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Synthesis and characterization of a novel mesoporous silica functionalized with [1,5 bis(di-2-pyridyl)methylene thiocarbohydrazide] and its application as enrichment sorbent for determination of antimony by FI–HG–ETAAS

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ABSTRACT

A simple, sensitive, low-cost and rapid flow injection (FI) on-line sorption preconcentration/hydride generation system has been synchronously coupled to an electrothermal atomic absorption spectrometer (ETAAS) for the determination of trace amounts of Sb in aqueous environmental samples (river and sea water samples). The system is based on retention of the analyte onto a micro-column filled with a novel mesoporous silica functionalised with [1,5 bis(di-2-pyridyl) methylene] thiocarbohydrazide placed in the injection valve of the FI manifold. The adsorption capacity of the resin for Sb was found to be 160.8 μmol g^{-1}. Chemicals and flow variables affecting the continuous preconcentration of antimony, the direct generation of antimony hydride and the final determination of this element by ETAAS were evaluated. The optimized operating conditions selected were: sample pH 5.0, sample flow rate 2.5 ml min^{-1}, eluent flow rate 5.4 ml min^{-1}, eluent 2.0% thiourea in 4.0% nitric acid. Under the optimum conditions, the calibration graph obtained was linear over the range 0.025–2.5 μg L^{-1}. At a sample frequency of 20 h^{-1} and 120 s preconcentration time, the enrichment factor was 22. The detection limit of the method (3σ) was 1 ng L^{-1} for a 5.0 mL sample volume and the precision was 0.9% (RSD) for 11 replicate determinations at 1.0 μg L^{-1} Sb. The preconcentration factor and detection limit can be improved by increasing the preconcentration time, which can be increased at least up to 5 min. The accuracy of the proposed method was demonstrated by analyzing two certified reference materials and by determining the analyte content in spiked environmental water samples. The results obtained using this method were in good agreement with the certified values of the standard reference materials and the recoveries for the spiked river and sea water samples were 91.3–109.9%.

1. Introduction

The importance of trace elements as environmental contaminants and their diffusion at planetary level over the past centuries has already been highlighted with studies performed on various environmental matrices [1]. Trace elements are released into the environment by a large number of natural mobilization processes, and also during the last few centuries by a number of uncontrolled human activities [2]. This has clearly been seen by analyzing a variety of environmental records, such as marine and lake sediments, snow, ice [3]. We have focused our attention on natural waters [4,5] because of the importance of these matrices in the global transport of trace elements.

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 (EPA) [6]. Dissolved antimony is present in surface water at very low concentration levels, typical concentrations of Sb in unpolluted water samples are less than 1 μg L^{-1} [7]. However, the concentrations can be substantially elevated to the 100 μg L^{-1} level in the vicinity of anthropogenic sources [8]. For this reason, the monitoring and subsequent removal of antimony from aqueous solution has been compulsory due to its toxicological effects [9,10].

Since the concentration of this element in water is very low, high sensitive analytical techniques are required, and so

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inductively coupled plasma mass spectrometry (ICP-MS) [11], inductively coupled plasma atomic emission spectrometry (ICP-AES) [12] and electrothermal atomic absorption spectrometry (ETAAS) [13] have been recommended for this purpose. Although ICP-MS is considered the most appropriate technique due to its super high sensitivity its application to monitoring surveys is rather limited by the high operational and maintenance cost involved with the use, especially when a large number of samples must be analyzed. Therefore, the provision of analytical protocols, that combines optimum analytical features with low analysis cost, is a continuous challenge for the analytical community. ETAAS appears as an attractive option because it is a well-established technique available in practically all laboratories, however high concentrations of matrices, such as Na, K, Mg and Ca, in seawater can cause serious spectral interferences, which can seriously affect the accuracy of the analytical results. On the other hand, its selectivity and detection power are sometimes inadequate to comply with the requirements for the determination of trace elements in natural water samples. For this reason separation and preconcentration steps are a frequently used sample pretreatment technique for the determination of low concentrations of elements by ETAAS.

One of the most frequently used methods for the preconcentration of antimony is liquid–liquid solvent extraction [14]. Ammonium pyrrolidine dithiocarbamate (APDC) and N-benzoyl-N-phenylhydroxylamine are the ligands usually employed in the liquid–liquid extraction [15]. As an alternative to liquid–liquid extraction, solid phase extraction (SPE) or liquid–solid extraction can be also used for antimony pre-concentration. SPE has been developed as a convenient and inexpensive alternative to other extraction techniques and is widely used for the separation and pre-concentration of analytes [16]. Commonly, SPE is applied in flow-injection analysis (FI). The extraction columns filled with anion or cation exchanger, complex forming resin, activated or modified alumina among others are connected on-line to the detector. The retention of Sb in conventional solid supports, such as C_{18} [17], knotted reactor [18], Al_2O_3 [19] or C_8 [20] can be selectively done after complexation with several organic compounds such as APDC. Also Polyorgs 31 complexing sorbent [21], Duolite GT-73 [22], chelating celluloses [23], AmberliteXAD-8 [24], high surface area titanium dioxide [25], silica gel chelating resin [26,27] have been used as solid supports.

The choice of selective adsorbent is a critical factor to obtain full recovery and high enrichment factor. In the last years, mesoporous silica has been proposed as a novel solid phase extractant. These materials are characterized by their high surface areas, uniform and controllable pore sizes, and the periodic order of their pore packing. A high concentration of surface Si–OH groups has been regarded as a strong point for binding guest molecules [28,29]. The modification with organic chains has become a larger focus of interest in such applications. The primary adsorption mechanism of ions to mesoporous silica is perceived to be surface complexation with functional groups, so the performance is mainly determined by the nature and the concentration of these groups, which could be different due to the modification and functionalization of the mesoporous silica. Nowadays, work has progressed in developing diverse chemical varieties of mesoporous silica which suggests a wide range of possible SPE materials, including different chemical possibilities and applications in SPE methods.

On the other hand, hydride generation (HG) in situ trapping of the analyte in the graphite surface is other alternative technique to reduce salt effect on the analytical signal. HG as a means of sample introduction with the elements into volatile compounds offers some advantages: separation of the analyte from the matrix and also higher sensitivity and selectivity by removing non-volatile interferent species which remain in solution. In addition, “in situ” trapping procedures which utilize the graphite furnace both a trapping device and an atomization cell have been described [30]. These procedures provide the most sensitive ETAAS methods available for the determination of volatile hydride forming elements. In general, HG of classical hydride forming elements is negatively affected by the presence of some transition and noble metals that may produce severe interferences [31]. In order to avoid interference effects the use of additives is largely employed. Recently a comprehensive and critical review of analytical methods developed during the last years for interferences remove in HG is presented by Ramesh et al. [32]. Numerous inorganic and organic acids as well ligand/donor species combined with different reaction conditions (pH, amount of THB, HG apparatus design) have been adopted in order to achieve better control of interferences. Thiourea is one of the most popular and effective masking agent in the HG determination of antimony. Furthermore, it is well documented that the difference in efficiency to produce hydrides depends on the state of oxidation of the element; for this reason the pentavalent form of antimony is usually reduced to its trivalent oxidation state before its determination. L-Cysteine, potassium iodide and thiourea are the prereducing agents most frequently used for previous reduction of Sb(V) owing to the low acid concentrations required in the hydride generation [33].

The purpose of this study is to develop a matrix removal/enrichment system for the determination of antimony in environmental water samples. For this purpose, a novel chelating resin, [1,5 bis(di-2-pyridyl) methylene thiocarbohydrazide] bonded to mesoporous silica (DPTH-ms) was prepared and studied. In the present study, we have probed that the DPTH-ms micro-column is a convenient pre-concentration device for determining traces of Sb in seawater as well as in other natural waters prior to its determination by HG–ETAAS.

2. Experimental

2.1. Instrumentation

Elemental analysis was performed with a LECO CHNS-932 Elemental Analyzer (LECO, Michigan, USA). The Mass spectrum was obtained with a Trace DSQ Mass spectrometer from Thermo Electron Corporation (Massachusetts, USA), the sample was introduced by means of a DIP (direct introduction probe). IR Spectra were recorder on a Perkin Elmer Spectrum 100 FTIR spectrometer (Perkin Elmer, Concord, Canada), samples were measured by using potassium bromide pellets, in which the concentrations for the samples were 2% (wt/wt) approximately.

A Perkin Elmer Zeeman AAnalyst 600 atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT, USA) with a longitudinal Zeeman effect background correction system in conjunction with a Perkin Elmer FIAS-400AS manifold was used in this study. A Perkin Elmer hollow cathode lamp operated at 15 mA was used as the radiation source. The antimony absorbance was measured at 217.6 nm with a 0.2 nm spectral band pass. A transversely heated graphite tube with integrated pyrolytic graphite platforms was

Table 1
Optimized furnace program used for Sb determination.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (mL min^{-1})
1	20	1	1	250
2	20	1	1	250
3	2000	0	5	0
4	2300	1	3	250

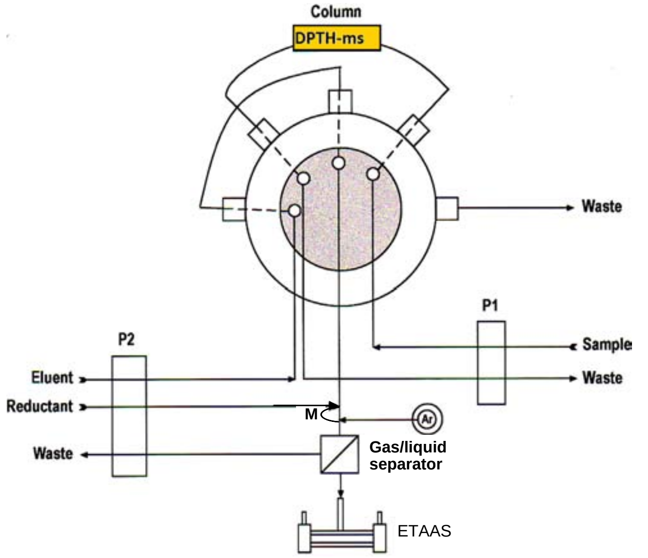


Fig. 1. Schematic diagram of FI system for the preconcentration and separation of antimony; P1 and P2, peristaltic pumps; M, mixing coil; Ar, stream of argon and W, waste.

employed as atomizer. This atomizer was used with thermal treatment for permanent modifier deposition according to the procedure reported by Moreda Piñeiro et al. [34]. The graphite furnace temperature program is shown in Table 1 and the flow manifold of the FI–HG–ETAAS system is shown in Fig. 1 which consists of two peristaltic pumps, a reagent mixing chemifold, an expansive gas–liquid separator and a five-port way rotatory valve with a PTFE membrane of 0.5 μm pore diameter. The FI system and the ETAAS instrument were coupled and operated completely synchronously.

The micro-column containing the DPTH-ms was a glass tube (25 mm × 3 mm i.d.) packed to a height of 0.7 cm; at both ends of the micro-column, polyethylene frits (Omnifit, Cambridge, UK) were fixed to prevent material loss. This micro-column was placed in the sample loop of the five-port rotary valve.

2.2. Reagents and samples

High purity reagents were used in all experiments. All plastic and glassware were cleaned with hot concentrated nitric acid and stored soaked in 10% (wt/wt) nitric acid, they were rinsed several times with water immediately before use. Doubly de-ionized water (18 MΩ cm) obtained from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout.

For the synthesis of DPTH-ms, 3 aminopropyltriethoxysilane, and diglutaric aldehyde were purchased from Fluka (Buchs, Switzerland). Brij 76C18EO10, tetraethoxysilane (TEOS), thiocarbohydrazide and di-2-pyridil ketone were supplied by Aldrich Chemie (Steinheim, Germany). Ethanol and toluene were obtained from Carlo Erba (Milano, Italy). Hydrochloric and nitric acid were supplied by Merck (Darmstadt, Germany). A standard 1000 mg $L^{-1}$for Sb (III) solution Merck (Darmstadt, Germany) was used. Standards of working strength were made immediately prior to use by appropriate dilution as required. Doubly de-ionized water obtained from a Milli-Q water system Millipore (Bedford, USA) was used throughout. A pH 5 buffer was prepared by mixing 14.8 mL of sodium acetate 0.2 M Merck (Darmstadt, Germany) and 35.2 mL acetic acid 0.2 M Merck (Darmstadt, Germany). A 0.5% (wt/vol) sodium tetrahydroborate (III) (THB) Merck (Darmstadt, Germany) solution, prepared in 0.1% (wt/vol) NaOH Merck (Darmstadt, Germany), was used as reductant and a 2% (wt/vol) thiourea Merck (Darmstadt, Germany) solution in 4% (wt/wt) nitric acid was used as eluent.

The certified reference materials (CRMs) analyzed to determine the accuracy of the proposed procedure were from National Research Council of Canada (NRCC): TMDA 54.4 fortified Lake Water, and SLRS-5 Estuarine Water. Seawater and river water samples were collected in polypropylene bottles (previously cleaned by soaking for 24 h in 10% (wt/wt) nitric acid and finally rinsed thoroughly with ultrapure water before use). Samples were immediately filtered by using a membrane of 0.45 μm pore size cellulose nitrate filters from Millipore (Bedford, MA, USA). After that, the samples were stored in low density polypropylene bottles at 4 °C as recommended by Method 3010B from the Environmental Protection Agency (USA), for less than 3 days until analysis. For the analysis of these samples, aliquots of 20 mL of sample were placed in volumetric flasks of 25 mL, then 2.5 mL of buffer of pH 5 and de-ionized water were added up to the mark.

2.3. Synthesis of chelating resin

Mesoporous silica phase was synthesized at room temperature by using a non-ionic surfactant as the structure-directing agent. In a typical preparation, as this, 4.0 g of Brij 76 was dissolved in 20 g of water and 80 g of 2 M HCl solution with stirring. Then 8.80 g of TEOS was added to that homogeneous solution with stirring at room temperature for 20 h. The solid product was recovered, washed, and air-dried at room temperature. The synthesis is described elsewhere [35]. Yields are typically 95% (based on silicon).

Mesoporous silica was refluxed with 6 M HCl for 3 h to remove metals. Washed with de-ionized water and dried in an oven at 180 °C for 24 h. Activated mesoporous silica (ms) (10 g) was suspended in 100 mL of 10% (vol/vol) 3-aminopropyltriethoxysilane in dry toluene. The resulting product, aminopropyl mesoporous silica (AP-ms), was filtered off and washed consecutively with toluene and ethanol. This product was mixed with 100 mL of 3% (vol/vol) diglutaric aldehyde in de-ionized water and the reaction mixture was refluxed for 4 h. The solid obtained (GlutAP-ms) was filtered off, washed with de-ionized water and mixed with 1.5 g of thiocarbohidrazide previously dissolved in 100 mL of de-ionized water; ten drops of glacial acetic acid were added. After boiling and refluxing for 24 h the corresponding derivative (TCHGlutAP-ms) was obtained and suspended in 180 mL of 2% (wt/vol) di-2-pyridil ketone in ethanol. After refluxing for 24 h, the resulting product (DPTH-ms) was filtered off, washed with ethanol and dried in an oven at 50 °C. The reaction for DPTH-ms formation is shown in Fig. 2.

2.4. Treatment of the graphite tube with a permanent modifier

Pyrolytically coated graphite tubes were pretreated by injection 50 μL of a 1000 mg L^{-1} Ir standard solution into the tube, and submitting it to a temperature program based on a work reported by Moreda Piñeiro et al. [34].

Each injection was dried slowly by heating the atomizer at 150 °C with a ramp rate and hold times of 30 and 40 s, respectively. Then a second dried step at 200 °C with a ramp rate and hold times of 20 and 30 s was used. Following this, a reduction step at 2000 °C was applied during 5 s. This procedure was repeated 25 times, resulting in a total mass of 1250 μg of the modifier deposited on the tube graphite wall. A tube treated in this manner can pass through about 500 firing cycles.

2.5. Preconcentration and elution procedure

The FI manifold used for on-line preconcentration and elution is shown in Fig. 1. The FI system was operated as follows: during

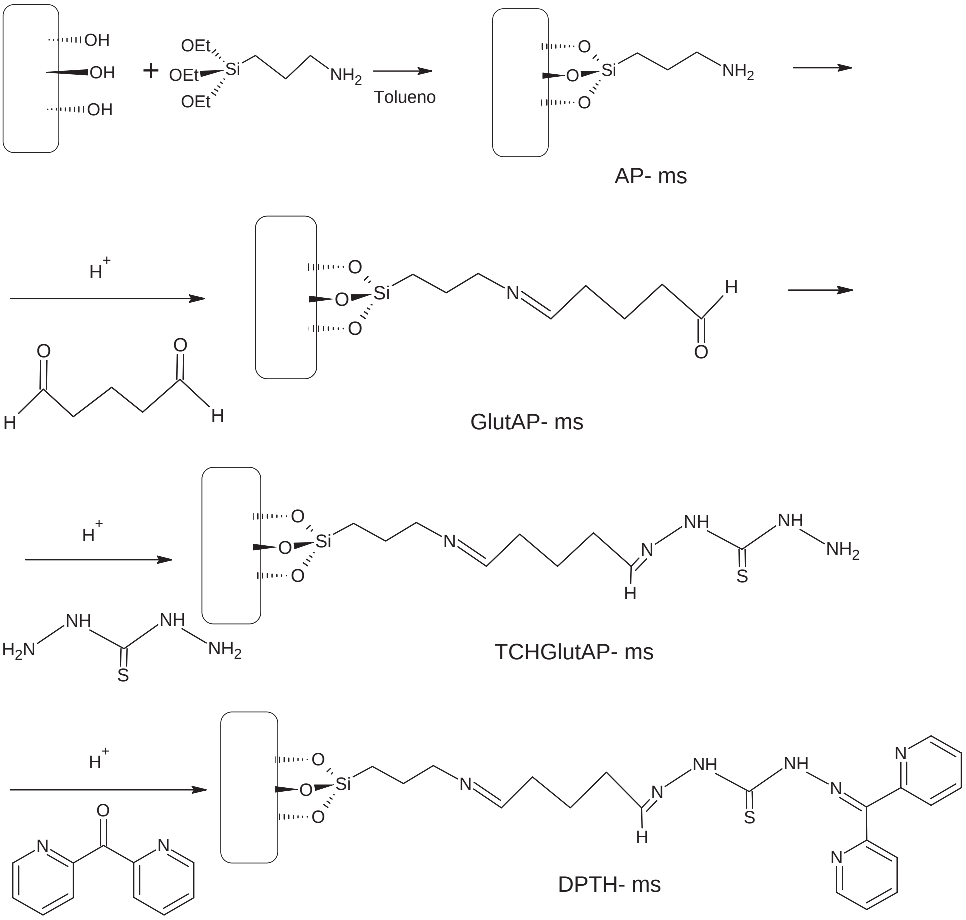


Fig. 2. Reactions for DPTH-ms formation.

the 120 s sample loading period, valve in the "fill" position, a 2.5 mL min^{-1} flow of sample (standard or blank) at pH 5 was pumped (via pump P1) through the micro-column (located in the loop of the valve). The antimony was retained on the sorbent micro-column while the sample matrix components were directed to waste. At the beginning of the 40 s elution stage, the valve position was changed and the sample pump P1 was stopped, when the valve is in the "inject" position, the eluent passes through the micro-column. Thus, the accumulated antimony was eluted at an elution rate of 5.4 mL min^{-1} and merges with 5.4 mL min^{-1} flow of reductant in the mixing coil, M, where direct generation of antimony hydride takes place. The gas generated and the solvent were then passed into the gas–liquid separator which provides a separation of gases from liquid. The liquid is drained and the generated hydride is swept into the graphite furnace by a stream of argon (70 mL min^{-1}) during 40 s. With this procedure, the FI system and the ETAAS instrument are coupled and operated completely synchronously. The furnace temperature program for antimony determination is shown in Table 1.

3. Results and discussion

3.1. Characterization of synthesized resin

The contents of carbon, hydrogen, nitrogen and sulfur in the DPTH-ms and AP-ms (aminopropyltriethoxysilane-mesoporous silica) measured with the CHNS elemental analyzer were 28.86% C; 4.813% H; 5.731% N; 1.997% S for DPTH-ms and 16.43% C; 5.494% H; 7.334% N, 0.0% S for AP-ms. The finding sulfur confirmed that the synthesis had been effective. It is interesting that the nitrogen-to-sulfur ratio is less than that predicted by theory; this may be largely explained to the fact that the yields of the different stages of the synthesis were limited and it is highly probable that intermediate structures existed between each stage.

The infrared spectrum (KBr pellets) is complicated because the large mass of silica and the aromatic portion of the molecule produce numerous bands, the overlap of which makes detailed assignments difficult. The band at 1280 cm^{-1} was attributed to C=S stretching and the bands at 1590 cm^{-1} and 2990 cm^{-1} were assigned to C=N and N–H stretching, respectively. These bands were assigned on comparison with the spectrum of pure DPTH as reference material. The spectrum exhibits several other bands, which are weak and difficult to assign, but those discussed above appeared to be the most useful.

The mass spectrum has been recorded by evaporation until 250 °C from DPTH-ms and the attribution of some peaks are showed in Table 2.

3.2. Adsorption capacity of the DPTH-ms resin

Adsorption capacity is an important factor to evaluate the sorbents, because it determines how much DPTH-ms is required for a given solution. The sorption capacity of the resin was determined by the batch process by equilibrating about 30 mg of DPTH-ms resin with solutions of 25 mL of 50 mg L^{-1} of individual metal ions for 24 h at pH 5 and pH 8 at 20 °C (without shaking). After this, the DPTH-ms was filtered from the standard and the analyte remaining in solution was determined by ICP-OES. The sorption capacity of the resin for each metal ion was calculated

Table 2
Identification of some peaks of the MS of DPTH-ms.

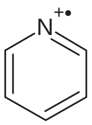
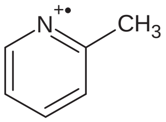
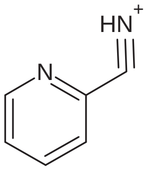
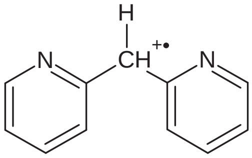
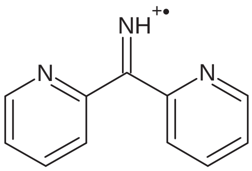
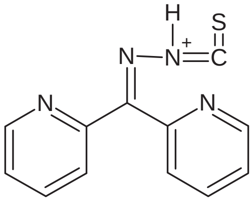
Attributions	Peak (*m*/*z*)
	79
	93
	105
	169
	183
	241

Table 3
Adsorption capacity of the resin at two different pH's.

Element	pH 5 (μmol g^{-1})	pH 8 (μmol g^{-1})
Ni	393.5	77.1
Sb	160.8	108.9
Cu	625.8	250.1
Co	337.0	264.3
Mn	718.4	382.6
Zn	193.1	–
Cr	421.5	–
Cd	189.4	158.6
Hg	155.4	45.1
As	80.6	33.4
Pb	99.5	–

from the difference between the metal ion concentrations in the solution before and after sorption. The absorption capacity calculated for Ni, Sb, Cu, Co, Mn, Zn, Cr, Cd, Hg, As and Pb are shown in Table 3.

On the other hand, the resin is stable over a wide pH range and the micro-column packed with this resin has a practically unlimited lifetime without the demand for generation, hence, the material can be stored and applied conveniently.

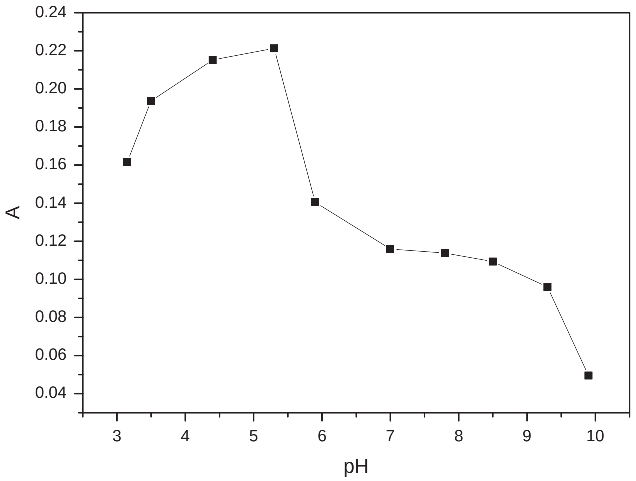


Fig. 3. Influence of pH on the preconcentration of antimony (peak height).

3.3. *Optimization of the experimental variables*

The configuration of the FI-system, and the effect of different parameters on the accumulation and recovery of Sb was studied in order to optimize conditions for achieving the best results. A one-at-a-time method was used for this purpose, changing one parameter each time while keeping the others constant. For measurements to be useful, it was considered that a relative standard deviation (RSD) of about 5% was acceptable. The best signal-to-noise (S/N) ratios were chosen as the optimization criterion. The scanning of each sample was repeated three times. The chemical and FI variables, and furnace program of the manifold were optimized using a standard solution of 1.0 μg L^{-1} Sb (III).

3.3.1. *Furnace program*

The trapping time onto the coated graphite tube for antimony hydride was investigated; the results obtained showed that a trapping time of 40 s was necessary, because the signal increased with the trapping time up to 40 s, and above this time the signal remained constant.

The atomization temperature (using a hold time of 5 s) was investigated. This temperature was varied over the range 1800–2000 °C in experiments conducted with a 1.0 μg L^{-1} Sb (III) solution of Sb, while running a blank in parallel. The optimum atomization temperature was determined to be 2000 °C because at lower temperature, broader peaks were observed. The effects of the temperature and hold times, on the efficiency of trapping antimony hydride onto the coated graphite tubes were also examined and it was found that these parameters have little influence on the analytical signal within the ranges 20–420 °C and 1–20 s, respectively. Thus, an adsorption temperature of 20 °C was selected, while a hold time of 1 s was adopted as being optimum (Table 1).

3.3.2. *Effect of pH on the collection of antimony*

Since the solution pH affects the extent of complexation with DPTH-ms, which in turn determines the percentage of analyte retained by the resin, the preconcentration of Sb from solutions buffered at different pH was studied. The pH from 3.0 to 5.0 was adjusted using sodium acetate–acetic acid buffer and from 5.0 to 10 using borax-boric acid buffer. As can be seen in Fig. 3, an optimum pH range between 4.4 and 5.3 was obtained, and pH 5.0 was selected for the determination of Sb. The influence of buffer volume was also studied. The results showed that more than 5.0 mL of buffer solution added in 50.0 mL of sample solution, no obvious variation took place in the extraction yield. A 5.0 mL aliquot of buffer solution was added in all subsequent experiments, and this volume was increased with the sample volume, proportionally.

3.3.3. Selection of eluent and its concentration

Choice of a suitable eluent is very important for the successful coupling of an FI on-line sorption preconcentration manifold to HG–ETAAS. A highly efficient eluent should be used to minimize the time required for quantitative elution and to facilitate eluate delivery. Three parameters were evaluated for their influence on the elution of the analyte from the resin, the type and concentration of the eluent, the eluent flow rate and the elution time. HCl, HNO_3, thiourea and their mixtures were tested as eluent. A mixture of thiourea and nitric acid was chosen as the eluent owing to its effective elution of the adsorbed antimony, its easy direct delivery through the peristaltic pump tubing and its low toxicity. The effect of HNO_3 concentration for elution of the analyte from the micro-column was studied by increasing HNO_3 concentration from 2% to 6% (wt/wt) and the results showed that under the specified experimental conditions a concentration of 4% (wt/wt) or higher of HNO_3 gave the maxima signal-to-noise ratios, and a concentration of 4% (wt/wt) was selected for further experiments. Keeping constant the HNO_3 concentration, the effect of the thiourea concentration for elution of analyte from the micro-column was also studied. Thiourea has demonstrated to be a good complexing agent that helps the elution of the retained analyte. In addition, thiourea stabilizes the trivalent form of antimony in the hydride formation and it might be useful to mask interfering metal ions. The thiourea concentration ranged between 0.5 and 5.0% (wt/vol). The Sb displayed maximum desorption with 2.0% (wt/vol) thiourea, higher concentrations of reagent did not lead to significant changes. Taking everything into account, it was decided to use 2.0% (wt/vol) thiourea in 4.0% (wt/wt) HNO_3 as the working concentration of the eluent. The effect of elution flow rate was studied between 2.7 and 6.6 mL min^{-1} for an elution time of 40 s, (the minimum time necessary for the trapping of the Sb in the graphite tube). The experimental results showed that an improvement in the signals was observed with the increase of the eluent flow rate up to 5.4 mL min^{-1}. High backpressures were not found due to the short time (40 s) employed for the elution. For further experiments an eluent flow rate of 5.4 mL min^{-1} was selected.

3.3.4. Optimization of antimony hydride generation

For complete conversion of antimony to the corresponding hydride, a considerable excess of TBH reagent is required. The THB concentrations studied were between 0.2% and 1.0% (wt/vol). An increment of the S/N ratio with the increase of THB concentration was observed up to 0.5% (wt/vol). Too high concentration of reductant could generate excessive hydrogen gas, which produced foam and consequently droplets reached the membrane of the gas liquid separator wetting it. Furthermore, the NaOH concentration to stabilize THB solution was also studied. The experimental results showed an improvement in the S/N ratios with the increase of NaOH concentration up to 0.1% (wt/vol). The reason for this observation should be attributed to the fact that the reduction by $NaBH_4$ is preferentially performed in acidic medium, nevertheless, the employment of NaOH solution is simply to stabilize the $NaBH_4$ by avoiding its adverse reaction with water during the storage.

The influence of the reductant flow rate was studied as well. The effect of reductant flow rate was studied between 2.7 and 6.6 mL min^{-1}. The experimental results showed that an improvement in the signals was observed with the increase of the reductant flow rate up to 5.4 mL min^{-1}. For further experiments an eluent flow rate of 5.4 mL min^{-1} was selected.

3.3.5. Effect of sample flow rate

The sample flow rate should be optimized to ensure quantitative retention along with minimization of the time required for sample processing. The influence of the sample flow rate was studied in the range 1.8–2.5 mL min^{-1}, using a constant flow rate of eluent and reductant of 5.4 mL min^{-1} and a constant sample volume of 3.60 mL, in order to keep constant the mass of analyte arriving at the micro-column. The kinetic properties of the sorbent as well as the flow impedance created in the micro-column should be considered and properly balanced in the choice of an appropriate sample loading flow rate. The experimental results showed an improvement in the signals with the increase of loading flow rate up to 2.5 mL min^{-1}, flow rates higher than 2.5 mL min^{-1} were not tested due to high backpressures encountered. For further experiments, a sample loading flow rate of 2.5 mL min^{-1} was employed.

3.3.6. Effect of the sample loading time

The effect of the sample loading time on the analytical signal of a 1 $\mu g\,L^{-1}$ of antimony was studied at a sample flow rate of 2.5 mL min^{-1}. The signal increased linearly at least up to 5 min preconcentration time. The sensitivity was increased by increasing the sample loading time; nevertheless, when the sample loading time is longer results in lower sampling frequency. In addition, it is less cost-effective since it will require the use of larger quantities of chemicals. Taking this into account, a pre-concentration time of 2 min was selected to achieve a good sensitivity and sampling frequency. A longer loading time can be employed for samples with low concentration of analyte.

3.4. Performance of the method

Under the optimal conditions described above, performance data of the on-line HG–FI–ETAAS system for antimony were obtained. For 2 min preconcentration time and a sample flow rate of 2.5 mL min^{-1}, the following linear calibration graph was obtained, $y = 0.324x + 0.010$ (y, absorbance signal/peak height; x, concentration/$\mu g\,L^{-1}$), from 0.025 $\mu g\,L^{-1}$ to 2.5 $\mu g\,L^{-1}$of Sb (III) with a regression coefficient of 0.9902. Peak height was chosen as analytical signal because the slope of the calibration graph was higher than with peak area (and so the sensitivity). A complete cycle of the FI-operation is ca. 180 s which gives a sample throughput of about 20 h^{-1}. The detection and determination limits, defined as the concentration of analytes giving signal equivalents to three and ten times, respectively, the standard deviation of the blank signal plus the net blank intensity, were 1 ng L^{-1} and 25 ng L^{-1}, respectively. Blanks of 0.0070 ± 0.0011 were obtained. The precision for aqueous standards evaluated as the relative standard deviation for eleven determinations (RSD $n = 11$) was 0.9% for 1.0 $\mu g\,mL^{-1}$ and the enrichment factor (EF) defined as the ratio of the slopes of the linear section of the calibration graphs with and without preconcentration (changing the micro-column by other unfilled) was 22.0. The preconcentration factor and quantification limit can be improved by increasing the preconcentration time which can be increased at least up to 5 min.

Although is difficult to compare the figures of merit for the developed method directly with results from other workers, because of different experimental conditions such as column dimensions, sample flow rate, etc., some estimates can be made. For comparison, the analytical performance data of some recent similar methods reported in the literature were listed in Table 4. As can be seen, both precision and sensitivity (detection limit) for

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

Sample	Technique	Preconcentration	Analytes	Eluent	Detection limit ($\mu g\ L^{-1}$)	Presicion (%)	Recovery (%)	Ref.
Fortified lake water and seawater	FI–HG–ICP-MS	DPTH-gel	Sb,Bi,Sn	4% HNO_3	0.011	1.1	97–107.5	[36]
Lake water	FI–HG–ETAAS	A quarts tip and PTFE capillary	Sb	Helium	0.015	0.9	93	[37]
Sea and host spring water	HG–ETAAS	–	As, Cd, Sb, Se	HCl	0.05	Lower than 10.0		[31]
Seawater	HG–ETAAS	Tip quartz capillary tube	As, Sb, Se	HCl 6.5 M	0.006	Lower than 12.0	Close to 100	[38]
Enviromental samples	FI–ETAAS	PSTH-Dowex	Sb	HNO_3 2M	2.0	3.1	98	[39]
Seawater	ETAAS	Titanium dioxide	As, Sb, Se	HNO_3 2M	0.15	1.0	72–107	[40]
Lipid-rich enviormental samples	FI-HG-AAS	–	Sb	10% HCl	0.021	6.0	–	[41]
Water samples	ETAAS	Liquid–liquid microextration	Sb, As	CCl_4	0.05	3.5		[42]
Natural water samples	ETAAS	Quartz capillary	Sb	HCl 1M	0.02	6.0	92	[43]
–	HG–AAS	Gas chromatographic column	Sb, As	0.1 M HCl	0.03	4.0	–	[44]
–	HG–GD–OES with HC and FC		Sb, As	HCl 2M	0.7	4.5		[45]
Sediment	FI–HG AAS		As, Sb, Se	4.7 HCl	0.121	4.4	96.0	[46]
Commercial homeopathic products	FA–HG–GPMAS		Sb	30% HCl	60.0	1.2	97.5–103.0	[47]
Natural water	ETAAS	Activated carbón	Sb	H_2O	5.0	3.0–5.3	97.0–110.0	[48]
Enviromental and pharmaceutical samples	AAS		Sb	HCl 1M	0.23	5.0		[49]
Natural water	SPE–FI–HG–ETAAS	DPTH-ms	Sb	4% HNO_3 2% Thiurea	1×10^{-6}	0.9	109.9–91.3	This work

Table 5
Analytical applications. Antimony determination in several certificated and non certificated environmental waters.

Water type	Certified ($\mu g\ L^{-1}$)	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)
SLRS-5	0.3[a]	–	0.31 ± 0.07	
TMDA 54.4	25.7 ± 0.5	–	27.8 ± 0.01	108.2
		20.0	47.8 ± 0.07	100.5
		40.0	66.8 ± 0.02	99.8
Seawater		–	0.07 ± 0.03	–
		0.5	0.59 ± 0.03	104.6
		1	0.983 ± 0.005	91.3
		1.5	1.621 ± 0.005	103.4
River water		–	0.399 ± 0.001	–
		0.5	0.92 ± 0.03	105.0
		1	1.38 ± 0.07	97.8
		1.5	2.03 ± 0.02	109.9
		2.0	2.44 ± 0.07	101.9

[a] Information value given in the certified table of the certified reference material.

the developed method were better to those reported using sorbent online separation/preconcentration.

3.5. Analytical applications

The accuracy and applicability of the proposed method to the analysis of environmental water samples were studied by examining two certified reference materials of environmental waters, TMDA 54.4 Fortified Lake Water (diluted 100-fold prior to use) and SLRS-5 River Water, and river and sea water samples collected from Málaga areas. The results, as the average of three separate determinations, are shown in Table 5. It can be seen that the determined concentrations of the reference samples are in agreement with the certified values, according to the *t*-test for a confidence level of 95% and they show sufficiently high recoveries. Because these standard reference samples have included trace elements such as transition metals, it can be said that there is not any interference from these metals at ng mL^{-1} concentrations. For the seawater and river water samples collected locally, an alternative verification process using the method of standard additions was conducted. From the results in Table 5, it was found that, the concentration values of the Sb added to sea water and river water samples were recovered by using DPTH-ms. Furthermore, in the sea water case, the accuracy achieved for the spiked samples demonstrates that the method is not affected by high salinity (approximately 35 g l^{-1}), and consequently offers accurate determination of antimony in sea water samples. On the other hand, the concentration of antimony found is well within the normal concentration ranges for this element in marine waters [5].

4. Conclusion

In this work, a new functionalized mesoporous silica has been synthesized, and a sensitive analytical methodology for Sb preconcentration and determination in different environmental waters: sea water, lake water and river water, has been developed. The method is rapid, easy, automatic, selective and with better precision and sensitivity than others found in the bibliography. The coupling of the resin DPTH-ms (SPE) with in situ trapping of stibine into Ir-treated tubes enhance both sensitivity and precision of the technique. DPTH-ms has demonstrated the good properties of the mesoporous silica (with higher surface area) as solid phase extractant, achieving better results than with DPTH bonded to silica gel (DPTH-gel) [36] even though in that work, a more sensitive technique (ICP-MS) was used. Besides, DPTH-ms coupled with HG–ETAAS is a low cost and environmentally friendly tool for elemental studies, given the volume of sample and reagents necessary. The use of the proposed procedure makes it possible to avoid complex sample pretreatment and preconcentration with organic solvents, which in turn may result in contamination or loss of the analyte. The application of our method has allowed us to obtain Sb concentrations in good agreement with certified data for the reference material (SLRS-5, TMDA 54.4).

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