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**High performance preconcentration of inorganic Se species  
by dispersive micro-solid phase extraction with a nanosilica-  
ionic liquid hybrid material**

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**Abstract**

A highly sensitive and efficient dispersive micro-solid phase extraction (D- $\mu$ -SPE) method was developed for inorganic Se speciation analysis. A novel ionic liquid (IL)-nanomaterial hybrid consisting of 1-dodecyl-3-methylimidazolium bromide-functionalized nanosilica was used for the efficient retention of Se(IV) complexed with ammonium pyrrolidine dithiocarbamate, followed by elution with an ethyl acetate/Triton X-114 mixture and determination by electrothermal atomic absorption spectroscopy. The Se(VI) species was selectively determined by difference between total inorganic Se and Se(IV) after pre-reduction. The IL-nanomaterial hybrid was characterized by Fourier transform infrared spectroscopy and transmission electronic microscopy. Likewise, Se(IV) sorption capacity of the retention material and maximum amount of IL loaded on its surface were determined. Several factors concerning the functionalization, extraction and elution steps were optimized, yielding a 100% extraction efficiency for Se(IV) under optimal conditions. A limit of detection of 1.1 ng L<sup>-1</sup>, a relative standard deviation of 5.7% and a 110-fold enhancement factor were obtained. The D- $\mu$ -SPE method was successfully applied to several water samples from different origins and compositions, including rain, tap, underground, river and sea.

*Keywords:* Ionic liquid; Nanoporous silica; Selenium; Speciation; Preconcentration.

## 1. Introduction

The effect of Se on human health has a characteristic dual nature, i.e. it is an essential nutrient for plants, animals and humans, but it is also toxic at higher levels, with a very narrow concentration range between both situations [1, 2]. Furthermore, the importance of Se determination is linked not only to its total content, but also to its speciation, since bioavailability and toxicity are modified greatly depending on the different chemical species [3]. Se(IV) and Se(VI) are the most common species occurring in environmental samples, although total Se concentration in these samples is usually in the order of a few  $\mu\text{g L}^{-1}$  [4, 5]. Therefore, Se speciation analysis is a challenging task, because highly sensitive analytical methods are required for accurate determination. This can be performed by using modern elemental detection techniques such as inductively coupled plasma mass spectrometry (ICP-MS) or well-established detectors, e.g. electrothermal atomic absorption spectrometry (ETAAS), that can be coupled to efficient separation and preconcentration techniques [6].

Ionic liquids (ILs) comprise a new generation of alternative solvents which have found great usefulness in the development of efficient separation and preconcentration methods in elemental analysis [7]. Several ILs have been applied for preconcentration of Se species based on different liquid-liquid microextraction (LLME) techniques, including dispersive liquid-liquid microextraction (DLLME) [8], cold-induced aggregation microextraction (CIAME) [9], magnetic ionic liquid-based up-and-down-shaker-assisted dispersive liquid-liquid microextraction (MIL-UDSA-DLLME) [10] and vortex-assisted liquid-liquid microextraction (VA-LLME) [6], among others. Nevertheless, the main drawbacks concerning the use of ILs in LLME-based preconcentration can be summarized as: i) difficulty for efficient mixing with another liquid phase containing the analyte, ii) partial solubilization of hydrophobic ILs in water

and iii) the need of ILs denser than water for efficient separation of the extractant phase when traditional techniques are used (e.g. centrifugation or decantation) [11, 12].

A valid alternative to solve some of the above-mentioned difficulties and extend the application of ILs for preconcentration consists on their combination with solid materials having high surface areas, such as nanomaterials [13]. In fact, in recent years, significant innovations have been introduced in preconcentration with the use of nanomaterials in dispersive-solid phase extraction (D-SPE), and more specifically in dispersive micro-SPE (D- $\mu$ -SPE), where fast and efficient analyte retention is achieved with only a few micrograms of the dispersed solid phase. This also translates into a significant reduction of the amount of sorption material and solvents required for elution, which in turns contributes to the development of more environmentally friendly methods [14]. Based on this approach, different nanomaterials, e.g. nano- $\text{Al}_2\text{O}_3$  [15], nano- $\text{TiO}_2$  [16, 17], sulfonated polystyrene-coated ( $\text{Fe}_3\text{O}_4$ @PSS) magnetic nanoparticles [18], graphene [19] and 3-(2-aminoethylamino) propyltrimethoxysilane modified multi-wall carbon nanotubes [20], have been implemented in sample preparation methods for Se preconcentration and determination.

Functionalization of nanomaterials with ILs can proceed based upon chemical or physical phenomena. Chemisorption allows higher flexibility at the time of selecting an IL and more control over the functionalization degree, but also requires several reaction steps and reagents that might contribute to waste generation [21]. On the other hand, physisorption is usually simpler and faster, thus simplifying the functionalization process. In that case, when ILs containing cations with long alkyl chains are used, the formation of hemimicelles and admicelles on the surface of some nanomaterials has been proposed [22]. Therefore, the development of novel preconcentration methods

based on IL-nanomaterial hybrids constitutes an interesting alternative for taking advantage of the full scope of available ILs.

In this work, an efficient and selective D- $\mu$ -SPE technique based on the use of a novel IL-nanomaterial hybrid consisting of 1-dodecyl-3-methylimidazolium bromide ([C<sub>12</sub>mim]Br)-functionalized nanosilica for the separation and determination of inorganic Se species was developed. This method allowed the rapid and facile application of a water-soluble IL showing outstanding extraction properties, in aqueous media. The application of nanosilica as supporting material made use of its extensive surface area and allowed not only the miniaturization of the process, but also enormously facilitated the separation steps. Different factors affecting the functionalization, extraction and elution processes were optimized and the resulting method was successfully applied for the separation and determination of inorganic Se species in natural water samples having different matrices and complexities.

## 2. Experimental

### 2.1 Instrumentation

Measurements were performed with a Perkin Elmer (Überlingen, Germany) 5100 ZL atomic absorption spectrometer equipped with a transversely heated graphite atomizer and a Zeeman effect background correction system. A Se electrodeless discharge lamp (EDL) (Perkin Elmer) was used. All measurements were performed based on absorbance signals with an integration time of 3 s. Instrumental conditions are listed in Table 1. The characterization of the IL-nanomaterial hybrid was performed using a Spectrum 100 (Perkin Elmer) Fourier transform infrared (FTIR) spectrometer and a Carl Zeiss EM900 transmission electron microscope (TEM). A Horiba F-51 pH meter (Kyoto, Japan) was used for pH determinations and a centrifuge (Luguimac,

Buenos Aires, Argentina), model LC-15, was used for the separation of phases. Mixing was achieved using a vortex stirrer model Bio Vortex B1 (Boeco, Hamburg, Germany). A temperature-controlled ultrasound bath (40 kHz and 600 W) (Test Lab, Buenos Aires, Argentina) was employed for analyte elution.

## 2.2 Reagents

All reagents were of analytical grade, and the presence of Se was discarded within the working range. Inorganic Se(IV) and Se(VI) stock standard solutions (1000 mg L<sup>-1</sup>) as sodium selenite (Na<sub>2</sub>SeO<sub>3</sub>) (99%) (Sigma-Aldrich, Milwaukee, WI, USA) and sodium selenate (Na<sub>2</sub>SeO<sub>4</sub>) (98%) (Sigma-Aldrich), respectively, were prepared in 0.1 mol L<sup>-1</sup> HCl. Working standard solutions were prepared daily using ultrapure water. A 500 mg L<sup>-1</sup> palladium nitrate dihydrate solution [Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O] (≥ 99.99%) (Sigma-Aldrich) and 500 mg L<sup>-1</sup> copper(II) nitrate hemi(pentahydrate) [Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O] (≥ 99.99%) (Sigma-Aldrich) were prepared and used as chemical modifiers (see Table 1). These solutions were prepared in 0.1% (v/v) HNO<sub>3</sub> (Ultrex<sup>®</sup> II Mallinckrodt Baker, Phillipsburg, NJ, USA). Chemical structures of all ILs used in this work are presented in Fig. 1. 1-octyl-3-methylimidazolium chloride ([C<sub>8</sub>mim]Cl), 1-dodecyl-3-methylimidazolium bromide ([C<sub>12</sub>mim]Br) and 1-hexadecyl-3-methylimidazolium bromide ([C<sub>16</sub>mim]Br) were synthesized according to the method proposed by Baltazar et al [23]. Tributyl(methyl)phosphonium methyl sulfate ([P<sub>4,4,4,1</sub>]CH<sub>3</sub>SO<sub>4</sub>), citric acid (99.5%), ethanol (99.5%) and ethyl acetate (99.8%) were purchased from Sigma-Aldrich. Diluted 5% (w/v) aqueous solutions of the ILs were prepared with ultrapure water. Hydrochloric acid (37%) was purchased from Merck. Triton X-100 was from Anedra, while Triton X-114 was from Sigma-Aldrich. Complexing agents including ammonium pyrrolidine dithiocarbamate (APDC) (~99%),

sodium diethyl dithiocarbamate (DDTC) (99%) and ammonium diethyl dithiophosphate (DDTP) (95%) were from Sigma-Aldrich. Solutions of APDC, DDTC and DDTP at 1% (w/v) in absolute ethanol were prepared daily. Silica nanopowder (99.8%) with 12 nm primary particle size and a 175-225 m<sup>2</sup> g<sup>-1</sup> surface area (BET, as declared by the manufacturer) was purchased from Sigma-Aldrich. Ultrapure water (18 MΩ·cm) was obtained from a Milli-Q water purification system (Millipore, Paris, France). All glassware was washed in 5% (v/v) HNO<sub>3</sub> solution for 24 h and thoroughly rinsed with ultrapure water.

### *2.3 Preparation and characterization of nanosilica-IL hybrids*

For functionalization, 1 mg of powdered nanosilica was initially suspended in 4 mL of ultrapure water in a centrifuge tube. Then, a volume of 40 μL of 5% (w/v) IL aqueous solution was added to the suspension and vortex stirring was applied for 10 s. Afterwards, the tube was centrifuged for 3 min at 3000 rpm and the supernatant was manually removed with a Pasteur pipette.

The functionalization of silica nanoparticles (NPs) with [C<sub>12</sub>mim]Br was evaluated using different techniques. FTIR spectra (4000 – 400 cm<sup>-1</sup>) were obtained from a KBr pellet containing the powdered samples. An average of 30 scans per sample was taken for peak identification. TEM images of dried aqueous dispersions were obtained working with the microscope at 80 kV, with a high-resolution Gatan SC1000-832 CCD camera. The amount of IL adsorbed on the nanoparticles was evaluated by weight difference before and after the impregnation of the nanosilica with an excess of IL. All hybrid materials were washed twice with ultrapure water and dried at 80 °C for two hours prior to characterization.

### *2.4 Sample collection*



For the collection of tap water samples, domestic water was allowed to run for 20 min, after which a volume of approximately 1000 mL was collected in an HDPE bottle. Analysis of tap water was performed immediately after sampling. River, sea, rain and underground water samples were collected in clean, HNO<sub>3</sub>-washed HDPE bottles that were rinsed three times with the sample prior to collection. For river, sea and underground water, sample volumes of 500 mL were collected at a depth of 5 cm below the surface. Immediately after sampling, sample aliquots were filtered through 0.22 µm pore size PTFE membrane filters (Millipore Corporation) and stored at 4 °C. Sand residues present in seawater were separated by centrifugation before filtration. River samples were collected at Uspallata city (Mendoza, Argentina), while seawater was collected at Viña del Mar city (Valparaíso, Chile). Rain samples were collected during a raining event in Mendoza city (Mendoza, Argentina) and underground water was obtained from a well in Lavalle city (Mendoza, Argentina). All sampling materials were previously washed overnight with a 1.5 mol L<sup>-1</sup> HNO<sub>3</sub> solution and then rinsed with ultrapure water.

### *2.5 General D-µ-SPE procedure for Se(IV) determination*

A volume of 5 mL of sample, or a 2 µg L<sup>-1</sup> Se(IV) standard solution (for optimization), were adjusted to pH 4 using 300 µL of 0.1 mol L<sup>-1</sup> citrate buffer and 20 µL of a 1% (w/v) APDC solution in ethanol were also added, followed by vortex-assisted mixing for 10 seconds to allow complex formation. Afterwards, the treated sample was added to the IL-nanosilica hybrid in a glass centrifuge tube and the mixture was vortex-stirred for 3 min. Phase separation was achieved by centrifugation at 3000 rpm during 5 min and the supernatant was removed using a Pasteur transfer pipette. The small fraction of liquid remaining in the wet solid phase was eliminated by evaporation.

Finally, the analyte was eluted with 100  $\mu\text{L}$  of a 0.5% (w/v) Triton X-114 solution prepared in ethyl acetate, at a temperature of 60  $^{\circ}\text{C}$  and assisted by an ultrasonic bath. The eluate was separated from the solid phase by centrifugation (5 min at 3000 rpm) and then directly injected into the graphite furnace of ETAAS for Se determination under the conditions shown in Table 1.

### *2.6 Determination of total inorganic Se and Se(VI) species*

For total inorganic Se determination, a pre-reduction step was necessary. A volume of 1.5 mL of concentrated HCl was added to a 5 mL sample aliquot and the mixture was heated on a hot plate at 100  $^{\circ}\text{C}$  for 30 min to reduce Se(VI) to Se(IV). After cooling at room temperature, the same procedure described for Se(IV) determination was applied to determine total inorganic Se. Finally, the concentration of Se(VI) was calculated by subtracting Se(IV) from total inorganic Se.

## **3. Results and discussion**

### *3.1 Functionalization of nanosilica and selection of ionic liquids*

Several factors involved in the functionalization process of nanosilica with ILs were optimized before Se preconcentration in order to assure the highest coating of the nanomaterial surface. This study was performed using 5 mL of a 200  $\mu\text{g L}^{-1}$  Se(IV) standard solution.

Water-soluble ILs with different cations belonging to the imidazolium or phosphonium families were assayed as functionalization agents by evaluating their effect on Se extraction. Extraction percentages as a function the type of IL are shown in Fig. 2. Even though satisfactory extractions were achieved in all cases (66 - 97%), the best results were obtained with  $[\text{C}_{12}\text{mim}]\text{Br}$ . This is assumed to be the consequence of a

balance between hydrophobicity and solubility of the IL; the former as a factor affecting the extraction of the low polar Se(IV)-APDC complex and the latter concerning the availability of the IL to functionalize the nanosilica. [C<sub>12</sub>mim]Br was the imidazolium-type IL with the longest alkyl chain that was completely soluble in water. On the other hand, [C<sub>16</sub>mim]Br is more hydrophobic, but it did not exhibit full solubility in water at room temperature. Therefore, it can be assumed that the amount of [C<sub>16</sub>mim]Br available for nanosilica functionalization was lower than that of [C<sub>12</sub>mim]Br. In addition, [P<sub>4,4,4,1</sub>]CH<sub>3</sub>SO<sub>4</sub> was less effective than [C<sub>12</sub>mim]Br for Se(IV) extraction.

The concentration of [C<sub>12</sub>mim]Br and the contact time between the IL and nanosilica were also studied. These two factors determined the impregnation of the pores occurring in the nanosilica and the functionalization of its surface, thus conditioning the performance of the IL-nanomaterial hybrid for Se(IV) retention. The results showed that a 100% extraction efficiency was obtained when 1 mg of nanosilica was exposed to 4 mL of a solution at 0.01% (w/v) [C<sub>12</sub>mim]Br during 10 s, which loaded the nanosilica surface with 400 µg of the IL. Further increases in the amount of [C<sub>12</sub>mim]Br and contact time did not increase Se(IV) extraction. Therefore, to ensure a 100% extraction efficiency, 800 µg of [C<sub>12</sub>mim]Br and a contact time of 10 seconds were selected. The different results obtained for Se(IV) extraction can be explained by the formation of hemimicelles and/or admicelles of the IL on the nanosilica surface. Initially, a monolayer (hemimicelle) of IL is formed, thus conferring the surface with a hydrophobic character, as a consequence of the alkyl chains exposed to the sample solution. Then, as the concentration of IL increases in the functionalization media, the formation of a second layer results in the formation of admicelles, with a characteristic amphiphilic nature. Therefore, the formation of hemimicelles and/or admicelles of

[C<sub>12</sub>mim]Br added a low polar character to the nanosilica surface, thus leading to the efficient retention of the Se(IV)-APDC complex.

Furthermore, the influence of the pH during functionalization of the nanosilica with the IL on Se(IV) extraction was studied. No significant differences in Se(IV) extraction efficiency were observed within the pH range between 2 and 11. This could be attributed to the existence of both electrostatic and hydrogen bond interactions between nanosilica and [C<sub>12</sub>mim]Br. Thus, independently of the charge of the nanosilica surface, interactions with the IL might be feasible, either by formation of hydrogen bonds between silanol groups of the surface and the imidazolium ring of the IL, or by a combination of hydrogen bonding and electrostatic forces occurring at pH values around or above the isoelectric point (pI) of the nanosilica [24]. Since the pH did not significantly modify the extraction of Se, its adjustment was not required and an additional step was avoided.

### *3.2 Characterization of the [C<sub>12</sub>mim]Br-nanosilica hybrid material*

Characterization of the sorbent material was performed by FTIR spectroscopy and TEM. Fig. 3a shows the FTIR spectra of pure nanosilica, [C<sub>12</sub>mim]Br and the [C<sub>12</sub>mim]Br-nanosilica hybrid. With the exception of the main peaks corresponding to the untreated nanosilica, the spectrum of the [C<sub>12</sub>mim]Br-nanosilica hybrid showed peaks corresponding to C-H stretchings (2853 and 2928 cm<sup>-1</sup>), C-H angular deformations (697, 834 and 1108 cm<sup>-1</sup>) and an imidazole ring characteristic nC=N<sup>+</sup> signal at 2076 cm<sup>-1</sup>. These peaks -although slightly displaced because of the different chemical environments- confirmed the successful functionalization of the nanosilica surface with [C<sub>12</sub>mim]Br. Also, TEM micrographs (Fig. 3b) revealed that the shape and size distribution of silica NPs were preserved after functionalization with the IL. The formation of clusters with a higher number of NPs was observed with IL-functionalized

silica NPs in comparison to untreated nanosilica (Fig. 3c). This might be the result of a decrease in the repulsive interactions between NPs, most probably as a consequence of the modification of the negatively charged surface of the nanosilica to a non-polar character, due to the presence of the alkyl chains of the  $[C_{12}mim]^+$  cation.

Finally, the adsorption capacity of nanosilica towards the IL was determined by weight difference. A capacity of  $824 \pm 33 \mu\text{g } [C_{12}mim]Br \text{ mg}^{-1}$  nanosilica was obtained, thus confirming that the high surface area of the nanosilica was able to adsorb a great number of IL molecules during the functionalization.

### *3.3 Optimization of extraction conditions and selectivity of Se species*

As previously mentioned, the IL-nanosilica hybrid prepared in this work had a surface with a non-polar character. Therefore, derivatization of Se(IV) species with a chelating agent was required in order to diminish its polarity and make its retention feasible. Three chelating agents were compared for the extraction of Se(IV) from aqueous samples: APDC, DDTC and DDTP (Fig. 1). These reagents were chosen because they are selective to Se(IV) under defined conditions and form low polarity chelates. Studies to select which of the reagents would allow the best Se extraction were performed at pH values reported in previous works [6, 25, 26]. These were: 2.5 for APDC, 5 for DDTC and 1 for DDTP. Also, the extraction was evaluated at two concentrations for each chelating agent. The results (Fig. 4a) showed that 100% extraction efficiency was achieved only with APDC, which might be attributed to the lower polarity of the Se(IV) complex formed with this reagent in comparison with those obtained with DDTC and DDTP.

After APDC was selected as chelating agent, the effect of its concentration on analyte extraction was assayed. Different APDC concentrations ranging from  $0.2 \text{ mg L}^{-1}$

to 2000 mg L<sup>-1</sup> (w/v) were evaluated (Fig. 4b). An APDC concentration of 40 mg L<sup>-1</sup> was found to be suitable for total extraction. In order to ensure total formation of the Se(IV)-APDC complex, an excess of APDC was assured using a concentration of 80 mg L<sup>-1</sup>. Furthermore, a decrease in the extraction efficiency was observed at high concentrations of APDC, which can be ascribed to a competition between the free chelating reagent and the Se(IV)-APDC complex for the sorption sites of the [C<sub>12</sub>mim]Br-nanosilica hybrid.

The pH of the sample medium is usually recognized as one of the key factors determining the performance of preconcentration methods, as it strongly influences the extraction of many analytes, especially when the formation of a complex is involved. In this work, the pH played a decisive role in the selective formation of the Se(IV)-APDC complex (Fig. 5). A pH of 4 was optimal for both the efficient extraction of Se(IV) species and the selective complex formation and separation of Se(IV) and Se(VI). It must be pointed out that partial deterioration of selectivity was observed at pH values between 1 and 3. However, by choosing a pH of 4 for the experiments, the determination of Se(IV) and Se(VI) species was highly selective. Both citric acid/citrate and HPO<sub>4</sub><sup>2-</sup>/H<sub>2</sub>PO<sub>4</sub><sup>-</sup> buffers were tested up to 0.1 mol L<sup>-1</sup>, finding no significant effect on analyte extraction. Therefore, a citric acid/citrate buffer was used throughout the experiments.

The selectivity of Se(IV) preconcentration in presence of Se(VI) was evaluated by means of a recovery study. As previously mentioned, Se(IV) was quantitatively extracted at pH 4, while Se(VI) did not form a complex with APDC. The study was performed within the following concentration ranges for each Se species: 0.25 - 25 µg L<sup>-1</sup> for Se(IV) and 2 - 50 µg L<sup>-1</sup> for Se(VI). This resulted in different Se(IV)/Se(VI)

molar ratios from 0.01 to 200. High selectivity and good accuracy were achieved under optimal conditions, with recovery values between 96.0% and 108% for Se(IV).

Also, time values required for efficient complex-formation, extraction and centrifugation were evaluated. The Se(IV)-APDC complex was formed instantaneously, while efficient extraction and centrifugation demanded at least 2 and 3 minutes, respectively. Thus, 10 s for complex formation, 3 min for extraction and 5 min for centrifugation were selected for the development of further experiments. These conditions ensured maximum extraction and a fast preconcentration.

The minimal amount of sorbent material required to obtain the highest extraction efficiency was also studied in this work. Different amounts of the [C<sub>12</sub>mim]Br-nanosilica hybrid were assayed for the extraction of Se(IV) from 5 mL of 200 µg L<sup>-1</sup> Se. Total extraction was achieved with sorbent resulting from 1 to 50 mg of nanosilica as starting material. Therefore, 1 mg of nanosilica was used for experiments. This demonstrates that, despite the existence of other materials with higher surface/mass ratios, (e.g. MCM-41 [27] or SBA-based materials [28]), which would probably also yield excellent results with minimal quantities, the nanosilica used in the present work constitutes an excellent and cost-effective alternative to achieve high extraction efficiency with low amounts of sorbent. Likewise, the Se extraction capacity of the [C<sub>12</sub>mim]Br-nanosilica hybrid was evaluated and it was found to be 470 ± 20 µg of Se(IV) per g of the hybrid material.

#### *3.4 Elution of Se(IV) from the [C<sub>12</sub>mim]Br-nanosilica hybrid material*

The analyte had to be eluted from the solid sorbent before Se determination by ETAAS. Thus, several approaches and eluents were assayed. Ethyl acetate, methyl isobutyl ketone (MIBK), ethanol and methanol were tested as possible organic

extractants. Likewise,  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$  and  $\text{HClO}_4$  were evaluated as acid and oxidant agents with the aim of decomposing the organic chelate and favor the release of Se. Also,  $\text{NaOH}$  and  $\text{KOH}$  were selected to establish an alkaline media that lead to the dissociation of APDC-Se(IV) complex. Furthermore, several combinations of the above mentioned solutions along with the application of radiation emitted from a UV lamp were also studied. Among these possibilities, ethyl acetate showed the highest back-extraction efficiency (50%), most probably as a result of non-polar interactions between the solvent and APDC-Se(IV) complex. Moreover, since ethyl acetate presents the lowest polarity among the assayed eluents, high removal of the adsorbed mixed hemimicelles of  $[\text{C}_{12}\text{mim}]\text{Br}$  can be expected. On the other hand, different practical drawbacks were observed with the rest of the extractants, including: low back-extraction (with inorganic acids and MIBK), incomplete separation of the sorption material after centrifugation (with ethanol and methanol) and significant damage of the analytical sensitivity in the ETAAS determination (with  $\text{NaOH}$ ,  $\text{KOH}$  and  $\text{H}_2\text{O}_2$ ).

As mentioned earlier, the highest back-extraction efficiency achieved with ethyl acetate was 50%, which can be considered as a limited value. Moreover, significant deficiencies in terms of reproducibility were obtained, mainly because of poor dispersion of the solid extractant in the organic phase. To solve this drawback, the addition of a surfactant to the organic eluent was studied. Surfactants of the Triton family, including X-114 and X-100, as well as  $[\text{C}_8\text{mim}]\text{Cl}$  and  $[\text{C}_{12}\text{mim}]\text{Br}$  were evaluated at different concentrations. The highest performance (75% back-extraction and high reproducibility) was obtained with 0.5% (w/v) Triton X-114. This improvement can be explained by a more efficient re-dispersion of the  $[\text{C}_{12}\text{mim}]\text{Br}$ -nanosilica hybrid material upon Triton X-114, which ultimately led to a higher contact area with the eluent and a more efficient back-extraction of Se.



Eluent volume was an important variable to be evaluated because the lower the volume, the higher the preconcentration factor; but efficient contact between the eluent and the sorbent material had to be verified. Different eluent volumes were assayed and optimal conditions involved the use of 100  $\mu\text{L}$  of 0.5% (w/v) Triton X-114 prepared in ethyl acetate. Eluent volumes lower than 100  $\mu\text{L}$  did not allow full re-dispersion and contact with the sorbent material, while higher volumes resulted in a decrease of the preconcentration factor due to significant analyte dilution. Therefore, 100  $\mu\text{L}$  of the eluent mixture was chosen for further experiments. Mixing and contact time stand as two fundamental parameters concerning the elution step. Vortex stirring was discarded at this stage as the sorbent material was adhered to the inner walls of the tubes, avoiding contact with the eluent. Therefore, ultrasound was chosen for efficient re-dispersion of the sorbent material and elution of Se(IV). The elution time and temperature were also optimized for temperatures between 20 and 60  $^{\circ}\text{C}$  (to avoid the evaporation of ethyl acetate) and times ranging from 5 to 30 min. A more efficient and faster back-extraction of Se was observed when the temperature was increased. Consequently, final conditions for elution included ultrasound at 60  $^{\circ}\text{C}$  for 10 min.

### *3.5 Re-utilization of the hybrid nanomaterial*

The possibility of reutilizing the IL-nanomaterial hybrid was studied in this work with 2  $\mu\text{g Se L}^{-1}$  standard solutions. It was observed that the sorption material could be re-used up to 3-fold sorption-elution cycles without loss of extraction efficiency. In order to achieve this performance, a washing step with ethyl acetate was necessary to eliminate any fraction of analyte remaining after elution, followed by a drying step. Finally, considering the time required to recondition the sorbent material, coupled with the fact that an additional volume of organic solvent was required for this task and that

only 1 mg of nanosilica was used, it was chosen not to reutilize the material for further experiments.

### 3.6 ETAAS conditions for Se determination

The optimized temperature program for the determination of Se is presented in Table 1. Problems related to a decrease in the sensitivity during the determination of Se by ETAAS have been previously reported with the Se(IV)-APDC complex, even when Pd was used as matrix modifier. These effects have been attributed to the high volatility of the complex [29], which results in analyte losses during the pyrolysis step. An alternative to classical chemical modifiers is the injection of Cu into the graphite furnace of ETAAS. This element has been proposed as an effective tool to overcome the aforementioned problem, even when high pyrolysis temperatures are used [6]. Therefore, Cu and Pd were evaluated in the range of 5-25  $\mu\text{g}$ . The combination of 10  $\mu\text{g}$  Pd and 10  $\mu\text{g}$  Cu was chosen to achieve the highest analytical sensitivity. Furthermore, different injection volumes of the final eluent solution containing the analyte were evaluated. Taking into account the capacity of the graphite furnace and the sensitivity of the measurements, 60  $\mu\text{L}$  of the 0.5% (w/v) Triton X-114 solution (in ethyl acetate) used for Se elution was found to be optimal.

It is important to point out that the organic matrix, composed of Triton X-114, co-extracted APDC and the IL initially retained onto the nanosilica during functionalization, caused a significant reduction in Se sensitivity when standard ETAAS conditions were applied. Thus, with the aim of optimizing the measurements, different pyrolysis stages were applied to slowly and effectively decompose the matrix, while avoiding analyte volatilization. Three pyrolysis stages were included in the temperature program to achieve this goal. The first two were fixed at 180  $^{\circ}\text{C}$  and 600  $^{\circ}\text{C}$ ; whilst optimization of the last one was studied within the 1000  $^{\circ}\text{C}$  - 1600  $^{\circ}\text{C}$  interval. A

pyrolysis temperature of 1300 °C was found to be the most suitable to achieve the highest signal when a 100 µg Se L<sup>-1</sup> (as Se(IV)-APDC) solution in 0.5% (w/v) Triton X-114 in ethyl acetate was injected. Once the pyrolysis temperature was optimized, the atomization temperature was evaluated between 1700 °C and 2300 °C, and the highest sensitivity was obtained at 1800 °C.

### 3.7 Study of potential interferences

The effect of potential interferences on Se preconcentration and determination was analyzed. For these experiments, solutions of 2 µg Se L<sup>-1</sup> containing diverse concomitant ions at concentration levels at which they might occur in the samples, or higher, were subjected to the optimized procedure and measured by ETAAS. The tolerance limit was defined as the amount of interferent that modified the recovery of Se(IV) in more than 5%. Common cations such as Na<sup>+</sup> and K<sup>+</sup> were observed to be tolerated up to 10000 mg L<sup>-1</sup>, Ca<sup>2+</sup> up to 2000 mg L<sup>-1</sup> and Mg<sup>2+</sup> and Zn<sup>2+</sup> up to 1000 mg L<sup>-1</sup>. Furthermore, anions commonly present in water samples, such as Cl<sup>-</sup> and Br<sup>-</sup> did not interfere in concentrations up to at least 20 g L<sup>-1</sup>, while NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were tolerated in concentrations as high as 5000 mg L<sup>-1</sup>. Moreover, the absorbance signal of the blank measurements was not significantly modified by the potential interfering ions.

### 3.8 Analytical performance

An external calibration curve for the determination of Se(IV) species was drawn by analyzing a series of Se standards submitted to the preconcentration method. A lineal interval was observed from concentrations near the limit of detection (LOD) up to at least 4.10 µg/L with a correlation coefficient of 0.9986. The LOD, calculated as the concentration corresponding to three times the standard deviation of the intercept [30], was 1.1 ng L<sup>-1</sup>. The enhancement factor (EF), calculated as the ratio of the slopes of

calibration graphs after and before preconcentration, was 110. An extraction efficiency of 100% was obtained under optimized conditions. The relative standard deviation (RSD) for six replicate measurements at  $2 \mu\text{g Se L}^{-1}$  was 5.7%.

Furthermore, a comparative evaluation of the analytical performance obtained with the proposed method with respect to others reporting the use of ILs and/or nanomaterials for Se microextraction and preconcentration in water samples is shown in Table 3. Thus, analytical figures of merit, such as the LOD, are comparable or better than previously reported procedures. Also, the consumption index (CI) obtained in the present work, defined as the quotient between the sample volume and the enhancement factor [31], is the lowest compared to the other works. This is a remarkable characteristic of the proposed method as it demonstrates a higher efficiency for the preconcentration procedure and its potential for extending its application to other types of samples that are usually more limited, such as biological. Likewise, in direct comparison with the work by Nyaba et al. with a nano- $\text{Al}_2\text{O}_3$ -Aliquat-336 hybrid, the hereby proposed method shows a more straightforward and facile functionalization process, which brings important advantages such as simplification of the overall process, considerable time reduction, limited consumption of reagents and minimal waste generation. Moreover, among all the methods mentioned in Table 3, the proposed one was applied to highly complex samples such as seawater. Surely, in terms of matrix composition and salinity, this is one of the most complicated aqueous samples to perform elemental speciation analysis on.

### *3.9 Validation studies and determination of Se species in water samples*

With the objective of validation, the proposed method was applied for the determination of total Se in a certified reference material (CRM). SRM 1643e – Trace

elements in water, from NIST, with a declared Se concentration of  $11.97 \pm 0.14 \mu\text{g L}^{-1}$ , was subjected to the optimized procedure, with a previous 6-fold dilution to ensure a final concentration within the linear range of the technique. The Se concentration found in the CRM was  $11.92 \pm 0.19 \mu\text{g L}^{-1}$ , indicating the acceptable accuracy of the method ( $p < 0.01$ ). In addition, a recovery study was performed on all analyzed samples (Table 4), with results in the range of 95.5 – 106% for Se(IV) and 95.0 – 104% for Se(VI). These figures are indicators of the reliability of the proposed method for speciation analysis of inorganic Se, even in complex matrices, such as seawater. Moreover, since no matrix effects were observed in these samples, external calibration was applied for quantification of Se species.

Finally, the method was applied for Se speciation analysis and determination in real water samples, with the results shown in Table 4. Concentrations found for each Se species were in good agreement with those reported by other authors for similar samples [26, 32, 33].

#### 4. Conclusions

Typical limitations shown by many ionic liquids for the development of microextraction techniques, such as those derived from their solubility in aqueous media and low density, have been overcome in this work by using them in conjunction with a nanomaterial. Thus, the first application of a water-soluble IL-nanomaterial hybrid for Se preconcentration and separation of its inorganic species is reported. The formation of mixed hemimicelles of the water-soluble IL  $[\text{C}_{12}\text{mim}]\text{Br}$  onto the surface of nanosilica was demonstrated to be an excellent tool to obtain a highly efficient solid phase extraction material. By means of the developed D- $\mu$ -SPE technique, the use of IL and solvent was minimal, making it an environment-friendly method. Also, an excellent

enhancement factor and outstanding extraction efficiency were achieved and a minimal amount of the IL-nanosilica hybrid was required. Moreover, the successful application of the proposed method for the analysis of complex matrix samples, such as seawater, was demonstrated. Therefore, the proposed method can be considered as a cost-effective, accurate and simple alternative to be implemented in many laboratories working on environmental routine analysis and inorganic Se speciation.

### **Acknowledgements**

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**Figure captions**

**Fig. 1** Chemical structures of the ILs and chelating agents used in this work. (a): [C<sub>8</sub>mim]Cl; (b): [C<sub>12</sub>mim]Br; (c): [C<sub>16</sub>mim]Br; (d): [P<sub>4,4,4,1</sub>]CH<sub>3</sub>SO<sub>4</sub>; (e): ammonium pyrrolidine dithiocarbamate (APDC); (f): sodium diethyl dithiocarbamate (NaDDTC); (g): ammonium diethyl dithiophosphate (NH<sub>4</sub>DDTP).

**Fig. 2** Influence of the type of IL used to prepare the IL-nanosilica hybrid on Se(IV) extraction. (Error bars represent the standard deviation with n = 3)

**Fig. 3** (a) FTIR spectra of IL, nanosilica and IL-functionalized nanosilica. Marked signals (from left to right): 2928 and 2853, 2076, 1108, 834 and 697 cm<sup>-1</sup>. (b) TEM micrograph of [C<sub>12</sub>mim]Br-nanosilica hybrid. (c) TEM micrograph of pure nanosilica.

**Fig. 4** (a) Effect of the type of chelating agent on Se(IV) extraction (light gray: 0.05% (w/v), dark gray: 0.2% (w/v)). (b) Evaluation of Se(IV) extraction upon different APDC concentrations. Concentration of Se(IV) was 2 µg Se L<sup>-1</sup>. (Error bars represent the standard deviation with n = 3)

**Fig. 5** Effect of pH on the selectivity of Se(IV) and Se(VI) extraction. (Error bars represent the standard deviation with n = 3)

**Table 1**

ETAAS instrumental and experimental conditions for Se species determination.

Wavelength	196.0 nm			
Spectral bandwidth	2.0 nm			
Lamp (EDL) current	210 mA			
Matrix modifier	10 $\mu\text{g Pd}$ [as $\text{Pd}(\text{NO}_3)_2$ ]			
	10 $\mu\text{g Cu}$ [as $\text{Cu}(\text{NO}_3)_2$ ]			
Graphite furnace temperature program				
Step	T ( $^{\circ}\text{C}$ )	Ramp time (s)	Hold time (s)	Argon flow ( $\text{mL min}^{-1}$ )
Drying 1	110	1	30	250
Drying 2	130	15	30	250
Pyrolysis 1	180	90	30	250
Pyrolysis 2	600	90	30	250
Pyrolysis 3	1300	10	15	250
Cooling	300	1	15	250
Atomization	1800	0	3	0
Cleaning	2400	1	2	250
D- $\mu$ -SPE conditions				
Sample volume	5 mL			
APDC concentration	80 $\text{mg L}^{-1}$			
pH	4.0			
Nanosilica amount	1 mg			
Extraction time	5 min			
Extraction stirring mode	Vortex			
Eluent	0.5% (w/v) Triton X-114 prepared in ethyl acetate			
Eluent volume	100 $\mu\text{L}$			
Elution time	10 min			
Elution stirring mode	Ultrasound			

**Table 2**

Selectivity of the proposed method for the determination of Se(IV) and Se(VI) species.

Se(VI)/Se(IV) molar ratio	Se(IV)			Se(VI)		
	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)
0.01	25	24.8	99.2	0.25	0.26	104
0.025	10	10.2	102	0.25	0.24	96
0.25	2	0.48	96.0	0.5	1.99	99.5
1	2	1.94	97.0	2	1.95	97.5
5	0.5	0.51	102	2.5	2.40	96.0
10	0.25	0.24	96.0	2.5	2.54	102
50	0.25	0.25	100	12.5	11.9	95.2
100	0.25	0.26	104	25	25.7	103
200	0.25	0.27	108	50	49.2	98.4

**Table 3**

Analytical methods reported for Se preconcentration using ILs, nanomaterials or IL-nanomaterial hybrids.

Method	Sample	Extractant	Speciation analysis	LOD (ng L <sup>-1</sup> )	Enhancement factor (EF)	RSD (%)	Consumption index (CI) (mL)	Sample volume (mL)	Reference
IL-CIAME-UV-Vis	Rice and water	[C <sub>4</sub> mim][PF <sub>6</sub> ]	No	1500	25	1.2	1	25	[9]
Online IL-DLLME-ETAAS	Water and garlic	[P <sub>6,6,6,14</sub> ][Cl]	Yes	15.0	20	5.1	0.267	4.0	[8]
D-μ-SPE-EDXRF	Mineral, tap, lake and sea water, lobster pancreas and pig kidney	Graphene	Yes	32	1013	5.1-6.6	0.049	50	[19]
In situ reduction and adsorption on Pd NPs-ETAAS	Ground water	Pd NPs	Yes	25	100	N.R. <sup>a</sup>	1	100	[5]
SPE-HG-AFS	River water	Nano-TiO <sub>2</sub>	Yes	24	N.R. <sup>a</sup>	Se(IV) = 7.8 Se(VI) = 7.0	4.2	100	[17]
SDSPME-ICP-MS	River water	Aliquat-336-Al <sub>2</sub> O <sub>3</sub> NPs	Yes	1.4	850	1.9	0.059	50	[31]
D-μ-SPE-ETAAS	Tap, rain, river, underground and sea water	[C <sub>12</sub> mim]Br-nanosilica	Yes	1.1	110	5.7	0.045	5.0	This work

<sup>a</sup> Not reported. [C<sub>4</sub>mim][PF<sub>6</sub>]: 1-butyl-3-methylimidazolium hexafluorophosphate; [P<sub>6,6,6,14</sub>][Cl]: Trihexyl(tetradecyl)phosphonium chloride;

CIAME: Cold-induced aggregation microextraction; SDSPME: Suspended dispersive solid phase microextraction.

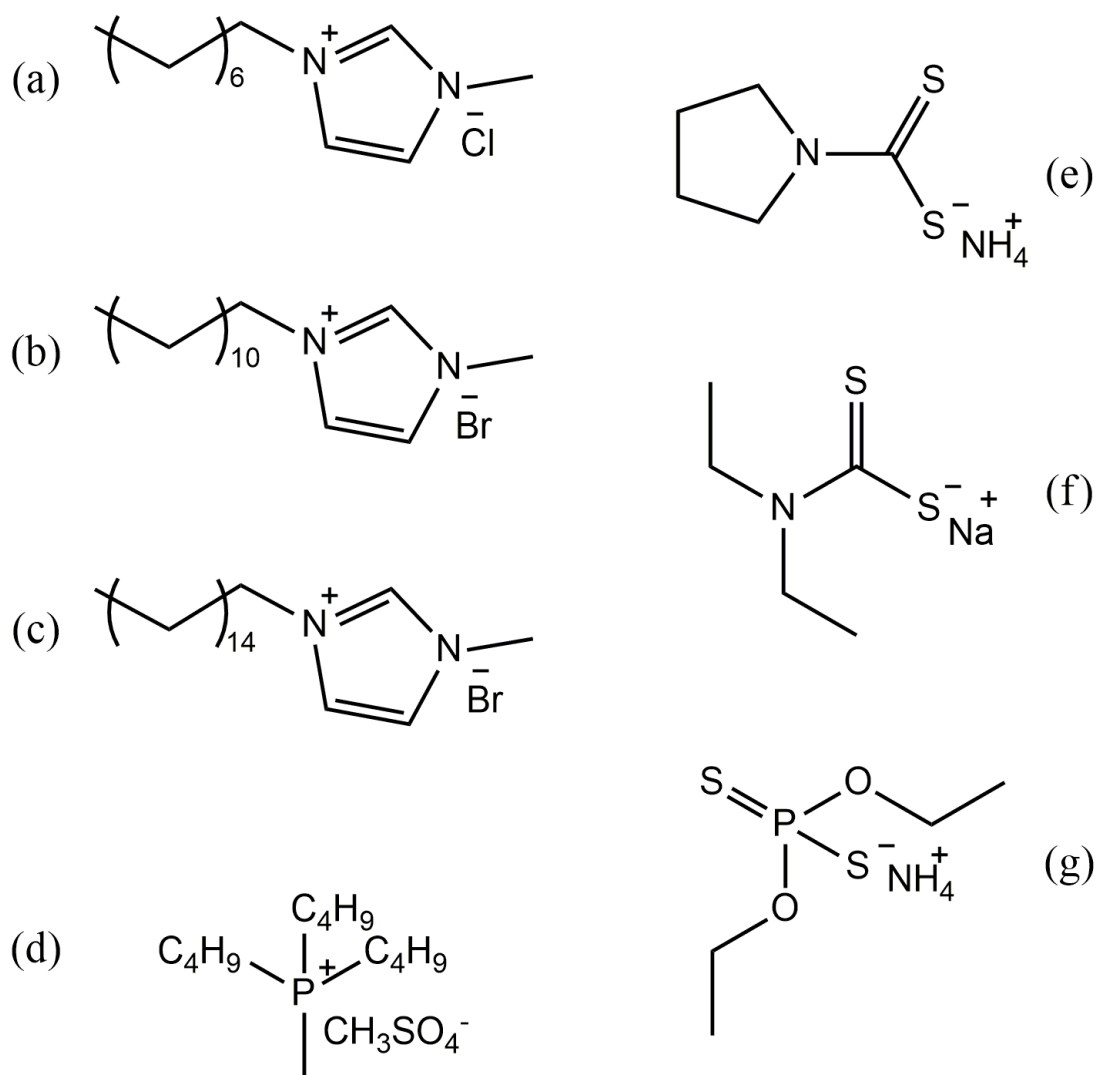
**Table 4**

Results of Se speciation analysis of several water samples and recovery studies (95% confidence interval; n=6).

Water sample	Se added as ( $\mu\text{g L}^{-1}$ )		Se(IV) Found ( $\mu\text{g L}^{-1}$ )	Recovery (%) <sup>a</sup>	Se(VI) Found ( $\mu\text{g L}^{-1}$ )	Recovery (%) <sup>a</sup>
	Se(IV)	Se(VI)				
Tap	-	-	$0.73 \pm 0.03$	-	$0.66 \pm 0.02$	-
	2.0	-	$2.64 \pm 0.09$	95.5	$0.62 \pm 0.02$	-
	-	2.0	$0.75 \pm 0.03$	-	$2.74 \pm 0.08$	104
Rain	-	-	$0.33 \pm 0.02$	-	$0.29 \pm 0.04$	-
	2.0	-	$2.31 \pm 0.07$	99.2	$0.29 \pm 0.03$	-
	-	2.0	$0.32 \pm 0.03$	-	$2.33 \pm 0.08$	102
Underground	-	-	$1.09 \pm 0.06$	-	$0.48 \pm 0.05$	-
	2.0	-	$3.0 \pm 0.1$	95.5	$0.47 \pm 0.05$	-
	-	2.0	$1.10 \pm 0.07$	-	$2.38 \pm 0.08$	95.0
River	-	-	$0.37 \pm 0.02$	-	$0.10 \pm 0.01$	-
	2.0	-	$2.49 \pm 0.08$	106	$0.11 \pm 0.01$	-
	-	2.0	$0.39 \pm 0.03$	-	$2.09 \pm 0.05$	99.5
Sea	-	-	$0.23 \pm 0.02$	-	$0.25 \pm 0.03$	-
	2.0	-	$2.36 \pm 0.09$	106	$0.24 \pm 0.03$	-
	-	2.0	$0.25 \pm 0.02$	-	$2.17 \pm 0.07$	96.0

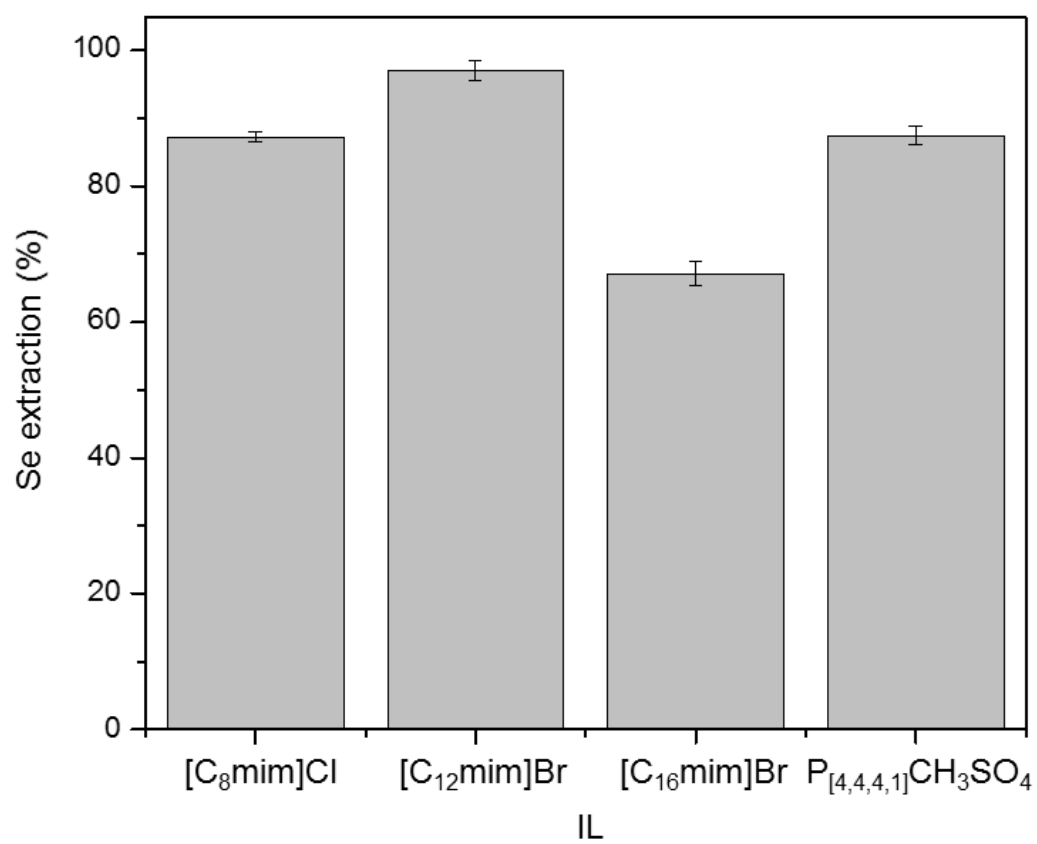
<sup>a</sup> $100 \times [(\text{found} - \text{initial}) / \text{added}]$

Fig. 1



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Fig. 2

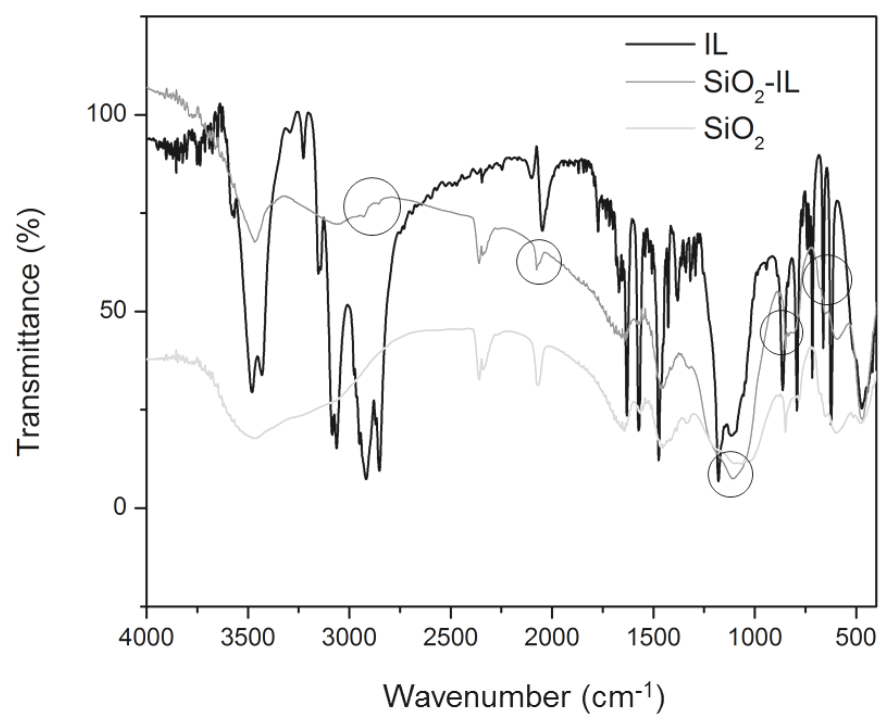


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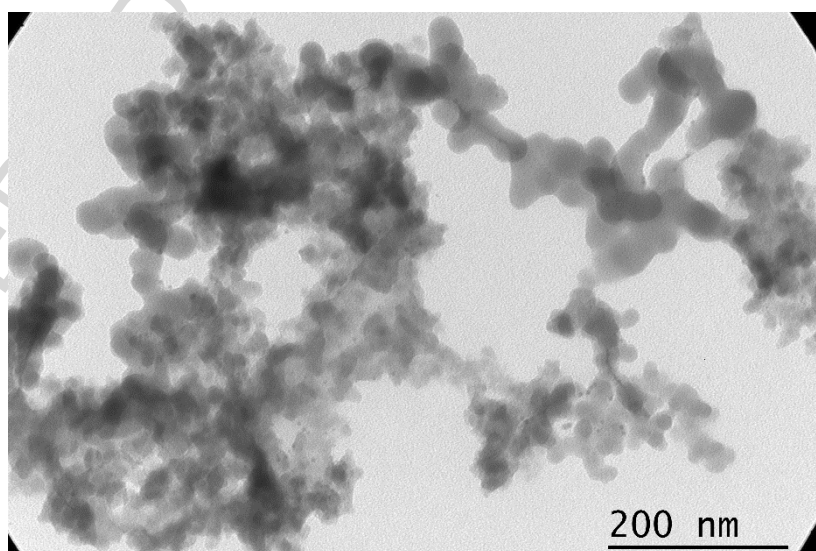


Fig. 3

(a)



(b)



(c)

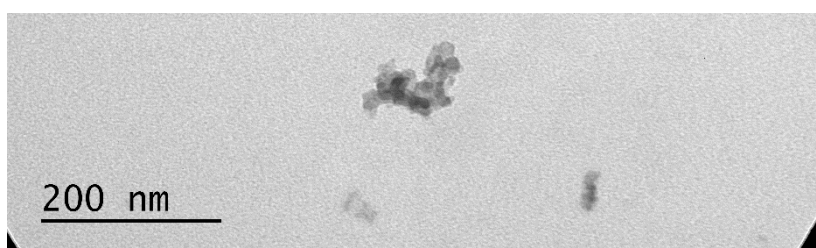
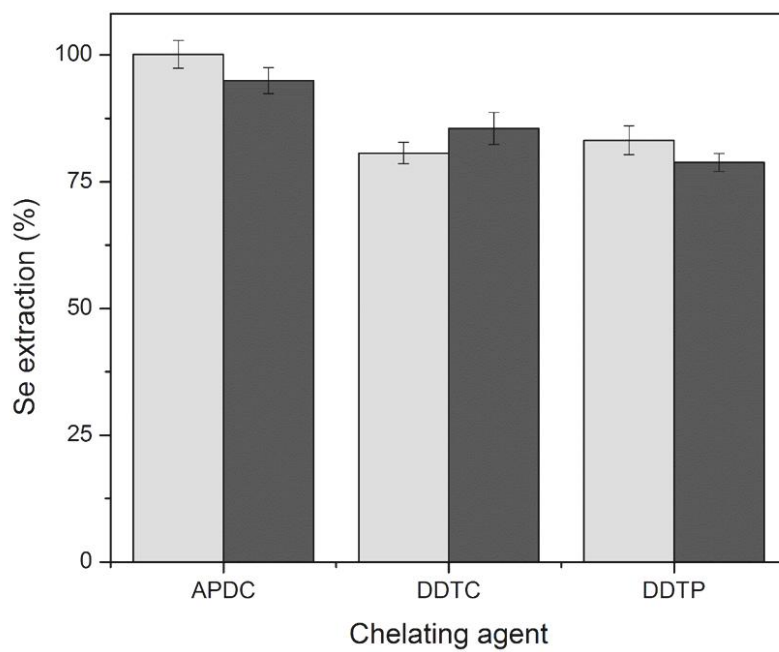


Fig. 4

(a)



(b)

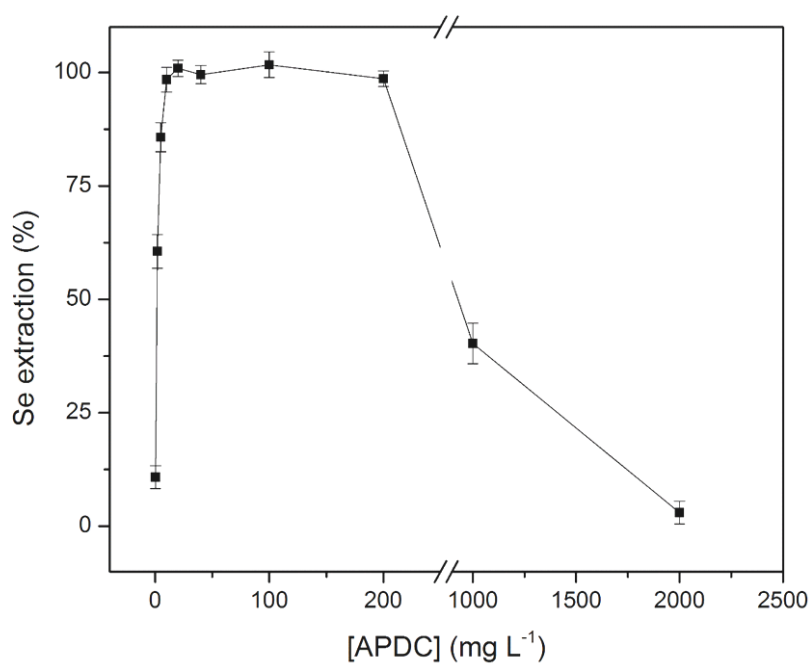
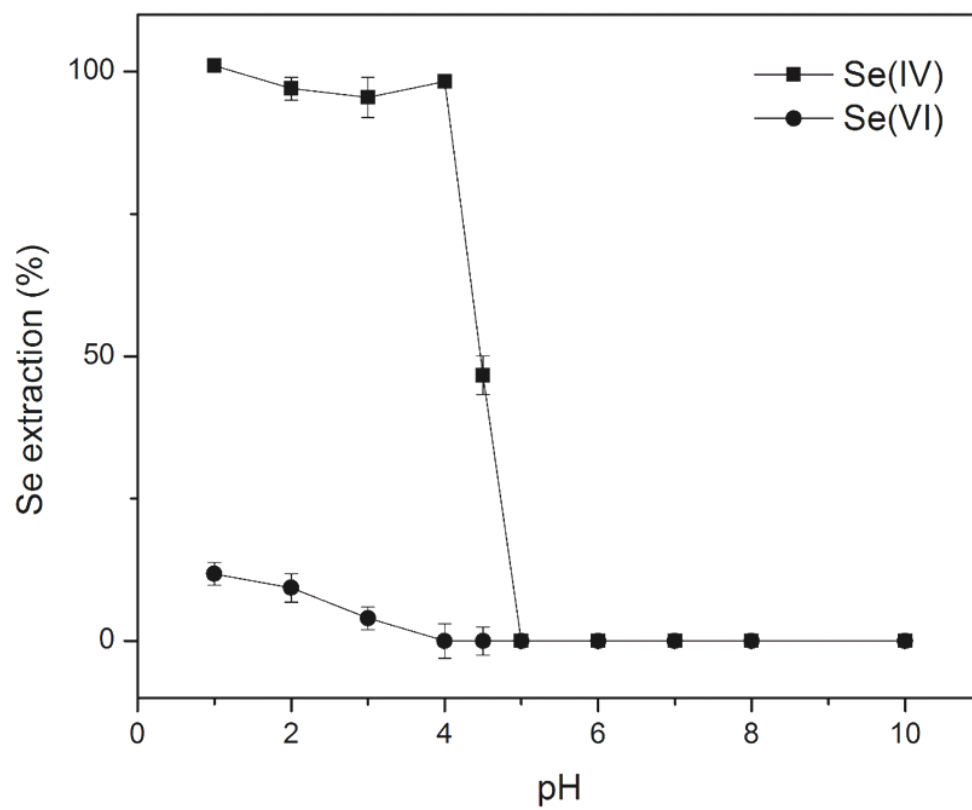
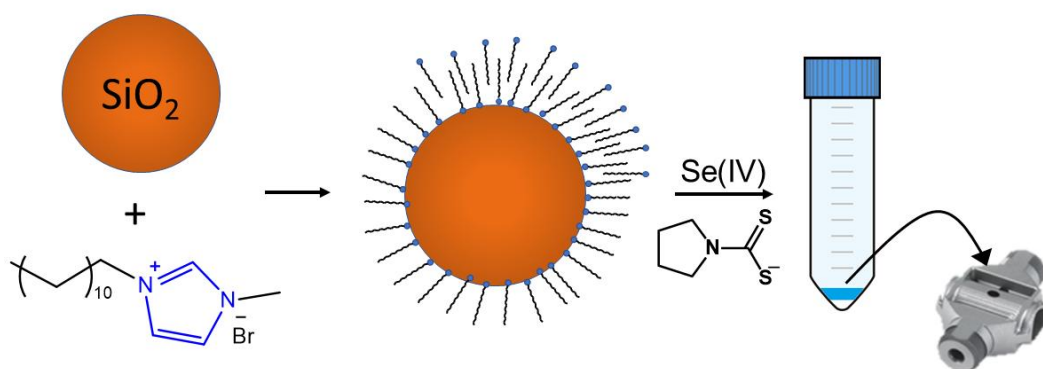


Fig. 5



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Graphical abstract

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**Highlights**

- Novel hybrid material made of nanosilica and a water-soluble ionic liquid.
- Retention mechanism of ionic liquid on nanosilica was studied.
- Combining ionic liquids and nanomaterials solved limitations for microextraction.
- Inorganic Se species preconcentration and speciation analysis were achieved.
- Successful analysis of tap, rain, underground, river and sea water samples.

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