the process [7]. However, in both cases the amount of reagents and solvents needed is excessive, and even if ultra-sensitive quantification techniques are used the limit of detections are often not low enough as to determine Ag in the samples [8-9]. As an example, there is no certified reference material available for determination of Ag traces in seawater, and limit of detection of existing methods is often not-low-enough to offer reliable data on silver concentration in seawater.

Numerous analytical methods have been developed in the last years to improve the determination of trace metals focused on the miniaturization and automation of the sample preparation step [10-12]. However, in the case of Ag innovative solutions that could overcome the drawbacks of LLE or SPE are limited to cloud point extraction [13]. Micro-extraction methods have allowed the reduction of samples handling and the amount of solvents needed, but they also have improved metals pre-concentration, leading to lower limits of detection [14-16]. In particular, hollow fiber liquid phase micro-extraction in the three phase configuration (3HFLPME) has gained increasing attention over other liquid micro-extraction methods due to the stabilization of the organic solution in the fiber pores [17]. In 3HFLPME two aqueous solutions: the sample and the acceptor solution are separated by an organic solution containing an organic reagent that transports the metal from the sample to the acceptor solution [18].

Among the applications of HFLPME for metals determination in seawater analysis, determination of Ni using di-2-ethylhexylphosphoric acid (DEHPA) as extractant and simultaneous pre-concentration of Cd, Cu, Ni, Pb and Zn using 1,10-didecyl-diazo-18-crown-4-ether (Kryptofix 22DD) can be highlighted [19,20]. Applications of HFLPME for Ag determination in fresh-waters have been explored in the form of 3 phases solvent bar micro-extraction (3SBME) using tri-isobutyl phosphine sulphide (TIBPS) as extractant; notwithstanding, its applicability is limited in the presence of high  $\text{Cl}^-$  concentration [21]. Despite the potential of 3HFLPME for metals pre-concentration, its application to routine determination of metals in seawater is limited by the loss of organic solution from the fiber pores with time [22].

Recent use of room temperature ionic liquids (RTILs), which are organic salts that are liquid at working temperature, as additives for the organic solution in 3HFLPME has supposed a breakthrough for the stability of the organic solution in the fiber pores [23-25]. RTILs have been used to enhance pre-concentration of several metals as Au, Cd, Cr, Ni, or Pb [24,26-28]. This is supported by higher viscosity, temperature stability, low volatility and negligible miscibility in water for RTILs [22]. Particular interest must be paid in the case of functional ionic liquids, which can be used not only as additives but also as the extractant [29]. This is the case of tri-octylmethylammonium chloride (Aliquat 336 ®) that presents the possibility to

exchange  $\text{Cl}^-$  by  $\text{AgCl}_2^-$  and  $\text{AgCl}_3^{2-}$  from the sample [30]. For this reason, the 3HFLPME can be substituted by a simpler 2 phases solvent micro-extraction bar (2SBME), that directly pre-concentrates the metals into the fiber lumen, improving the performance of the extraction system and its reproducibility. In this work the parameters that affect 2SBME of Ag in seawater have been optimized for further quantification of  $\text{ng L}^{-1}$  silver in seawater samples.

## 2. Material and Methods

### 2.1. Reagents and solutions

All reagents were analytical-reagent grade unless otherwise stated. Kerosene (97.5%), tri-octylmethylammonium chloride (Aliquat 336 ®) (99%) and dodecan-1-ol (97%) were purchased from Fluka (Buchs, Switzerland). Sodium hydroxide (98%), hydrochloric acid (35%), sodium chloride (99.5%), calcium chloride (99%), magnesium chloride (99.5%), sodium dihydrocarbonate (99%), potassium bromide (99.5%), sodium sulphate (99%) were obtained Panreac (Barcelona, Spain). 1-pyrrolidine-dithiocarbamate (APDC) and diethylammonium-diethyldithiocarbamate (DDDC) were purchased from Merck (Darmstadt, Germany). Aqueous solutions of silver were prepared from a  $1000 \text{ mg}\cdot\text{L}^{-1}$  standard solution obtained from Merck (Darmstadt, Germany) and samples for optimization studies contained  $10 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ . Pure water obtained by a Millipore Quantum Ultrapure water supplier (Millipore, USA) was used exclusively. Argon for atomic spectrometry was obtained from Air Liquid (Madrid, Spain).

Synthetic seawater samples for optimization studies were prepared dissolving NaCl,  $\text{MgCl}_2$ , KCl,  $\text{CaCl}_2$ ,  $\text{NaHCO}_3$ ,  $\text{H}_3\text{BO}_3$ , KBr, and  $\text{Na}_2\text{SO}_4$  in deionized water [31]. Acceptor solutions of Aliquat 336 ® were prepared using kerosene as a solvent and dodecan-1-ol as matrix modifier.

### 2.2. Apparatus

Polypropylene Accurel PP S6/2 hollow fibers of  $0.2 \text{ }\mu\text{m}$  pore size and  $1800 \text{ }\mu\text{m}$  internal diameter were used in this study (Membrana, Germany). Samples were stirred using an IKA-Big Squid magnetic stirrer (Ika-Werke, Germany). Analytical signal of silver was registered using a continuum source atomic absorption spectrometer model ContrAA (Analytikjena, Germany), using graphite furnace atomizer (GFAAS). Transversally heated graphite furnaces made in pyrolitic graphite and equipped with L'Vov platform were used for atomization (Analytikjena, Germany).

### 2.3. Procedure

For 2-phases solvent bar micro-extraction (2SBME), a 4 cm long piece of capillary hollow fiber was cut using a blade. One of the fiber ends was thermally sealed by a hot tip with the assistance of tweezers, and the fiber lumen was filled with the acceptor solution until it dropped through the fiber pores, using a syringe. Thus, the other fiber end was sealed to make up the

solvent bar. The solvent bar was immersed into deionized water and stirred for 5 minutes to rinse the excess of acceptor solution in the fiber wall. Finally, the 2SBME was left free in the sample during extraction time for pre-concentration of silver. After extraction, the acceptor solution was recovered into a vial for further measurement in GFAAS.

Each sample was analysed by triplicate, by using three different aliquots. Three solvent bars were simultaneously added to each aliquot, providing nine experimental data for each sample. Hollow fibers were discarded after use to avoid memory effects.

#### 2.4. Instrumental determination.

Concentration of silver in the acceptor solution was measured by graphite furnace atomic absorption spectroscopy, at a wavelength of 328.1 nm and setting up the spectrometer detector between pixels 98-102. Atomization conditions were optimized to maximize the analytical signal, modifying drying, ash and atomization temperature. Since the acceptor solution consists in a kerosene solution of Aliquat 336®, two drying steps were needed. The atomization program is showed in table 1.

Volume of sample injected was 20µL and 3 replicates of each acceptor solution sample were analysed.

#### 2.5. Mechanism of Ag extraction

Selection of Aliquat 336® for extraction of Ag in sea-water samples was based on the speciation of Ag. In the case of sea-water silver appears in the forms of  $\text{AgCl}_2^-$  and  $\text{AgCl}_3^{2-}$  [30], and Ag extraction with Aliquat takes place by ion exchange of  $\text{Cl}^-$  ion from Aliquat 336® by the corresponding Ag chlorinated complexes [32].

#### 2.6. Optimization of silver extraction

Stability of the extraction system in the solvent micro-extraction bar was evaluated using synthetic seawater samples containing 10 µg L<sup>-1</sup> silver at pH=2 and 10% Aliquat 336 ® dissolved in kerosene and 10% dodecan-1-ol as acceptor solution. The use of synthetic seawater samples for optimization allowed evaluating the response of the method in the presence of main ions present in seawater samples that could interfere during extraction. Kerosene was chosen as a solvent for Aliquat 336®, because it has been proved to be suitable for hollow fiber liquid phase micro-extraction in previous studies. Samples were stirred for 60 minutes at 800 r.p.m. Fiber length was 4 cm, and the mass of acceptor solution recovered after extraction was weighted.

Univariate optimization of physic-chemical factors affecting the extraction of Ag was carried out, modifying one of the factors each time, keeping the rest constant. Optimized factors were, sample pH, Aliquat 336® and dodecan-1-ol concentration in the acceptor solution, stirring

speed and time of extraction. In all cases samples for optimization contained  $10 \mu\text{g L}^{-1}$  Ag. During optimization of chemical parameters and stirring speed, the recovered acceptor solution was diluted to avoid saturation of the detector. Only in the case of application to real samples, acceptor solution was directly measured without further dilution.

During optimization and for application to seawater analysis, 37 mL beakers were filled up with the sample to ensure solvent bars were completely immersed in the sample. Synthetic seawater was used to simulate the matrix of real samples. Efficacy of the extraction was measured from the analytical signal of Ag measured, for the acceptor solution, obtained in the different studied conditions.

### 3. Results

#### 3.1. Optimization of Ag extraction

Recovery of acceptor solution for 10 solvent micro-extraction bars after extraction was  $90.1 \pm 5.9$  mg, and an analytical signal for silver of  $0.259 \pm 0.019$  was obtained in graphite furnace atomic absorption, showing the repeatability of the system and its suitability to support the extraction system.

First, concentration of Aliquat 336® in the acceptor solution was optimized keeping pH=2 in the sample, 10% dodecan-1-ol in the acceptor solution and 30 minutes extraction for 800 r.p.m. stirring speed. As it can be seen in figure 1, the analytical signal was enhanced by the increase of Aliquat 336® in the acceptor solution up to a concentration of 5%; however, at higher concentration the extraction of Ag decreased due to the high viscosity of Aliquat 336® that difficulties the diffusion of the Ag-Aliquat 336® complexes through the fiber pores, as it happens with other extractants as DEHPA [20]. For this reason 5% Aliquat was kept for further experiments.

Next, the effect of the sample pH was evaluated, showing that the highest analytical signal was reached at pH=2 (Figure 2). Additionally, the best reproducibility was also obtained at this pH, which was used for optimization of the rest of the parameters.

A key factor for the use of Aliquat 336® is the addition of dodecan-1-ol to the acceptor solution, to allow solubility of Aliquat 336® in kerosene. Figure 3, shows how the response of the method against dodecan-1-ol concentration presented a profile similar to Aliquat 336®. The best performance was obtained for 5% dodecan-1-ol, and at higher level the viscosity of the acceptor solution was increased leading to a lower diffusion through the fiber pores.

Once the chemical variables were optimized, the effect of stirring speed and time of extraction were evaluated. In the case of stirring speed, the analytical signal was increased with the increasing stirring rate due to a better contact of the sample and solution in the fiber pores. As it

can be seen in figure 4, the analytical signal was stabilized after 800 rpm. maybe because at this rate the limiting factor was not the reaction between chlorinated Ag complexes and Aliquat 336® but the diffusion of the Ag-Aliquat 336® complexes through the fiber pores. As it can be observed (Figure 4), the analytical signal remains constant up to 1600 rpm., showing that the use of an ionic liquid as Aliquat 336® improved the stability of the organic phase in the fiber pores if compared with other systems in which kerosene is used as a solvent for HFLPME [18]. In this case a stirring speed of 800 rpm was selected. Finally the effect of time was also studied, showing an increase in the first 60 minutes to be stabilized after this time (Figure 5). Compared with other HFLPME methods for pre-concentration of silver, the proposed 2SBME offers a better performance in shorter times [21].

Summarizing, optimum conditions were: sample pH=2, 5% Aliquat 336® and 5% dodecan-1-ol in the acceptor solution, stirring rate 800 rpm. and 60 minutes extraction time. These conditions were used for calibration and determination of silver in real sea-water samples.

### 3.2. Analytical features

For calibration of the 2SBME, standard solutions were prepared in a synthetic sea-water matrix and treated using the same extraction procedure as for the samples.

Calibration curve showed a slope of 0.0339 and an intercept of 0.0092 with a regression coefficient of  $R^2 = 0.9966$ . Limit of detection  $0.09 \text{ ng L}^{-1}$  was calculated as the concentration that offered by the average signal of 10 independent blanks samples plus 3 times their standard deviation. The response of the method showed to be linear in the range  $1 \text{ ng L}^{-1}$  to  $50 \text{ ng L}^{-1}$  [33].

### 3.3. Application to real samples

In order to prove the applicability of Aliquat 336® based 2SBME for extraction of silver traces in sea-water samples, results obtained by the proposed method were compared with results obtained by the reference method of liquid-liquid extraction using 1-pyrrolidine-dithiocarbamate (APDC) and diethylammonium-diethyldithiocarbamate (DDDC) in a 10,000 class Clean Room followed by determination with ICP-MS [6].

Silver concentration was analysed in five samples from the Gulf of Cádiz (Spain). Samples were collected using clean sampling techniques, through a polytetrafluoroethylene tube and filtered on-line through a  $0.45 \mu\text{m}$  pore sized nylon filter. Before analysis, the samples were acidified to pH=2. Results from both methods were compared using a t test ( $t_c = 3.18$ ,  $n=3$ ,  $\alpha=0.05$ ). As it can be seen in table 2, results obtained by the proposed 2SBME method are in accordance with those obtained by the reference method in the level of  $\text{sub ng L}^{-1}$ .

Regarding operational conditions, 2 SBME allowed simplifying the sample preparation process if compared with liquid-liquid extractions (Table 3). Extraction experiments were carried out in a 10,000 class Clean Room to avoid samples contamination due to excessive sample handling. As the SBME extraction does not require participation of the operator during extraction, up to 6 samples could be extracted simultaneously, offering 18 extraction replicates in 60 minutes. Considering the amount of reagents needed and waste generated, on the one hand, the proposed SBME less amount of sample and requires only a few  $\mu\text{g}$  of ionic liquid, which are used for determination in AAS; on the other hand, the reference method requires higher amount of reagents followed by ICP-MS determination.

Additionally, the proposed method has been compared with other methods proposed for Ag determination in seawater samples (Table 3). Regarding micro-extraction methods, the proposed SBME offers the lowest limit of detection up to the date [13, 18], offering similar LOD as the ion exchange followed by ICP-MS determination [7].

#### 4. Conclusion

The use of an ionic liquid Aliquat 336® for silver extraction, allows the use of 2 phases solvent bar micro-extraction (2SBME) simplifying the set-up of hollow fiber liquid phase micro-extraction used in metals analysis. This is the first HFLPME approach used for determination of silver ultra-traces in sea-water, which is supported by the capability of Aliquat 336® to exchange  $\text{Cl}^-$  for  $\text{AgCl}_2^-$  and  $\text{AgCl}_3^{2-}$ . Finally, Stability of the system is enhanced in comparison with other HFLPME used for metals due to the presence of the ionic liquid.

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Figure 1. Effect of Aliquat 336 ® concentration in the acceptor solution on Ag extraction. 30 minutes extraction, sample pH=2, dodecan-1-ol 10%, stirring speed 800 rpm.

Figure 2. Effect of the sample pH on the extraction of Ag. 30 minutes extraction, 5% Aliquat 336 ®, dodecan-1-ol 10%, stirring speed 800 rpm.

Figure 3. Effect of dodecan-1-ol concentration on the efficiency of Ag extraction. 30 minutes extraction, 5% Aliquat 336 ®, pH=2, stirring speed 800 rpm.

Figure 4. Effect of stirring speed on the efficiency of Ag extraction. 30 minutes extraction, 5% Aliquat 336 ®, dodecan-1-ol 5%, pH=2.

Figure 5. Evolution of Ag extraction with time of extraction. 5% Aliquat 336 ®, dodecan-1-ol 5%, pH=2, 800 rpm.

Table 1. Temperature program for atomization of Ag in the acceptor solution

Step	Temperature (°C)	Ramp (°C/s)	Hold (s)
Dry	80	10	20
Dry	90	10	10
Dry	260	50	30
Pyrolysis	300	--	10
Gas adaption	300	--	5
Atomization	1600	1500	3
Clean-out	2500	500	6

Table 2. Application of IL- 2SBME to analysis of silver in seawater samples

Sample	Ag this method (ng L <sup>-1</sup> )	Ag <sub>t</sub> ref. method <sup>1</sup> (ng L <sup>-1</sup> )	t <sup>2</sup>
Gulf of Cádiz 1	0.62±0.08	0.59	0.64
Gulf of Cádiz 2	1.46±0.16	1.21	2.70
Gulf of Cádiz 3	1.35±0.25	0.91	3.08
Gulf of Cádiz 4	0.26±0.02	0.31	-4.16
Gulf of Cádiz 5	0.31±0.03	0.28	1.68

<sup>1</sup> Extraction using 1-pyrrolidine-dithiocarbamate (APDC) and diethylammonium-diethyldithiocarbamate (DDDC) in a 10,000 class Clean Room followed by determination with ICP-MS. <sup>2</sup>t<sub>c</sub>= 3.18, n=3, α=0.05.

Table 3. Comparison of the proposed Aliquat 336<sup>®</sup> based SBME with other methods for determination of Ag in seawater

Instrumental determination	Average time per replicat	Amoun t of sample	Amoun t of reagent	Solvent	Extractant	LO D (ng	Ref .
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		e (min)	(mL)	(mL)			L <sup>-1</sup> )	
This method (IL-2SBME)	GFAAS	3.3	12.3	0.09	Kerosene	Aliquat 336 <sup>®</sup>	0.09	
Liquid-Liquid extraction	ICP-MS	21	100	9	Chloroform	APDC/DDDC	0.17	[3]
Hollow fiber liquid phase micro-extraction	GFAAS	10	50	0.02	Dihexylether	Tri-isobutylphosphine sulfide	1.16	[18]
Cloud point extraction	GFAAS	7.5	10	0.03	Triton X-114	--	2.00	[13]
Ion exchange	ICP-MS	9	12	--	--	Chelex-100	0.07	[7]
Solid phase extraction	ICP-MS	25	20	1	Nitric acid	Chitosan	0.70	[34]

Figure 1

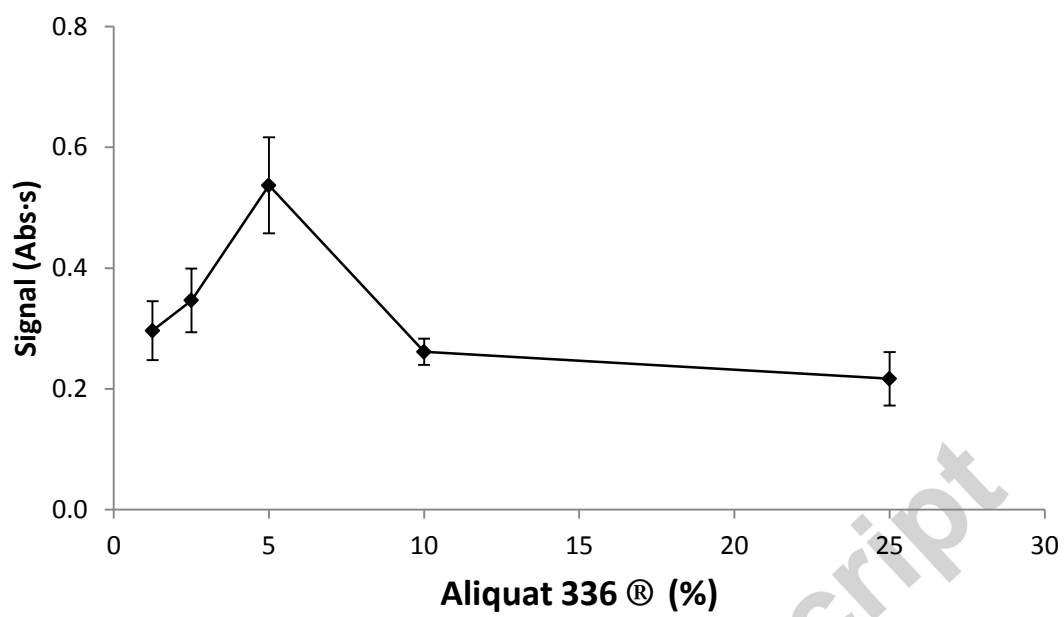
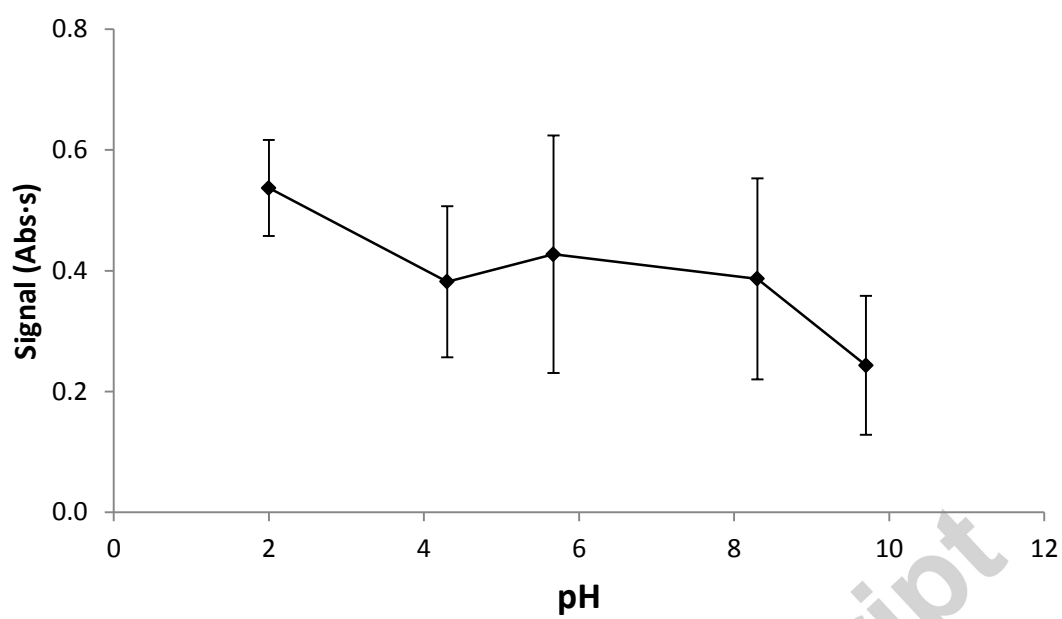
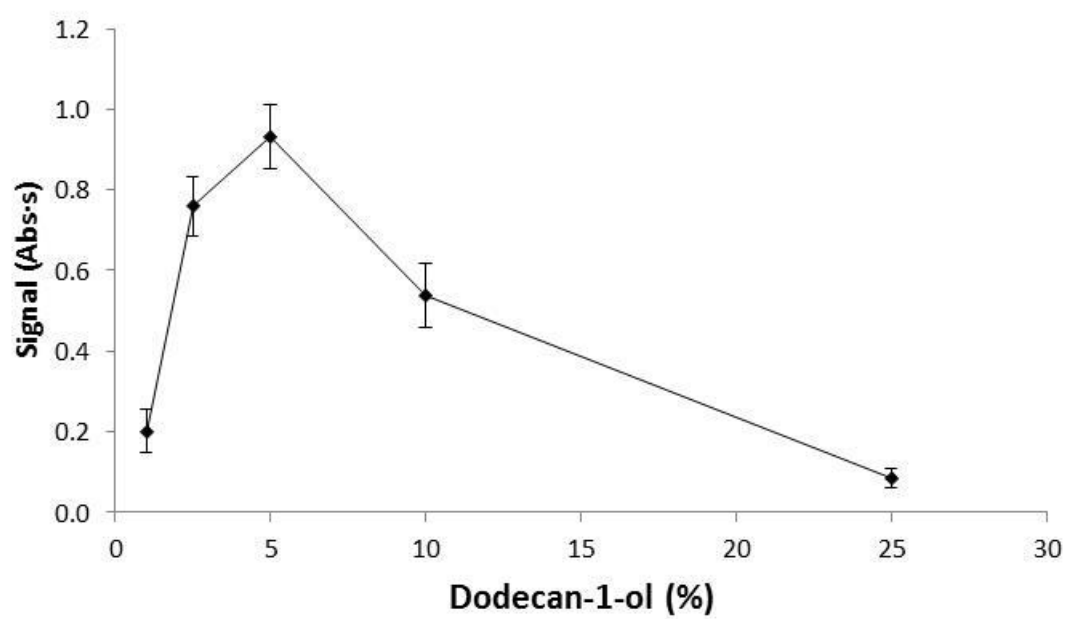


Figure 2



Accepted manuscript

Figure 3



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Figure 4

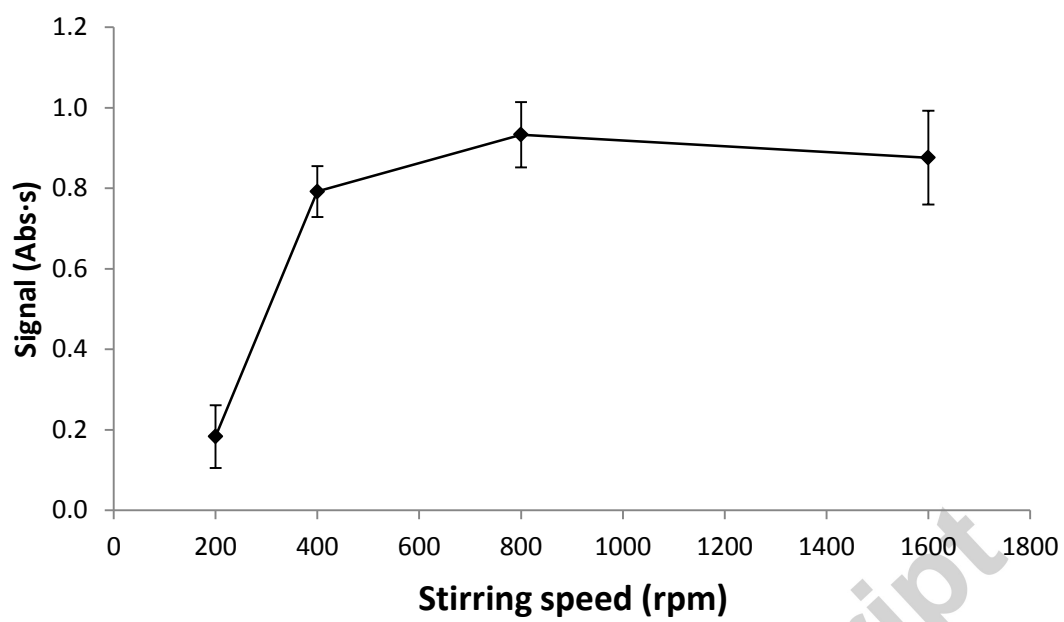
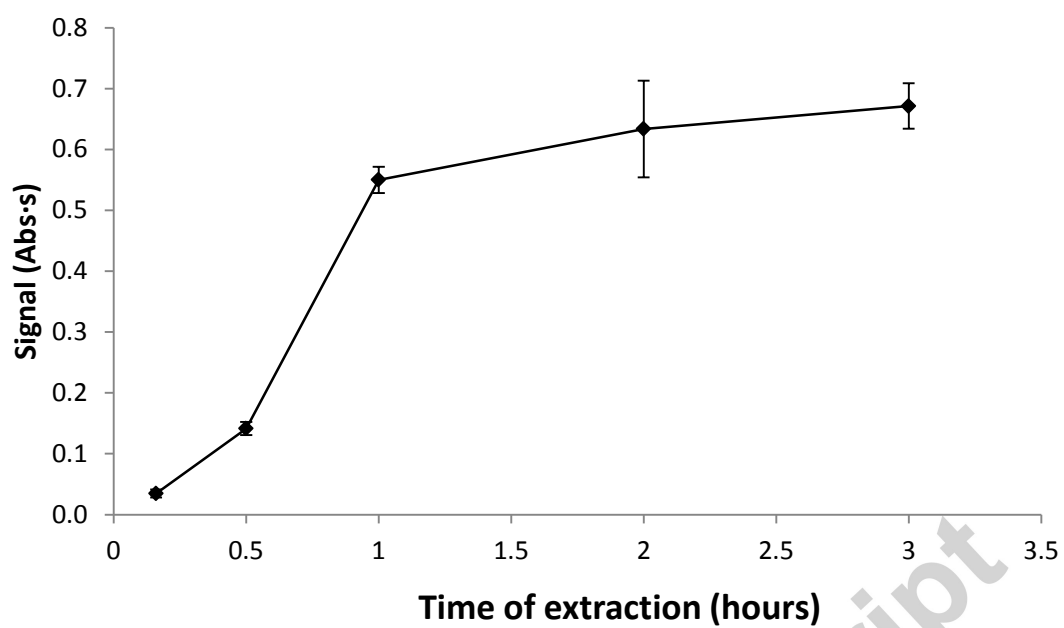
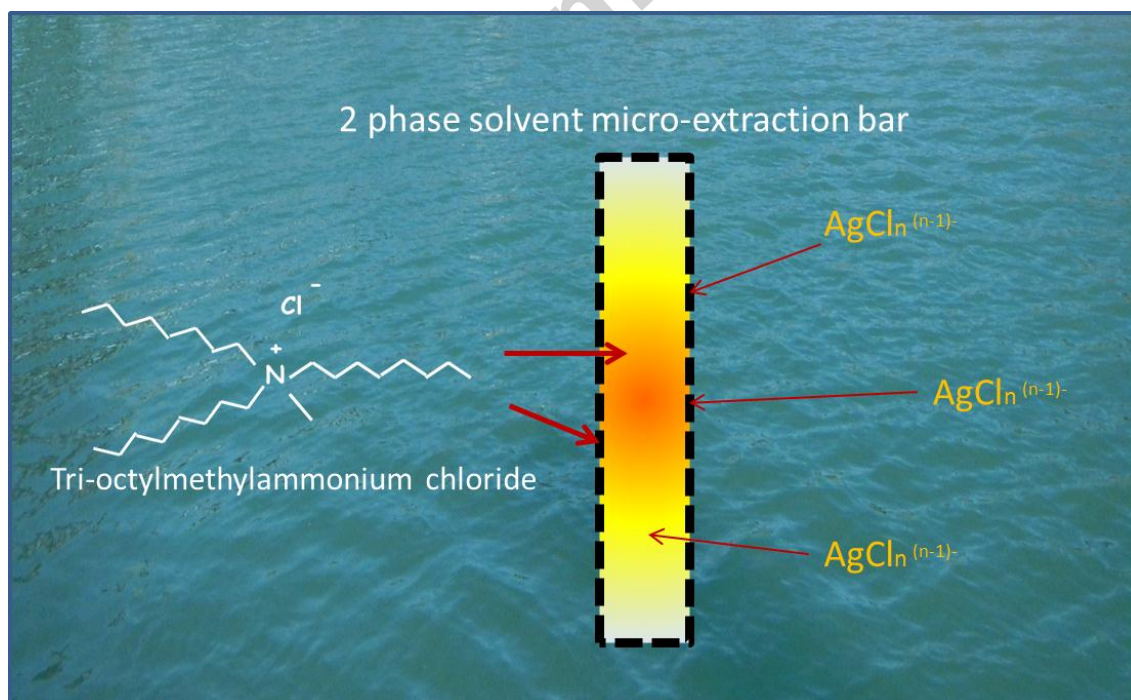


Figure 5



Graphical Abstract



**Highlights**

- Ionic liquid based 2SBME allows Ag pre-concentration in seawater samples.
- Using Aliquat 336® 2SBME with GFAAS offers a limit of detection 0.1 ng L<sup>-1</sup>
- Ionic liquid 2SBME is alternative to existing methods for Ag analysis in seawater

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