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In situ trapping of As, Sb and Se hydrides on nanometer-sized ceria-coated iron oxide–silica and slurry suspension introduction to ICP-OES

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ABSTRACT

A procedure is developed for the analysis of sub-μg L^{-1} levels of arsenic, antimony and selenium after preconcentration of their hydrides. The study highlights the capability of an aqueous suspension of a nanometer-sized magnetic ceria, in the presence of iodide, to function as a sorbent for the *in situ* trapping and preconcentration of the hydrides of certain metalloids. After extraction, the material is magnetically separated from the trapping solution and analyzed. A slurry suspension sampling approach with inductively coupled plasma-optical emission spectrometry (ICP-OES) is employed for measurements, as the quantitative elution of the adsorbed metalloids is not feasible. The whole analytical procedure consists of five steps: (i) pre-reduction of As, Sb and Se, (ii) generation of the hydrides AsH_3, SbH_3 and SeH_2, (iii) *in situ* collection in the trapping suspension of magnetic ceria, (iv) isolation of the particles by applying a magnetic field, and (v) measurement of As, Sb and Se concentrations using ICP-OES. Under the established experimental conditions, the efficiency of trapping accounted for $94 \pm 2\%$, $89 \pm 2\%$ and $98 \pm 3\%$ for As, Sb and Se, respectively, signifying the effective implementation of the overall procedure. The applicability of the procedure has been demonstrated by analyzing tap and lake water and a reference material (soft drinking water). The obtained analytical figures of merit were satisfactory for the analysis of the above metalloids in natural waters by ICP-OES.

1. Introduction

Antimony is an element of environmental concern due to its toxicity and biological effects and is therefore considered as a priority pollutant by the US Environmental Protection Agency. Dissolved antimony is present in surface water at very low concentration levels, less than 1 mg L^{-1} [1]. Arsenic is widely distributed in the environment both because of natural sources (e.g. volcanic activity) and anthropogenic applications [2]. Considered and classified as human carcinogen substances, inorganic forms of arsenic are the predominant forms found in water [3]. Finally, there has been increasing interest in trace determination of selenium because of its dual role, as an essential nutrient at low concentrations (10–40 mg/ml in serum) or a highly toxic compound (selenosis) at an intake greater than 5 mg/kg of Se (in the mammals of a seleniferous region) [4].

During the last three decades, hydride generation atomic spectrometry has become the most popular technique in atomic spectroscopy to enhance sensitivity and selectivity for the determination of classical hydride forming elements, such as Sb, As and Se and transition and noble metals [5–12]. The process involves a hydride generation device coupled with atomic spectrometry and consists of few distinct steps: (i) generation of the hydride (s), (ii) collection and transfer of the hydride(s), (iii) atomization and excitation and (iv) detection of the signal(s). An essential advantage of hydride generation is the separation of the analyte (s) from the matrix, which enables their preconcentration with a concomitant increase in sensitivity and reduction or even elimination of interference.

Trapping is a relatively simple and cost-effective way to increase sensitivity. Trapping materials should be capable of absorbing, holding and releasing analyte species easily with minimum loss. The metal hydrides and volatile species interact with the trapping material in order to be retained and then released for detection. Atomization after trapping is accomplished either on line or in a separate atomizer to which the released species are transported. Oxidized multiwall carbon-nanotubes have excellent sorbent characteristics, which can be utilized in diverse applications as well as for arsine trapping [13–15].

The use of inductively coupled plasma-optical emission spectroscopy (ICP-OES) as an atomic spectroscopy technique offers the advantages of selectivity, reproducibility and in some cases sensitivity. These advantages are always associated with sample pretreatment and sample introduction to ICP-OES. Slurry introduction

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is well-established for the direct determination of trace metals and metalloids in solids with ICP-OES [16–19]. The introduction of slurry into ICP-OES reduces sample preparation time by combining matrix destruction, atomization and excitation into a single step. It also reduces sample contamination and minimizes analyte losses during preparation or due to incomplete release from the matrix. Slurry introduction can also overcome difficulties relating to sorbent material, which exhibit irreversible retention of analytes. Some researchers have coined the general term "on-bead detection" to describe the concept, which has been properly developed by directly transporting analyte loaded beads into the detection device, for measurement [20,21].

Iron-oxide magnetic nanoparticles are superparamagnetic; hence, they can be removed from a matrix quickly, along with target compounds adhered to them, using a magnetic field [22]. These characteristics make them highly useful in novel separation processes and suitable for the rapid adsorption of the analyte(s) from large volumes of solutions with high enrichment factors [23–25]. Recently, a novel sample pretreatment technique was developed by combining modified silica-coated magnetic nanoparticles with a cationic surfactant and atomic absorption spectrometry for the determination of heavy metals in environmental water samples [26].

Ceria has been reported to have good adsorption capacity for the removal of some anions and high resistance against attacks by acid [27]. Furthermore, cerium is a cost-effective element with rather large reserves among rare earth elements. Ceria nanospheres show an excellent adsorption capacity for heavy metal removal, for instance, As(V) and Cr(VI) [28,29]. The adsorptive properties of ceria vary significantly with morphologies, sizes, shapes and surface areas [30]. Ceria-coated iron oxide–silica has also been demonstrated to be capable of preconcentrating metals and metalloids and can be used for analytical purposes [31].

The principle behind the approach applied herein is based on a seminal work dating back to thirties, which reported the detection of iodide making use of its catalytic effect on the reaction between arsenious acid and ceric sulfate, in sulfuric acid solution [32]. As recently as in the mid-1980s, it was proven that a mixture of Ce^{4+}/I^{-} was efficient adsorbing solution for the simultaneous trapping of hydrides [33]. In this work, a procedure is developed for the analysis of trace concentrations of As, Sb and Se after preconcentration of their hydrides in a magnetic ceria aqueous suspension. Following the *in situ* trapping, the material, free from potential sample matrix components, is magnetically separated from the suspension and analyzed with a slurry suspension sampling approach and ICP-OES. The applicability of the procedure is demonstrated by analyzing tap, lake water and a reference material; the obtained analytical figures of merit are satisfactory. To the best of our knowledge, this approach, which combines the trapping properties of a suspension of magnetic nanometer-sized ceria for certain hydride-forming elements, in combination with slurry sampling into ICP-OES, has not been reported so far.

2. Materials and methods

2.1. Reagents and standards

Anhydrous iron(III) chloride ≥ 99.99% trace metals basis, anhydrous iron(II) chloride 99.998% trace metals basis, tetraethyl orthosilicate 99.999% trace metals basis, cerium (III) nitrate hexahydrate and hexamethylenetetramine ≥ 99.5% for the synthesis of nanosorbent were obtained from Aldrich (Sigma-Aldrich Hellas). Concentrated nitric acid (65%), hydrochloric acid (35%) and sulfuric acid (98%) for analysis as well as potassium iodide (suprapur) were supplied by Merck (Darmstadt, Germany). Dilute nitric acid solutions were used for slurry suspensions in acidic environment. Stock solutions of As(III), Sb(III) and Se(IV) (Merck), at concentrations of 1000 mg L^{-1} were used for the preparation of the final working standards solutions. Working standard solutions were prepared by appropriate dilutions of a mixture with 1.0 M HNO_3 at concentrations ranging from a few ng L^{-1} to 10 μg L^{-1}, for each analyte, depending on the analyte and the mode of calibration. A solution containing 2.0 M HNO_3 was introduced for periodical aspiration and rinsing of the nebulization system. Finally, a soft drinking water reference material (ERM CA021a, LGC Teddington, Middlesex, UK) was used to test the accuracy of the procedure for As, Se and Sb.

A 0.8% (w/v) sodium borohydride solution (99.99% trace metals basis Aldrich) was prepared daily, in 0.6% (w/v) sodium hydroxide stabilizing solution and used as reductant. A 2% (w/v) aqueous KI solution was prepared on daily basis and employed for the trapping of hydrides after mixing with magnetic nano-sized ceria. Thiourea solution was prepared by dissolving the solid chemical (Merck) in water to yield a concentration of 0.5 mol L^{-1}.

Throughout the work, de-ionized water of 18 MΩ cm^{-1} specific resistance was used, which was obtained from a Millipore Simplicity 185 system. All plastic and glassware were cleaned with hot concentrated nitric acid and stored soaked in 10% (v/v) nitric acid; they were rinsed several times with de-ionized water before use.

2.2. Instrumentation

A Thermo Scientific, USA IRIS Intrepid II XDL Thermo Electron Corporation dual viewing inductively coupled plasma – optical emission spectrometer was used, according to the operating conditions, tabulated in Table 1. A concentric nebulizer and a cyclone radial spray chamber were employed with a sample flow rate of 1.85 mL min^{-1}. For the measurements, a sensitive, non-interfered emission line per element was used with the instrument set in the axial mode. The transportation of sample solutions to the concentric nebulizer and to the conical spray chamber of the ICP was performed by a peristaltic pump. Sonication was carried out in an Elma low power sonic bath (Elma GmbH & Co., Singen, Germany) with a nominal power output of 50 W.

A three-channel GBC 3000 HG hydride generator (GBC, Braeside, Australia) was used for a continuous flow vapor system with a U-shaped gas–liquid phase separator. The acidified sample, at a rate of 6.0 mL min^{-1} as well as the alkaline sodium borohydride and 1.0 M HCl, at 2.5 mL min^{-1} were continuously pumped in three separate streams to a junction, where the reaction occurred. A knotted PTFE tubing reactor was used to reduce the dispersion.

Table 1
Operating conditions for ICP-OES measurements of slurry suspension and specifications of the IRIS Intrepid XDL with dual viewing.

Operating conditions – specification	Value-characteristic
Focal length	75 cm
Spectral range	165–1000 nm
Spectral bandwidth	200 nm
Integration time	10 s
Detector	Solid state charge injection device – CID
RF generator	27.12 MHz, crystal controlled
RF generator	2 kW
Plasma viewing	Dual
Shear gas	Argon
Nebulizer	Concentric glass, 28 psi
Spray chamber	Cyclone radial spray
Plasma torch	Fully demountable
Nebulizer gas flow	0.65 L min^{-1}
Auxiliary gas flow	0.5 L min^{-1}
Sample uptake	1.85 mL min^{-1}
Number of measured replicates per sample	3

Pure argon was maintained at 1.1 L min^{-1} for mixing and purging in order to transfer the hydrides to the trapping solution containing 10 mL of the adsorbing material.

2.3. Synthesis and characterization of ceria-coated silica–iron oxide

The details about the synthesis and characterization of iron oxide, silica iron oxide and ceria coated silica–iron oxide can be found in a work published previously [31]. Briefly, final concentrations of 37.5 mM and 0.5 M of $Ce(NO_3)_3 \cdot 6\,H_2O$ and hexamethylenetetramine, respectively in 20 mL de-ionized water, were mixed with 0.3 g of nanometer-sized magnetic-silica and stirred for 24 h, at 90 °C. The magnetic ceria nanopowder obtained by applying an external magnetic field (B-field = 0.25 T), was washed with de-ionized water and ethanol and finally was oven dried.

2.4. Preparation of suspension of magnetic ceria

For the preparation of ceria dispersion, 100 mg of magnetic silica–ceria was first ground with an agate mortar and pestle and then 100 mL of de-ionized water was added. The dispersion was sonicated in an ultrasound bath cleaner (50 W), for 20 min. After that, the obtained dark-orange dispersion was let stand undisturbed for 1 h and the upper less dark dispersion was collected and centrifuged at 1000 rpm with a Hettich Universal centrifuge (Hettich GmbH, Tuttlingen, Germany) for 5 min to remove any largish particles. The resulting homogeneous colloidal aqueous suspension of magnetic ceria was reduced to a final concentration of 2 mg mL^{-1} by removing the bulk water while retaining the sorbent by a neodymium magnet (B-field = 0.25 T). From this suspension, appropriate dilutions were made to study the effect of the dispersion content. The particle size of the as-prepared sorbent was in the range of 100–250 nm [31].

2.5. Analytical procedures

The whole analytical procedure consists of five steps: (i) pre-reduction of As, Sb and Se, (ii) generation of the hydrides AsH_3, SbH_3 and SeH_2, (iii) their *in situ* collection in the trapping suspension of magnetic nano-sized ceria, (iv) isolation of the particles by applying a magnetic field and (v) measurement with ICP-OES. Blank, standard solutions and samples went through the same procedure.

2.5.1. Pre-reduction of As, Sb and Se

The pre-reduction to the hydride-forming oxidation states followed the procedures described elsewhere [34,35]. Briefly, to a beaker containing 50 mL of sample solution, 35 mL of conc. HCl was added so that the final concentration of HCl was ~5 mol L^{-1}. The solution was heated at 90 °C for 20 min and after cooling, 8 mL of 0.5 M thiourea was added. The content of beaker was transferred quantitatively to a 100-mL volumetric flask and filled up to the mark with de-ionized water. The solution was analyzed within 30 min after the addition of thiourea.

2.5.2. Hydride generation and in situ trapping of hydrides

The samples, standard and blank solutions already treated as described above, were propelled along with sodium borohydride and hydrochloric acid into the hydride generator to effect the formation of hydrides. A 10-mL solution containing 1% KI and 2.5 mg of magnetic ceria were placed in a 12-mL test tube with a diameter of 2 cm, wherein the outlet of the hydride generator was submerged. The generated hydrides were trapped *in situ* in the suspension and the sample matrix was driven to the waste in the gas–liquid separator. The trapping solution was prepared just before its use to avoid preliminary oxidation of iodide. After the completion of the entrapment, the nanosorbent with the retained analytes was harvested *via* an external magnetic field (B-field = 0.25 T) and the system was prepared for the next sample. Between sample loadings, 10 mL of 10% (v/v) HNO_3 were flushed through the hydride generator in order to wash the system and minimize potential memory effects. The trapping efficiency was calculated as the percent ratio of the mass of analyte in 50 mL of the original sample to its mass in the final volume of slurry.

2.5.3. ICP-OES measurements

After separation, the remaining nano-sized material was used for the preparation of slurry by dispersing it in 2.5 mL of 1.0 M HNO_3 under ultrasonication (50 W) for 5 min to maintain the stability of the slurry. For ICP-OES measurements, the slurry was directly introduced into the plasma, where the particles were disintegrated and the target analytes were atomized and excited. After aspiration of each suspension, a 2 M HNO_3 solution was flushed through the nebulizer-torch system to remove any residual sample, prevent clogging and minimize the chance of any possible memory effect.

2.6. Sample preparation

Tap water samples were taken from Ioannina water-supply system and surface water was sampled form Pamvotis Lake located in the vicinity of Ioannina town. Samples were filtered through paper filters, then acidified to 0.1% (v/v) by the addition of concentrated HNO_3 and stored at 4 °C, until analysis.

3. Results and discussion

3.1. Pre-reduction of metal ions

It is well documented that the difference in efficiency to produce hydrides depends on the state of oxidation of the element. The presence of higher oxidation states of As, Sb and Se makes it necessary to convert them to hydride-forming oxidation states, before the generation of hydrides. Hexavalent selenium is frequently reduced to the tetravalent state by heating the sample with HCl. However, heating with concentrated HCl does not reduce pentavalent As and Sb. Thiourea, in combination with HCl has been proven to be an efficient pre-reduction agent in the multi-element determination of the hydride-forming elements by ICP-OES. Therefore, in our study, established conditions for the reduction of the elements of interest were adopted drawing upon previous investigations, without undertaking further research on this subject [34,35]. The pre-reduction conditions adopted were the following: final concentration of HCl in the sample, 4.9 mol L^{-1}; heating, 90 °C for 20 min; addition of 8 mL of 0.5 M thiourea, after cooling.

3.2. Study of the operational parameters

The formation and *in situ* entrapment of hydrides in magnetic ceria suspension was studied by optimizing the concentrations of the reducing reagent and hydrochloric acid and the trapping conditions. A one-at-a-time method was used for this purpose, changing one parameter each time while keeping the others constant. The best signal-to-noise (S/N) ratio of ICP-OES was chosen as the optimization criterion. Each sample was measured in triplicate and the measurements were acceptable, if relative standard deviation (RSD) was less than 5%.

3.2.1. *Optimization of hydrides generation*

Hydrides were formed in aqueous solutions by the reaction of analyte ions in the acidic medium with the reducing agent, which was a solution of sodium borohydride stabilized with NaOH. Based on the recommended conditions of the instruction manual, 0.6% (w/v) sodium borohydride in 0.6% (w/v) sodium hydroxide (as stabilizer) was used initially as the reductant to study the conditions of hydrides generation [36].

For the acidification of the reaction medium, HCl was added to the sample at the appropriate concentration. Because of the pre-reduction procedure applied in a previous step, the concentration of HCl introduced into the hydride generation is definitely lower than the initial one (it was calculated to be 4.2 M, considering the final dilution to 100 mL). To accommodate the need for additional HCl for the generation of hydrides, different concentrations of acid up to 3.0 M were studied and propelled through the respective channel of the hydride generator. For arsenic, an increase in the analytical signal was observed with the simultaneous increase in the concentration of HCl up to 1.0 M, acquiring a plateau thereafter. At a constant HCl concentration of 1.0 M, the analytical signal increased with a rise in borohydride content to 0.6% and reached a plateau, when 0.7% sodium borohydride was employed. To compensate for the presence of other hydride-forming metals, 0.8% sodium borohydride could be selected. However, higher concentrations, close to 1.0%, led to excessive foaming making their use prohibitive.

Similar changes in the analytical signal were observed with the determination of antimony. At 0.8% sodium borohydride, when the concentration of the acid was kept below 1.0 M, the signal was low. That, however, was not the case with selenium, which exhibited constantly decreasing analytical signal at increased concentrations of HCl above 1.0 M. As a compromise, 1.0 M HCl and 0.8% sodium borohydride were used along with the acidified sample, as described above, in order to generate the hydrides of the three elements.

3.2.2. *Study of the trapping conditions*

The ceria-iodide system was chosen because of its fast and efficient oxidizing action, based upon the catalytic effect of iodide [32]. Ceria has high oxygen mobility at its surface and a large oxygen diffusion coefficient, which facilitates the conversion between valence states Ce^{4+}/Ce^{3+} allowing oxygen to be released or stored in its crystalline structure [37,38]. Therefore, it is most likely that the catalytic and oxygen storage/release capacity of the ‘oxygen-rich’ adsorbing material are responsible for the *in situ* trapping of hydrides. Based on the above, it can be hypothesized that the volatile hydrides are oxidized on the surface of ceria and the metalloids released would form the respective oxyanions, which remain adsorbed on the positively-charged particles below their point of zero-charge (6.9) [31] and are then removed from the aqueous sample along with them.

The effect of KI content up to 2.0% as trapping medium was studied using 2.5 mg of iron oxide–silica–ceria. Fig. 1 demonstrates the role of KI in the trapping suspension. In the absence of KI, no emission signal is noticed and therefore the trapping of metalloids does not occur. A final content of 1.0% is efficient to obtain the highest emission signal on ICP after trapping, highlighting the role of iodide ions. Acidification of the trapping suspension, containing 1.0% KI with sulfuric acid up to concentrations of 1.5 M was detrimental to the trapping process and therefore it was not used for subsequent experiments.

Next, the signal intensities in ICP-OES were studied as a function of the content of magnetic silica–ceria in the trapping medium. Employing 50 mL of a mixture of As (4.0 μg L^{-1}), Sb (2.0 μg L^{-1}) and Se (2.0 μg L^{-1}), an optimum of nanosorbent amount was achieved by increasing the amount of ceria in the trapping medium. Emission signals increased steadily until the dispersed nano-sized material reached the content of 2.0 mg in 10 mL of a dispersion containing 1.0% KI, thus demonstrating sufficiency to trap the formed hydrides. The enhancement of signal with the increase in the ceria content can be reasonably explained by the increasing number of active sites of particles available for analytes. Increasing further the quantity of nano-sized ceria does not improve the emission signal. However, a suspension of 2.5 mg/10 mL was chosen as trapping medium since it can compensate for higher concentrations of metal ions in real samples. As regards bare iron oxide and iron oxide–silica, which constitute the backbone of the magnetic ceria, they are almost inactive as trapping materials of the hydrides under investigation (Fig. 2) signifying the dominant role of ceria on the trapping of hydrides.

Stripping of metalloids from solid substrates could presumably be facilitated by an acid. In the present study, 30%, 35% and 45% of As, Sb and Se, respectively were possible to be measured with an eluent consisting of 2.0 M HNO_3. The incomplete elution implies no involvement of exchange process between the adsorbed metalloids and H^+. To overcome the problem of irreversible trapping, the introduction of sample slurry into the plasma could be a potential solution. In this context, the amount of the nanosorbent was investigated in association with the resuspending volume for the slurry suspension introduction. The optimal conditions were established by varying the dispersing volume of 1.0 M HNO_3 while keeping constant the amount of the sorbent, at 2.5 mg. High and stable signal intensities, acceptable standard deviations and hence, reproducible sample pretreatment with low risk of clogging of the aspiration system of ICP-OES were achieved when the content was 2.5 mg/2.5 mL of 1.0 M HNO_3. Slurry nebulization is, therefore, viable since it is able to prepare samples of fine particle size, in a reproducible manner. If the acid volume is increased, the slurry of particles, albeit less viscous, is not as homogenous as required for an acceptable precision because of the insufficient mixing and unstable homogenization of slurry [39]; at the same time, the preconcentration factors deteriorate. Volumes lower than 2.5 mL do not ensure smooth emission signals. The volume of 2.5 mL, which was finally used, results in a theoretical enrichment factor of 20 considering a 50-mL initial sample volume.

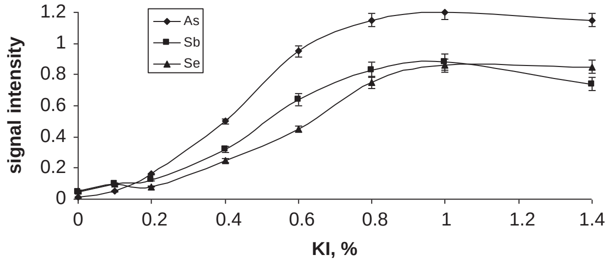

Fig. 1. Effect of KI on the trapping efficiency of magnetic nanometer-sized ceria on As, Sb and Se hydrides.

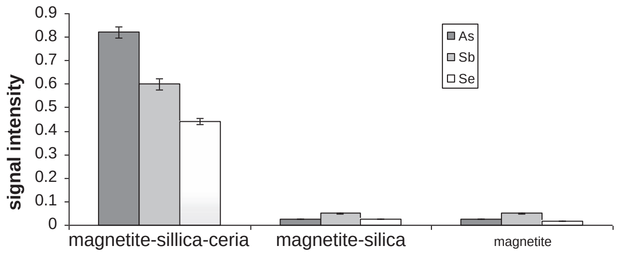

Fig. 2. Iron oxide–silica–ceria, iron oxide–silica and iron oxide as adsorbing phases for As, Sb and Se hydrides.

The stability of slurry was ensured by applying a 5-min ultrasonication before aspiration and maintaining it during aspiration. In this way, the particles were homogeneously distributed throughout the slurry and remained stable during the whole analysis, as was seen by naked eye.

3.3. *Effect of ionic strength and humic acids*

The effect of ionic strength on the generation of hydrides and their retention was studied using solutions of NaCl up to concentration of 500 mM. The preconcentration in ceria–KI suspension, in the presence of NaCl, had no noticeable effect ($RSD < 5\%$) on the monitored ICP-OES signals for As, Sb and Se. Therefore, the nanosized material based hydride trapping method can be practical and effective for all three metalloids studied, in most of the environmental water samples.

The effect of humic acid due to its occurrence in natural waters was studied up to a concentration of 10 mg L^{-1}. Practically no alteration to the ICP signals of the studied elements was noticed. Normally, the concentration of humic acid in freshwaters is lower than the maximum values examined in this work [40] indicating that its presence poses no thread to the reliability of the method if is going to be applied to real-life aqueous samples.

3.4. *Spectral interferences and calibration curves*

Ceria-modified iron oxide–silica, by its very nature, has the advantage over other sorbents, of not containing any organic matter, which may be responsible for any deterioration of atomization capability [41]. On the other hand, Fe, which is in overwhelming excess in the sorbent, is a line-rich element and the introduction of the nanometer-sized particles into the ICP in slurry form, may cause spectral interference to the signal of metalloids and therefore systematic errors. It has already been demonstrated that the presence of ceria composite material in plasma does not influence the atomization capacity and the overall performance of the method, when the slurry is aspirated [31]. In this work, the spectral bandwidth at 200 nm, where the prominent spectral lines of As, Se and Sb are located for ICP-OES measurements (Table 2) was found to be 7 pm. Relevant spectral scans, which were received over the region around the spectral lines, showed that an intense line at 206.791 nm corresponding to Fe is properly separated by the respective emission line of Sb. Therefore, the determining factor of the procedure for quantitation is the step of hydrides trapping.

Three-element calibration standards were used for all elements studied. Five-point calibration curves were drawn for the most sensitive spectral line of each analyte, using aqueous standard solutions, after proper trapping and formation of slurries in 2.5 mL of 1.0 M HNO_3. At the same time, de-ionized water was pumped through the hydride generation system to define the blank slurry, for slurry suspension introduction into ICP-OES. In this way, standard solutions and samples of the same matrix and chemical form were run to obtain qualitative performance data with ICP-OES. The slopes together with their corresponding standard errors, the linear correlation coefficients and the measuring wavelength for all elements are presented in Table 2.

The overall efficiency of the *in situ* trapping on ceria-modified iron oxide–silica and hydride generation were evaluated by comparing the mass of analytes in 50 mL of the original sample with their mass in the final volume of slurry. It was found that under the established experimental conditions, the efficiency of hydride trapping accounted for 94 ± 2%, 89 ± 2% and 98 ± 3% for As, Sb and Se, respectively, as compared with ICP-OES measurements of metal standard solutions. This signifies the effective implementation of the overall procedure. The analytes were quantitatively retained by the sorbent during the trapping step and under these circumstances the sample volume did not exceed the retention capacity of the sorbent. Moreover, keeping constant the concentration of the metalloids and doubling the volume of the sample, the trapping efficiency was invariably high but the time required was unusually long for routine uses.

3.5. *Analytical figures of merit and applicability*

The quantitation limits of the method for the studied metalloids – based on ten times the standard deviation of five blank solutions – are given in Table 2 and confirm the applicability, at sub-μg L^{-1} levels. The precision of the proposed slurry suspension microextraction method was evaluated by calculating the relative standard deviation obtained for five repetitive analyses of a 0.90 μg L^{-1} multi-element 50-mL solution and are 2.9%, 3.0% and 4.1% for As, Sb and Se, respectively.

The enrichment factors, defined as the ratio between the analyte concentration in the enriched solution and in the original one, are 19, 18 and 19 for As, Sb and Se, respectively. Considering the high signal intensity even in the presence of the slurry in plasma and the effective trapping of the studied elements, satisfactory enrichment is anticipated, which guarantees high sensitivity. In order to test the applicability of the proposed method, tap and lake water were collected and analyzed. The results, as the average of three separate determinations, are shown in Table 3. The accuracy was evaluated by determining the recoveries of the analytes from tap and lake water spiked at two concentration levels i.e. three and five times the quantitation limits of each element. The overall recoveries obtained after slurry suspension were calculated to be 95%, 96% and 102% for As, Sb and Se, respectively. A soft drinking water reference material was worked up and further demonstrated the accuracy of analytical results obtained by using the present method (Table 3).

A comparison of the analytical performance of the proposed method with other analytical approaches for the determination of As, Sb and Se is shown in Table 4. The analytical figures of merit of the method are comparable with those attained by other approaches involving different sample pretreatment procedures. Besides, the nano-sized iron oxide–silica–ceria is easy to prepare and the developed method is environmentally benign as it is free

Table 2
Spectral lines of ICP-OES measurements, trapping efficiency, calibration curves and limits of quantitation.

Analyte	Spectral line	Slope of calibration curve[a]	Efficiency of trapping (%)[b]	LOQ (μg L^{-1})	Correlation coefficient
As	189.042	0.04 ± 0.01	94 ± 2	0.44	0.9989
Sb	206.833	0.07 ± 0.02	89 ± 2	0.26	0.9989
Se	196.090	0.05 ± 0.01	98 ± 3	0.29	0.9985

[a] Slope ± standard error of calibration curve.
[b] Percent ratio of the mass of analyte in 50 mL of the original sample to its mass in the final volume of slurry.

Table 3
Mean concentrations ($n=3$) of As, Se and Sb in environmental water samples (μg L^{-1}).

Analyte	Tap water	Lake water[a]	Soft drinking water[b]
As	nd	0.65 ± 0.03	9.7 ± 0.5
Se	0.44 ± 0.03	14 ± 1.0	9.2 ± 0.5
Sb	0.31 ± 0.02	2.9 ± 0.2	5.1 ± 0.3

[a] pH: 8.0, dissolved oxygen: 7.5 mg L^{-1}.
[b] ERM CA021a. Certified values: As, 9.9 μg L^{-1}; Se, 9.5 μg L^{-1}; Sb, 4.9 μg L^{-1}.

Table 4
A comparison of analytical performance data with other data reported in the literature.

Sample	Technique	Preconcentration technique	Metals	Detection limits ($\mu g\ L^{-1}$)			Precision (%)	Recovery (%)	References
				As	Sb	Se			
Marine sediment and fortified lake water	ICP-OES	–	As, Hg, Se, Tl, Sn, Bi	3	–	4.3	–	–	[42]
Standard solutions	HG-ETAAS	Headspace single drop microextraction	As	0.045	–	–	8.6	–	[43]
Fortified lake water and seawater	FI-HG-ICP-MS	Silica gel functionalised with 1,5-bis(di-2-pyridyl) methylene thiocarbonohydrazide	Sb, Bi, Sn	–	0.011	–	1.1–1.5	97.0–107.5	[44]
Fresh water and marine sediment	FI-HG-ICP-TOFMS	–	As, Bi, Ge, Sb, Se, Sn	0.04	0.09	0.25	1.7–6.7	95.4–101.6	[45]
CRM, tap water	HG-ETAAS	CNT microcolumn	As	0.001	–	–	6.3	97.6–102.8	[46]
Seawater, groundwater	HG-AAS	–	As, Sb, Se	0.05	0.03	0.06	6.9–12.0	96.5–99.0	[47]
Tap water, lake water	HG-ICP-OES-slurry sampling	Magnetic nanoceria	As, Sb, Se	0.15	0.09	0.10	2.9–4.3	89–98	This work

of organic solvents and chelating agents and has the merits of simplicity and fast trapping kinetics.

4. Conclusions

The nano-sized ceria-coated silica–iron oxide was employed, for the first time, to trap As, Se and Sb hydrides capitalizing on the property of ceria to adsorb them in the presence of iodide, under certain experimental conditions. After *in situ* trapping, the material was magnetically separated from the suspension and analyzed with a slurry suspension sampling approach and ICP-OES. The preconcentration-separation and detection method was evaluated and demonstrated to be successful for the determination of trace amounts of the above elements in natural waters by ICP-OES. The process enables separation of As, Sb and Se from sample matrix, preconcentration and elimination of potential interfering substances. Analysis of real samples demonstrated the absence of interfering effects during hydride generation, trapping process and ICP measurements. The detection limits obtained are adequate for ordinary analyses and are similar to or even better than others found in the bibliography.

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