



## A comparative study of two nanosubstrates for the on-line solid phase extraction of antimony by FI-HG-AAS



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### ARTICLE INFO

#### Article history:

Received 23 March 2016

Received in revised form 3 May 2016

Accepted 4 May 2016

Available online 7 May 2016

#### Keywords:

Antimony  
Nanosubstrates  
Comparative study  
Preconcentration  
FI-HG-AAS  
Waters

### ABSTRACT

Nanoporous carbon (NPC) prepared from metal organic frameworks (MOFs) was studied to serve as a sorbent for preconcentrating Sb(III) at trace levels. The performance of NPC regarding sensitivity, enrichment factor, analytical throughput and recovery was compared with that of multiwalled carbon nanotubes functionalised with L-proline (pro-MWCNTs). In this study, Sb(III) was preconcentrated using both substrates using an on-line flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS) system. A low molecular weight polyethylene was added to the sorbent material to fill the preconcentration columns to avoid nanoparticle aggregation. A comprehensive study of the type and concentration of the reaction media and the eluent was carried out to select the best substrate not only in terms of adsorption capacity but also considering potential interferent control. The study evidenced that for Sb(III) retention, phthalate buffers (1.0 mM at pH = 6) resulted the best alternative. Under optimal conditions, both substrates exhibited high adsorption capacities: 343 mg Sb g<sup>-1</sup> NPC and 559 mg Sb g<sup>-1</sup> pro-MWCNTs. The preconcentration factors reached were: 258 and 420 for NPC and pro-MWCNTs, respectively. The high adsorption capacity of both substrate allowed reaching detection limits (3σ) of 1.47 and 0.52 ng L<sup>-1</sup> for NPC and pro-MWCNTs, respectively when using a sorbent column containing only 1.0 mg of sorbent. Precision, expressed as relative standard deviation (RSD) turned to be ~2% at the 0.1 μg L<sup>-1</sup> level (n = 10) for both substrates. Trueness test for the entire analytical procedure was performed by means of the Standard Reference Material (SRM) NIST 1643e (Trace elements in water) and results were in good agreement with the certified values. The system was evaluated for quantitative determination of Sb(III) in different kind of waters. The method is simple and relatively cheap in comparison with other methodologies.

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### 1. Introduction

Antimony is an element that raises concern from both the environmental and human health point of view [1,2]. It is a potentially toxic element even at very low concentrations and has no known biological functions. Elemental Sb is more toxic than its salts and inorganic species of Sb are more toxic than the organic ones. Trivalent compounds are about 10 times more toxic than Sb(V) species. The International Agency for Research on Cancer (IARC) has reported that there is sufficient

evidence for the carcinogenicity of antimony trioxide in experimental animals. On the other hand, the U.S. Environmental Protection Agency (USEPA) and the German Research Community have listed Sb as a priority pollutant but it has not been classified for carcinogenicity. In contrast to As, there is evidence that Sb is not detoxified via methylation in mammals, but the mechanism responsible for antimony's genotoxicity is not clearly known.

The permissible limit for this element in drinking waters prescribed by the USEPA is 6 μg L<sup>-1</sup> [3]. In surface unpolluted waters, dissolved Sb is found at concentrations <1 μg L<sup>-1</sup> [4]. To meet the need for reliable determination of Sb at such low levels, different substrates in conjunction with a variety of preconcentration systems coupled to atomic and/or plasma-based techniques were developed for its determination in natural matrices.

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Simplicity and convenience of operation make solid phase extraction (SPE) a superior alternative to more established techniques in a number of applications. Different substrates and methodologies were employed for preconcentration of metals and metalloids. A mesoporous substrate, namely, silica functionalised with 1,5 bis(di-2-pyridyl)methylene thiocarbonylhydrazide was applied as enrichment sorbent for the determination of Sb by flow injection-hydride generation-atomic electrothermal atomic absorption spectrometry (FI-HG-ETAAS) [5]; a preconcentration factor of 22 was reached. Li et al. [6] employed a magnetic solid phase extraction (MSPE) method using octyl-immobilised silica-coated magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles as adsorbent combined with inductively coupled plasma mass spectrometry (ICP-MS) for elemental quantification. The limits of detection achieved resulted to be 0.001 µg L<sup>-1</sup> and 0.004 µg L<sup>-1</sup> for Sb(III) and Sb(V), respectively. Other alternative methodology was adopted by Gao et al. [7] who reported a novel and sensitive approach for the direct determination of Sb in natural waters by photochemical vapour generation (PVG) in conjunction with ICP-MS. A detection limit of 0.6 pg g<sup>-1</sup> based on external calibration was obtained.

The scenario depicted above is probative of the continuous interest of the scientific community for developing more and more methods capable of determining antimony at very low concentrations.

Aminoacids and peptides were extensively employed by Holcombe and his group [8] in metal binding studies. The use of carbon nanotubes (CNTs) as SPE sorbents prior to atomic spectrometric determination of metal species was reviewed by Herrero Latorre and coworkers [9]. Our group has been studying the biosorption capabilities of aminoacids immobilised on controlled pore glass for elemental SPE [10,11] for many years. More recently, the work has progressed in the use of L-tyrosine immobilised on multiwalled carbon nanotubes (MWCNTs) for the selective determination of Tl [12] and Co [13], L-alanine for Ni [14], Pb [14] and Cd [15] and L-proline for Bi [16].

In this direction, it was deemed of interest to further investigate the capabilities of MWCNTs functionalised with L-proline (pro-MWCNTs) as an enrichment sorbent for Sb(III) and compare the performance of this sorbent with a novel one namely nanoporous carbon (NPC). The method involved the use of a SPE system for the retention of the analyte onto a micro-column and the on-line determination by FI-HG-AAS. The combination of SPE and FI-HG-AAS showed merits such as its good detection power, overall flexibility, acceptable throughput and low cost. We have focused our attention on the analysis of different kinds of waters because of the importance of these matrices in the global transport of antimony.

## 2. Experimental

### 2.1. Instrumentation and reagents

A PerkinElmer (Norwalk, CT, USA) AAnalyst 200 atomic absorption spectrometer provided with a quartz cell in an electrically heated mantle, in conjunction with a PerkinElmer Flow Injection Analysis System (FIAS 100) was used for Sb(III) determination. The gas-liquid separator (PerkinElmer) is a modular 'building block'-type made from chemically resistant plastic with an exchangeable PTFE membrane placed in the screw cap of the separator. An additional peristaltic pump, Minipuls 3 from Gilson (Villiers-le-Bel, France) was used to deliver the sample. Connections among components were made with 1.0 mm (i.d.) PTFE tubing. Tygon type pump tubing with internal diameters of 1.52 mm, 1.14 mm and 1.14 mm (Ismatec, Cole Parmer, Vernon Hills, IL, USA) were employed to propel reagents and eluent, reductant and sample, respectively.

A Sb hollow cathode lamp (PerkinElmer) operated at a current of 20 mA and a wavelength of 217.58 nm with a spectral band pass of 2.7 nm was used. Deuterium background corrector was used. Instrumental details and operating conditions are summarised in Table 1.

**Table 1**

Instrumental details and operating conditions of the FI-HG-AAS system for preconcentration and determination of Sb(III).

Instrument	PerkinElmer AAnalyst 200
Cell temperature	940 °C
HDL lamp current	20 mA
Measurement mode	Peak area
Slit width	2.7 nm
Wavelength	217.58 nm
Hydride generation	
NaBH <sub>4</sub> concentration	0.4% (w/v); NaOH 0.2% (w/v)
Reductant flow rate	3.5 mL min <sup>-1</sup>
Eluent (HCl) flow rate	6.6 mL min <sup>-1</sup>
HCl concentration	15% (v/v)
Carrier gas (N <sub>2</sub> ) flow rate	30 mL min <sup>-1</sup>

Deionised distilled water (DDW) was produced by a commercial mixed-bed ion-exchange system, Barnstead (Dubuque, IA, USA) fed with distilled water. All reagents were of analytical grade and the presence of Sb was not detected within the working range. A stock standard solution (100.0 mg L<sup>-1</sup>) of Sb(III) was prepared by dissolving a proper amount of Sb<sub>2</sub>O<sub>3</sub> (Carlo Erba, Italy) in 10% HCl. Diluted working solutions were prepared daily by serial dilutions of the stock solution. Sodium tetrahydroborate(III) solution (0.4%, w/v) was prepared daily by dissolving NaBH<sub>4</sub> (Merck, Germany) in deionised water, stabilising in 0.2% (w/v) NaOH and filtering through Whatman N° 42 filter-paper to eliminate turbidity. The resulting solution was stored in a polyethylene flask at 4 °C. The cation solutions used in the study of interferences were prepared from analytical-reagent grade chemicals. Buffer solutions of tartrate (Baker, USA), citrate (Carlo Erba), phthalate (Carlo Erba), acetate (Aristar, Argentina) and oxalate (Merck) at different pHs and concentrations were prepared from their respective acids. All of them were tested as reaction media. The eluents tested were: HCl (Merck), L-cysteine (ICN Biomedicals, USA), citric acid and tartaric acid.

All glassware and plastic bottles used were cleaned by rinsing with deionised water, soaking with a 10% (v/v) nitric acid solution for 24 h and then rinsing several times with deionised water. All standards were stored in polyethylene bottles (50 mL) or Falcon® tubes.

Multiwalled carbon nanotubes were purchased from Sun Nanotech Co. Ltd., Jiangxi, China. All chemicals (Merck) used for MWCNT functionalisation (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, SOCl<sub>2</sub>, DMF, THF, L-proline) were of analytical reagent grade and were used without further purification. NPC particles were synthesised through direct carbonisation of ZIF-8 (zeolitic imidazolate framework-8), according to our previous reports [17, 18].

### 2.2. Sample collection and treatment

Water samples were collected in different sites in Argentina. They include: tap, river, sea, thermal waters and effluents from mining activities. In addition, a water sample collected in Antarctica was analysed. This sample was collected at the Carlini Station (ex Jubany), 25 de Mayo Island (62°14'18"S, 58°40'0"W).

Collected samples were placed in poly(ethylene terephthalate), PET previously cleaned with 10% HNO<sub>3</sub>. Antarctic water was collected in a Teflon® flask. Samples were transported to the laboratory and stored in a dry and dark place until analysis. Water samples were filtered through a 0.45 µm polyvinylidene fluoride syringe filter (Minisart-Sartorius, Göttingen, Germany).

Antimony was reduced to Sb(III) with 5 ml of a solution containing 10% KI + 10% ascorbic acid and 1 mL of concentrated HCl. After addition of the reduction solution to the water samples they were left for about five minutes. Before the analysis was started an aliquot of the buffer solution at the optimised concentration and pH was added (final volume: 50 mL). Blank solutions were prepared by application of the entire

procedure to the reagent solution containing no sample. Samples were analysed as soon as it was possible.

### 2.3. Immobilisation procedure

**Sorbent A:** Oxidation of MWCNTs was carried out in a mixture of  $\text{H}_2\text{SO}_4\text{:HNO}_3$  (3:1). Commercial MWCNTs were soaked for 30 min in an ultrasound bath and then placed in a water bath at 55 °C for 4 h. The resulting oxidised MWCNTs were dialysed with DDW until complete elimination of the residual acid. L-Proline functionalised MWCNTs (pro-MWCNTs) were obtained by the chemical attachment of L-proline using the following procedure: the oxidised MWCNTs were dispersed in thionylchloride ( $\text{SOCl}_2$ ) with 2 mL of dimethylformamide (DMF) and the mixture was left to react while stirring at 70 °C for 24 h. The resultant solid material (COCl-MWCNTs) was centrifuged and then washed with tetrahydrofuran (THF). L-Proline and COCl-MWCNTs were mixed with THF at 45 °C for 4 days. The resultant material, pro-MWCNTs was resuspended with ethanol, filtered and dried. Fig. S1a and b show SEM images of (a) oxidised MWCNTs and (b) pro-MWCNTs.

**Sorbent B:** Different carbon nanomaterials such as active charcoal, graphite, carbon nanotubes, and graphene, have been successfully used in many research fields [19–21]. Nanoporous carbon particles with very high surface area can be prepared by simple carbonisation of monodispersed ZIF-8 crystals [17,18]. From  $\text{N}_2$  adsorption-desorption isotherms, the surface area of the used NPC particles was calculated to be around  $1250 \text{ m}^2 \text{ g}^{-1}$ . In order to obtain the functional groups necessary for analyte retention, this sorbent was oxidised as Sorbent A.

### 2.4. Substrates and microcolumns preparation

According to previous experiences [16] to avoid aggregation and an unacceptable higher back-pressure due the tight packing of the filling material we decided to fill columns (A and B) with the same amount of sorbent material as follows.

**Column A:** it was filled with a mixture of functionalised pro-MWCNTs and inert microparticles of Epolene® (Eastman Chemical Products, Inc., Kingsport, TN, USA), a low-density polyethylene wax that offers good high-temperature stability, low-temperature flexibility,

and very good compatibility with the use of mineral acids. The amount of each material was: ~1.0 mg of pro-MWCNTs and 10 mg of Epolene®.

**Column B:** this column was filled with a mixture of NPC and inert microparticles of Epolene® but using different proportions (~1.0 mg of NPC and 5.0 mg of Epolene®).

The dry packing method was employed for the preparation of both microcolumns. Then, they were connected to the system with PTFE tubing to form the preconcentration system. Microcolumns A and B were preconditioned by the blank solution prior to each cycle.

The sorbents resulted stable over a wide range of pH and the columns packed with both sorbent materials had a lifetime of (at least) 600 cycles of Sb(III) retention/elution without demand for generation or modification of the initial conditions.

### 2.5. On-line solid phase extraction procedure

The flow injection system and the experimental set-up are shown in Fig. 1. Before loading (and after each cycle of Sb(III) retention/elution) the system was washed with 1 mL of a 15% (v/v) HCl solution and then with 2.5 mL of DDW. An aliquot of sample was then loaded on the microcolumn delivered by Pump 1 at flow rate of  $3.0 \text{ mL min}^{-1}$  with FIAS-valve in load position. After that, FIAS-valve was switched to the elution position and Sb(III) retained was eluted with a 15% (v/v) HCl solution at a flow rate of  $6.6 \text{ mL min}^{-1}$ . The acidified eluate was on-line merged with the reductant (delivered by Pump 2 at flow rate of  $3.5 \text{ mL min}^{-1}$ ) into the reaction loop and subsequently carried to the gas-liquid separator. Reaction loop volume was kept as small as practicable to avoid broadening of the signal peak. The volatile stibine generated was separated from the solution and swept by  $\text{N}_2$  ( $30 \text{ mL min}^{-1}$ ) into the quartz cell and the determination was carried out.

### 2.6. Optimisation strategy

For achieving the best performance of the system, the effect of different parameters on the retention/elution of Sb(III) was assessed. To this end, not only to reach the best intensity of Sb signal (peak area) was taken into account but also the performance of the system in terms of interference control, elution efficiency, system stability and reproducibility.

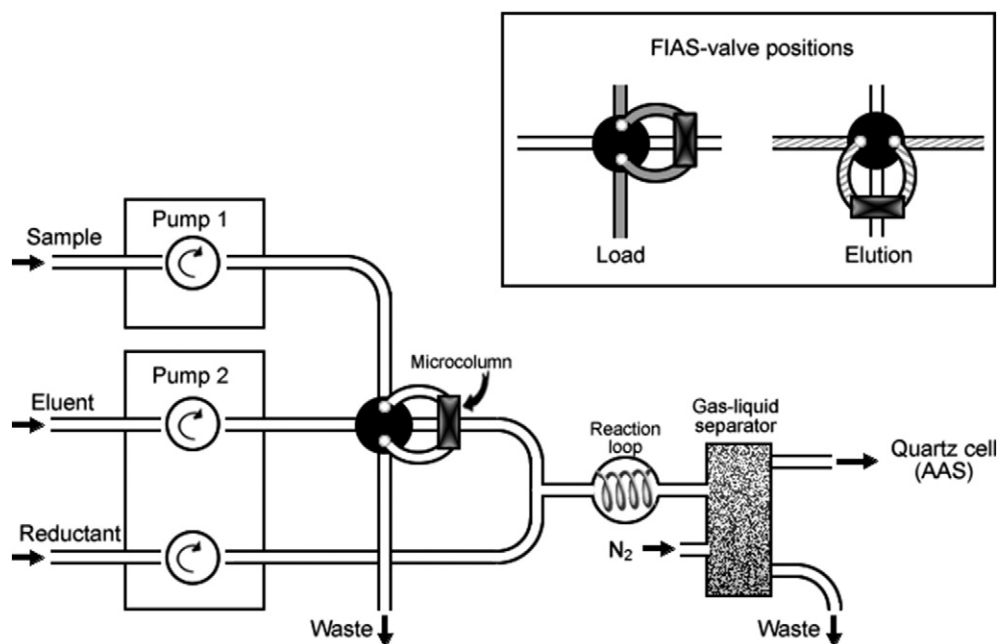


Fig. 1. Operational diagram of the FI-HG-AAS system used for Sb(III) preconcentration.

Optimisation of the retention step comprised type, concentration and pH value of buffers used as reaction media. Buffer solutions of citrate, oxalate, phthalate and acetate at different concentrations and pHs were tested, leading to 12 conditions. For the elution step four eluents namely, HCl, citric acid, L-cysteine and tartaric acid were tested leading to four conditions. Both variables (reaction media and eluent) were studied simultaneously and Table 2 summarises the conditions for each variable. Full combination of the variables led to 48 cases.

In order to evaluate the effect of concomitant ions on Sb(III) signal, two elements were tested as typical interferents: As(III) and Fe(III). Antimony signal was recorded in the presence and absence of each ion at  $1 \text{ mg L}^{-1}$  level.

When elution efficiency was tested, consecutive elution cycles were performed and Sb signal was recorded for each one. The objective was to evaluate if it was possible to reach a complete elution of the analyte in one step. Antimony signal in each reaction media was normalised with respect to Sb signal in water as reaction media.

### 3. Results and discussion

#### 3.1. Microcolumn characteristics

A careful evaluation of the optimum dimensions of the microcolumns led to the conclusion that to reach an efficient Sb(III) preconcentration as well as high and thinner peaks, a good compromise was to use a small (home-made) microcolumn of 2.3 mm (i.d.)  $\times$  20 mm (net length of substrate: 5 mm and a nominal microcolumn capacity  $\sim 22 \mu\text{L}$ ). On the other hand, the smaller the column cross-section was, the higher and narrower was the peak. Columns A and B had the same dimensions and the same amount of nanosubstrate but different amounts of Epolene®. This study showed that the retention of Sb(III) in column B was lower when increasing amounts of Epolene® were added. Consequently, the best proportion found was: 1.0 mg of NPC and 5.0 mg of Epolene®. To further avoid packing of the nanosorbents, both operations namely, loading and elution were performed countercurrently.

To check that Sb(III) was not retained by the low molecular weight polyethylene wax, a test microcolumn was filled only with  $\sim 10 \text{ mg}$  of this material and inserted in the preconcentration system. No Sb(III) retention was observed which evidenced that Sb(III) was only retained by sorbent A and sorbent B, and not by Epolene®. The same set of optimised parameters was applied to both nanosorbents because screening experiments showed that the results reached were similar.

#### 3.2. Elution profile

The elution of metals from retained aminoacids onto solid substrates in the presence of acids occurs fast with high recoveries. Column A was loaded with 5 mL of a  $10 \mu\text{g Sb L}^{-1}$  solution and Fig. 2 shows the time-dependent transient signal obtained when Sb(III) was removed using 15% HCl as eluent. The transient signals for a complete metal removal

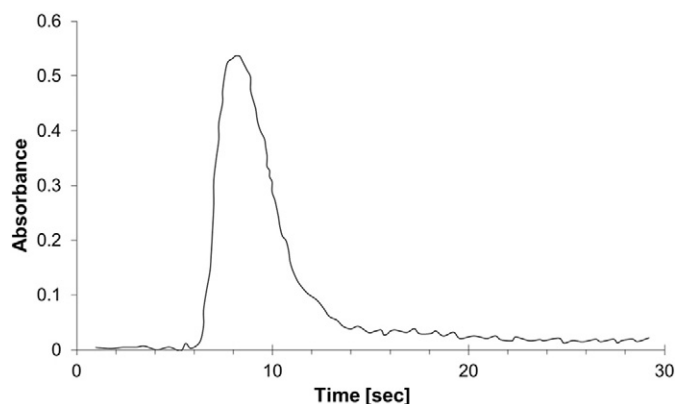


Fig. 2. Transient absorbance signal observed when on-line Sb(III) stripping with 15% HCl was carried out.

lasted less than 8 s, which corresponds (at an elution flow rate of  $6.6 \text{ mL min}^{-1}$ ) to 0.9 mL of eluent solution. The profile of Sb peaks resulted similar independent on the concentration tested in this study.

#### 3.3. Optimisation of experimental chemical and physical variables

Similar experimental results were obtained for both columns so, the graphs of Fig. 3 are the only depicted peaks obtained when the column filled with pro-MWCNTs was used. The four graphs in Fig. 3 show the results obtained for the preconcentration of  $10 \mu\text{g Sb L}^{-1}$  solutions, each graph corresponds to a specific eluent condition assessed.

The results denote that in general terms, the buffers that resulted adequate as reaction media were: phthalate > acetate > oxalate. Briefly, phthalate buffer showed the best performance (control of interferences) when As(III) and Fe(III) were tested as typical interferents. Tartrate and citrate buffers were discarded as reaction media because Sb signal resulted too low.

Fig. 4 shows the comparative efficiency of the eluents. It can be seen that 15% HCl resulted the best option to reach a complete elution of the analyte in one step. For L-cysteine, tartaric acid and citric acid, a complete recovery of Sb(III) was reached after two or three elution cycles. In addition, citric acid was disregarded as eluent because of the bad reproducibility of Sb signal (%RSD > 10) as well as the formation of foam in the gas-liquid separator. On the basis of the study described above, 1 mM phthalate buffer at pH = 6 (reaction media) and 15% HCl (eluent) were the selected conditions for further work.

The system optimisation also included the effect of flow rate on the Sb signal that was varied between 2.5 and  $7.5 \text{ mL min}^{-1}$ . Flow rates higher than this value were not tested due to the high backpressure observed. The results exhibited in Fig. 3 refer to flow rates of 3.0 and  $6.6 \text{ mL min}^{-1}$  for loading and elution, respectively ensuring a quantitative retention/desorption with the minimum sample processing time.

#### 3.4. Interference study

The determination of Sb(III) is prone to interferences in the presence of transition metals and hydride forming elements. The individual effects of potentially interfering metal species were assessed. The interference effects of metals such as Al, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn on the generation of stibine were considered because these elements compete with the analyte for reduction and catalyse  $\text{NaBH}_4$  decomposition. Another group of typical interferents is volatile hydride elements, (Periodic Group 14, 15 and 16); As, Bi, Se and Sn were checked as potential interferents. Using the optimised working conditions, the effect of potential interferents on Sb(III) signal was investigated for NPC and pro-MWCNTs and results are summarised in Table 3. Variations over  $\pm 5\%$  in the analytical signal of Sb(III) in the presence of other elements were taken as an interference. All samples analysed contained

Table 2  
Different conditions for each variable evaluated for optimisation.

Reaction media	Eluent
0.001 M phthalate buffer, pH 3	15% HCl
0.1 M phthalate buffer, pH 3	1 M citric acid
0.001 M oxalate buffer, pH 4	0.01 M L-cysteine solution
0.1 M oxalate buffer, pH 4	1 M tartaric acid
0.001 M tartrate buffer, pH 4	
0.1 M tartrate buffer, pH 4	
0.001 M acetate buffer, pH 5	
0.1 M acetate buffer, pH 5	
0.001 M citrate buffer, pH 5	
0.1 M citrate buffer, pH 5	
0.001 M phthalate buffer, pH 6	
0.1 M phthalate buffer, pH 6	

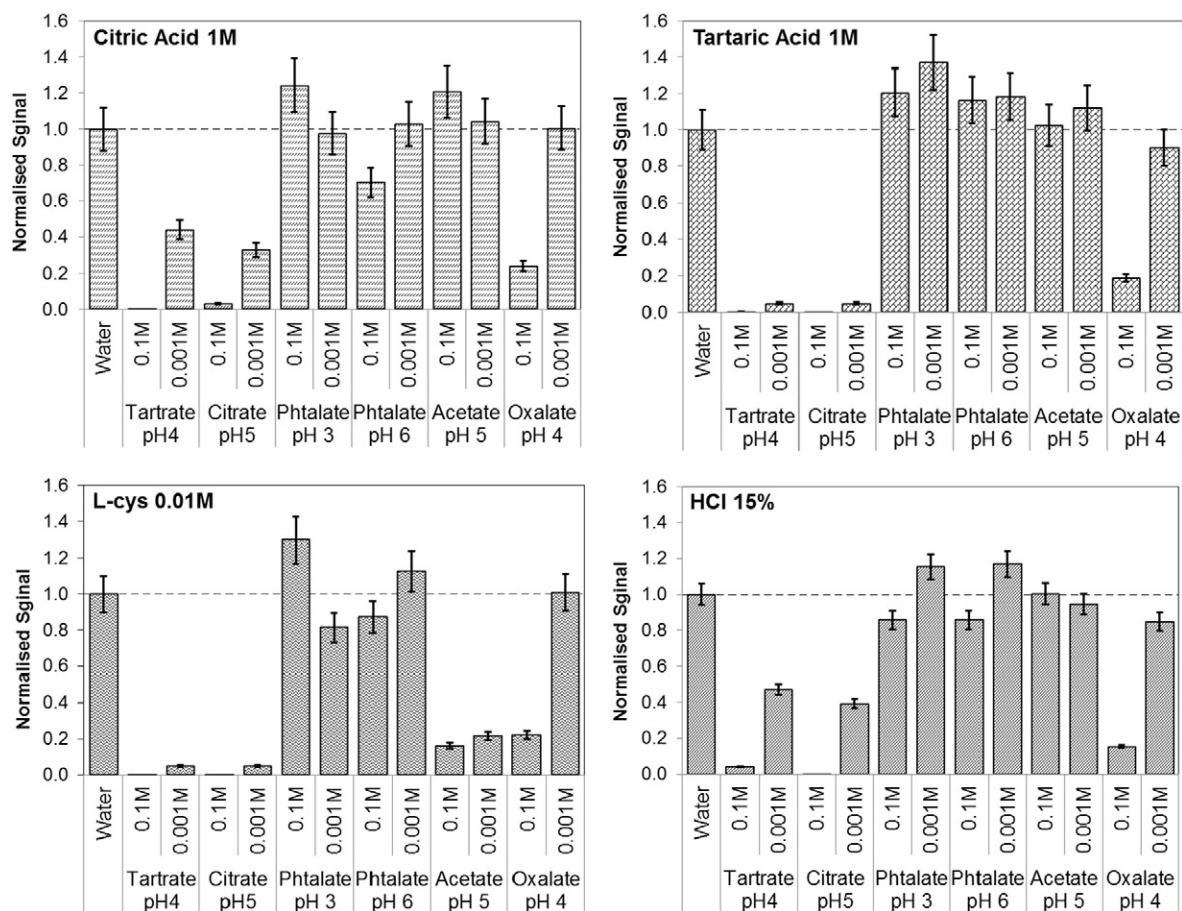


Fig. 3. Effect of different reaction media and eluents on Sb signal (normalised signal).

$10 \mu\text{g Sb L}^{-1}$  and the results are the average of three measurements. No enhancing effects were observed for the 14 elements tested. On the other hand, Bi, Cr, Sn and V produced signal depression of the analyte when both substrates were tested. In all cases depressions of Sb signal  $<20\%$  were observed. Based on the data obtained in this study, it is not possible to choose the most suitable substrate in terms of interference control because the results are similar.

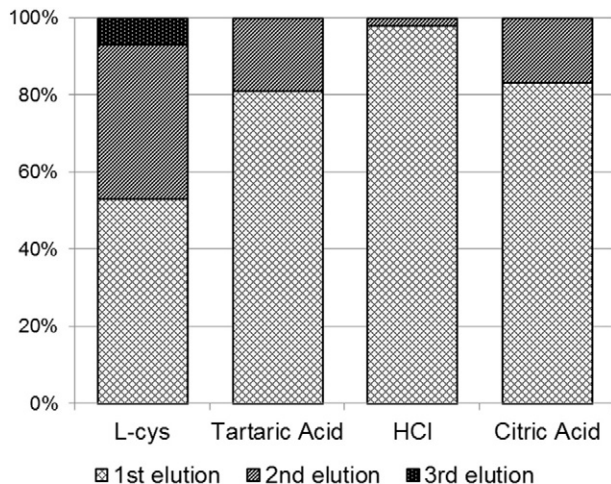


Fig. 4. Comparative efficiency of various eluents on Sb signal.

### 3.5. Quality parameters and method trueness

Under the selected physical and chemical variables detailed in the foregoing sections, the analytical performance of the FI-SPE-HG-AAS method using pro-MWCNTs (substrate A) and NPC (substrate B) for Sb(III) retention resulted as follows: the repeatability, expressed as relative standard deviation (RSD) was 2.1 and 2.4% (for substrate A and B, respectively) for ten replicate measurements for  $0.1 \mu\text{g L}^{-1}$ . The limits of detection (LODs) calculated as the concentration associated with three times the standard deviation of 10 independent measurements of the procedural blank ( $3\sigma$  criterion) were  $1.47 \text{ ng L}^{-1}$  (NPC) and

Table 3

Interferences of heavy metals and hydride forming elements in the determination of Sb(III). Results are percentage change in Sb signal ( $10 \mu\text{g Sb L}^{-1}$ ; interferent concentration:  $1 \text{ mg L}^{-1}$ ).

Interferent	NPC-CPS	Pro-MWCNTs
Al	0	-9.5
As	0	0
Bi	-15.9	-10.6
Cd	0	0
Cr	-9.9	-9.7
Cu	0	0
Fe	0	0
Mn	0	0
Ni	-6.5	0
Pb	-6.8	0
Se	0	0
Sn	-16.9	-19.8
V	-9.3	-9.2
Zn	0	0

0.52 ng L<sup>-1</sup> (pro-MWCNTs). The limits of quantification (10σ) resulted to be 4.85 and 1.72 ng L<sup>-1</sup> for NPC and pro-MWCNTs, respectively. The calibration curves were linear from levels close to the LOD up to 120 ng L<sup>-1</sup>. A good correlation coefficient has been obtained with R<sup>2</sup> = 0.998. According to Fillela et al. [2] typical concentrations of Sb in natural waters are <1 μg L<sup>-1</sup> while ocean surface concentrations are ~0.2 μg L<sup>-1</sup>. The LODs obtained for both nanomaterials evidence that the proposed method is fully able to determine Sb(III) in different categories of natural waters.

The sample throughput depends on the mode of operation and on the sample volume used for the analyte determination. The time required for the preconcentration of 5 mL of water sample at 3.0 mL min<sup>-1</sup> using an elution flow rate of 6.6 mL min<sup>-1</sup> was ~4 min (including washing and pre-conditioning times) resulting in a sample throughput of 15 samples per hour. This is more than satisfactory even for routine analysis.

Dynamic sorption capacity is an important parameter to evaluate and it was determined for each substrate by integrating the breakthrough curve. The results showed high values for both substrates: 343 mg Sb g<sup>-1</sup> NPC and 559 mg Sb g<sup>-1</sup> pro-MWCNTs. In consequence, high preconcentration factors (PFs) of 258 (NPC) and 420 (pro-MWCNTs) for a sample volume of 50 mL was obtained with respect to the Sb determination by FI-HG-AAS without preconcentration (changing the microcolumn by other unfilled).

Trueness test for the entire analytical procedure was performed by means of the Standard Reference Material (SRM) NIST 1643e (Trace elements in water). The standard addition technique was adopted for calibration by adding dilute solutions of Sb(III) to the analytical solutions (three replicates). Results were in good agreement with the certified values as follows: 58.30 ± 0.61 μg Sb L<sup>-1</sup> (certified) vs 56.8 ± 1.50 μg Sb L<sup>-1</sup> (found) according to the *t*-test for a confidence level of 95%.

### 3.6. Analytical application: Sb(III) in different categories of waters

As stated before in Section 2.2 samples were subjected to a reduction process. The same procedure was applied to the SRM. Table 4 summarises the results of the analysis of waters from different origins. Antimony concentration values for the real samples were obtained by a standard addition technique (three replicates). A recovery test was performed and recoveries between 98.1 and 103% were obtained. In the case of the sea water a recovery of 102% was obtained which demonstrates that the method is not affected by the high salinity of the sample. Concentrations of Sb in the analysed samples ranged from <LOD to 105 ng L<sup>-1</sup> (mine effluent).

## 4. Conclusions

Two nanosubstrates were used and compared for Sb(III) preconcentration. The on-line combination of NPC or pro-MWCNTs in a SPE-FI-HG-AAS system resulted fully able to determine Sb at ng L<sup>-1</sup> levels. The mixture of each substrate with a low molecular weight polyethylene wax (with no need for substrate immobilisation) avoided agglomerations and overpressures in the on-line system. NPC and pro-

MWCNTs microcolumns featured excellent chemical stability and retention efficiency without noticeable Sb(III) breakthrough for sample volumes of 50 mL, and with a long lifetime of up to 600 sorption/elution cycles.

The excellent dynamic sorption capacity of both substrates and the enrichment factors obtained render NPC and pro-MWCNTs ideal sorbents for the determination of Sb(III) and other elements at the very low concentrations usually expected in natural waters.

Research work in our lab is underway to expanding the proposed preconcentration method to the use of other nanomaterials for the determination of key pollutants in environmental matrices. Efforts will be addressed to the speciation analysis of elements of ecotoxicological interest.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.microc.2016.05.003>.

## Acknowledgements

PS thanks CONICET (Project PIP 486) and ANPCyT (Project PICT 1195) for funds.

Y. Y. and S. M. A. extend appreciation to the Deanship of Scientific Research support from the Visiting Professor Program of King Saud University.

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**Table 4**

Antimony concentrations (expressed in ng L<sup>-1</sup>) in different kinds of waters.

Sample	Sb concentration
Tap water (Buenos Aires)	<LOD
Tap water (Buenos Aires province)	51.6 ± 2.2
Sea water (Mar del Plata)	21.1 ± 0.8
River water 1 (Mendoza)	20.3 ± 0.9
Thermal water (Entre Ríos)	15.1 ± 0.7
Antarctic water (Carlini Station)	<LOD
Mine effluent 1 (Córdoba)	18.9 ± 0.9
Mine effluent 6 (Córdoba)	105 ± 5

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