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On-line flow injection solid phase extraction using oxidised carbon nanotubes as substrate for cold vapour-atomic absorption determination of Hg(II) in different kind of waters

Belén Parodi[a,b], Agustín Londonio[c,b], Griselda Polla[d], Marianela Savio[e], Patricia Smichowski[c,f]*

[a] *Instituto Nacional de Tecnología Industrial, Centro de Investigación y Desarrollo en Mecánica, Av. General Paz 5445- B1650KNA- San Martín, Buenos Aires, Argentina.*

[b] *Instituto de Investigación e Ingeniería Ambiental (3iA), Universidad de San Martín, Peatonal Belgrano 356, San Martín, Buenos Aires, Argentina.*

[c] *Comisión Nacional de Energía Atómica. Gerencia Química, Av. Gral Paz 1499, B1650KNA- San Martín, Buenos Aires, Argentina.*

[d] *Comisión Nacional de Energía Atómica. Gerencia Investigación y Aplicaciones, Av. Gral Paz 1499, B1650KNA- San Martín, Buenos Aires, Argentina.*

[e] *Instituto de Química de San Luis (UNSL-CONICET). Área de Química Analítica, Facultad de Química Bioquímica y Farmacia, Universidad Nacional de San Luis. Chacabuco y Pedernera, D5700BWQ-San Luis, Argentina.*

[f] *Consejo Nacional de Investigaciones Científicas y Técnicas, Av. Rivadavia 1917, C1033AAJ-Buenos Aires, Argentina.*

A study was made to investigate the concentrations of Hg(II) in different categories of water samples at ng L^{-1} levels. The capabilities of oxidised carbon nanotubes (ox-CNTs) were studied to assess if this substrate serves as an efficient material for Hg(II) preconcentration using an on-line flow injection cold vapour-atomic absorption spectrometry (FI-CV-AAS) system. Carbon nanotubes are characterized by a marked tendency to aggregation, which negatively affects the retention of Hg whenever integrated in flow systems as a packed column. For this reason, the preconcentration was carried out on a microcolumn filled with a mixture of ox-CNTs and a low molecular weight polyethylene. The preparation of the microcolumn was studied in detail. Concerning column design, the best performance was achieved when packing the substrate in a microcolumn of 2.25 mm (i.d) x 20 mm length. The effect of chemical and physical parameters including pH of the solutions, eluent type and concentration was systematically examined. Mercury was retained at pH 5.0 and 15 % (v/v) HCl was the best alternative for Hg(II) elution. Under optimal conditions, the adsorption capacity of the substrate was found to be 3.2 mg/g reaching a preconcentration factor (PF) of 150. The high adsorption capacity of this substrate allowed reaching a detection limit (3σ) of 1.9 ng L^{-1}, when using a sorbent column containing only 1.0 mg of ox-CNTs. The limit of quantification (10σ) resulted to be 6.3 ng L^{-1}. Precision, expressed as relative standard deviation (RSD) turned to be 1.6% at the 0.1 μg L^{-1} level (n=8). The system was evaluated for quantitative determination of Hg in river water, sea water and effluents.

*Corresponding author. Tel: +54 11 6772 7873; fax: +54 11 6772 7886.

E-mail address: smichows@cnea.gov.ar (P. Smichowski)

Introduction

Different sources are responsible for the presence of a toxic element such as Hg in environmental matrices. In urban areas, coal burning, refining, cement production, smelters, transportation, municipal solid waste incineration, and different kind of industries are responsible for the major inputs of anthropogenic emission of Hg.[1,2] Mercury is also emitted by natural sources namely, volatilisation of Hg^0 from surface waters, emissions from volcanoes and degassing of Hg from top soil and vegetation.[3] Studies carried out in size-classified road dust demonstrated that in Buenos Aires Hg is a traffic related elements (TREs).[4] It was mostly accumulated in the smaller fraction of road dust and its presence was linked with exhaust of liquid fuel combustion from vehicles.

In natural waters, Hg concentrations are extremely low (ppt levels) which requires the use of a very sensitive technique such as inductively coupled plasma mass spectrometry (ICP-MS) for its quantification. However, direct analysis of sea water samples by ICP-MS presents some difficulties due to the high saline content.[5] The alternative of sample dilution has the risk that the sensitive of the technique is not enough for its quantification at the concentrations typically found in sea water.

Cold vapour atomic absorption spectrometry (CV-AAS) and CV-atomic fluorescence spectrometry (AFS) have demonstrated to be appropriate techniques for Hg determination.[6] Notwithstanding an impressive number of analytical advantages, CV-AAS has a drawback because its detection power is sometimes inadequate to comply with the requirements posed by the determination of Hg in some environmental matrices such as waters. Therefore, it is not surprising that alternative ways to exploit the potential of this technique has been its combination with preconcentration systems involving specific substrates. In this way, the coupling of a microcolumn, filled with an effective substrate, flow injection-cold vapour-atomic absorption spectrometry (FI-CV-AAS) offers the possibility of reaching very low detection limits, acceptable throughput with a reasonable cost. This approach is a widely accepted and applied sample preparation technique due to its simplicity, offering a relatively fast extraction and preconcentration capabilities particularly attractive for avoiding the use of solvents. The appropriate selection of the sorbent is one of the most critical steps in solid phase extraction (SPE) method development. As substrates, carbon nanotubes (CNTs) have demonstrated to be an effective sorbent for metal and organometallic compounds preconcentration.[6-8] Their large sorption capacity is linked to the distortion of planar graphene sheets into a helical or cylindrical fashion. The main adsorption mechanism of metal ions to CNTs is considered to be surface complexation with functional groups, so the performance is mainly determined by the nature and the concentration of these groups. In addition, the surface of CNTs can be easily modified, resulting on functionalised adsorbents with distinctive properties.

Considering the above advantages, it was deemed of interest to further investigate the capabilities of ox-CNTs as a new substrate for Hg(II) determination using an on-line SPE procedure involving its coupling to FI-CV-AAS. The main factors influencing preconcentration and determination of Hg(II) were examined thoroughly, and they included characteristics of the microcolumn, sample pH, sample flow rate and volume, and eluent concentration and flow rate. The conditions were established and Hg(II) determination in different kinds of waters was successfully carried out reaching a high preconcentration factor.

Experimental

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 Hg(II) 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.) Teflon tubing. Tygon type pump tubing with an internal diameter 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. The experimental set-up of on-line preconcentration of Hg(II) is depicted in Fig.1.

A mercury electrodeless discharge lamp (PerkinElmer) operated at a current of 190 mA and a wavelength of 253.7 nm with a spectral band pass of 0.7 nm was used. Instrumental details and operating conditions are summarized in Table 1.

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 Hg was not detected within the working range. Commercially available 1000 mg L^{-1} standard solutions (Merck, Darmstadt, Germany) of Hg was used. Diluted working solutions were prepared daily by serial dilutions of the stock solution. Sodium tetrahydroborate(III) solution was prepared daily by dissolving $NaBH_4$ (Merck) in DDW, stabilizing in 0.1% (w/v) NaOH (Merck) and filtering through Whatman Nº 42 filter-paper to eliminate turbidity. The resulting solution was stored in polyethylene flask at 4 ºC. The cation solutions used in the study of interferences were prepared from analytical-reagents grade chemicals.

All glassware and plastic bottles used were cleaned by rinsing with deionised distilled 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 (Corning Inc., Tewksbury, MA, USA).

Sample collection and treatment

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

Collected samples were placed in poly(ethylene terephthalate)-PET bottles previously cleaned with 10% HNO_3. Antarctic water was collected in a Teflon® flask. Samples were transported to the laboratory and stored in a dry and dark place until analysis. The sea water, river water and effluent samples were filtered through a 0.45 µm polyvinyldifluoride syringe filters (Waters Corp., Milford, MA, USA) and just before the preconcentration step, the pH was adjusted at the corresponding optimum value. Samples were analysed as soon it was possible. Fadini and Jardim studied and compared the use of Teflon® and PET bottles for sampling and storage of waters prior to Hg determination[10]. They reported that undetectable levels of contamination, either by leaching from sampling vessels or metal losses, were detected when these materials were tested for mercury.

An issue of concern is the presence of Hg in waters in the form of various inorganic and organic species. Different oxidising agents, mixtures and procedures were reported for sample treatment.[11-13] In this study, samples were irradiated for 0.5 h with a 78-W UV lamp in order to photooxidise organo-Hg compounds.

Substrate and microcolumn preparation

The most used, effective and simple modification of CNTs is their oxidation using acids. The application of extreme conditions leads to the opening of the tube caps and the subsequent formation of holes in the side walls and, as a consequence, oxygen functional groups (e.g., -OH, -C=O, –COOH) are created[14]. Oxidation of CNTs was carried out in a mixture of H_2SO_4:HNO_3 (3:1). Carbon nanotubes were soaked for 2 h in an ultrasound bath and then placed in a water bath at 55 ºC for 7 h. The resulting ox-CNTs were dialyzed with DDW until complete elimination of the residual acid. The oxygen-containing groups created on CNTs surface increase their solubility in polar media. After this step, ox-CNTs were filtered and dried at room temperature.

A mixture of ~ 1.0 mg of ox-CNTs and 10 mg of tiny pellets of a low molecular weight polyethylene wax namely Epolene® (Eastman Chemical Products, Inc., Kingsport, TN, USA) was packed in a home-made microcolumn (20 mm length x 2.25 mm i.d. with a net length of substrate of 5.5 mm and a nominal microcolumn capacity ~22 µL) using the dry packing method. Several column dimensions were tested and the best results in terms of Hg(II) retention and quantitative elution were achieved with a microcolumn of the mentioned dimensions. The microcolumn was then connected to the system with PTFE tubing to form the preconcentration system. The microcolumn was preconditioned by the blank solution prior to each cycle. After the elution, the ox-CNTs were washed with 0.5 mL of a 15% (v/v) HCl solution and then with 2.0 mL of DDW.

Results and discussion

Characteristics of the column and the filling material

The preparation and dimension of the microcolumn is a key topic when CNTs are used as the filler material. Screening experiments showed that the characteristics of the sorbent and the column geometry greatly influenced Hg(II) preconcentration efficiency. On the other hand, it is known that CNTs are characterised by a marked tendency to aggregation, which negatively affects the retention of different elements whenever packed in a microcolumn and integrated in a flow system. Tests were undertaken to exploit if ox-CNTs packed in different home-made microcolumns and inserted in the flow-through system were adequate for Hg(II) preconcentration. The experiments showed limited success because of the high backpressure reached and consequently resulting in poor analytical performance. To surmount this limitation, Boonjob *et al.*[15] proposed an ingenious approach in a microsolid-phase extraction procedure based on the insertion of a dedicated stirred-flow sorptive microchamber integrated in a fully automated sequential injection (SI) assembly for expedient handling and reuse of carbon nanoparticles. In order to find a simpler procedure for Hg(II) preconcentration while avoiding further nanomaterial functionalisation, the mixture of ox-CNTs and a material with polymeric characteristics as a filler material was assessed as a new alternative to avoid ox-CNTs aggregation.

We performed a careful evaluation of the optimum dimensions of the microcolumn and especially, the characteristics of the filling material. These tests demonstrated that to reach an efficient Hg(II) preconcentration as well as higher and thinner peaks, a good compromise was: (*i*) using a small microcolumn of 2.25 mm (i.d) x 20 mm (ox-CNTs net length: 55 mm), and *(ii*) carefully assess the filler material and the way of packing it. We decided to pack the microcolumn with a mixture of ox-CNTs and inert microparticles of a low molecular weight polyethylene wax (Epolene®) to avoid sorbent aggregation and an unacceptable higher back-pressure due the tight packing of the filling material. Epolene® is a low-density polyethylene wax that offers good high-temperature stability, low colour, low-temperature flexibility, and very good compatibility with the use of mineral acids. According to our experiments, the optimal proportion was ~ 90 % of Epolene® and ~ 10% of ox-CNTs. In addition to the lack of aggregation, microcolumns resulted to be even better in terms of peak sharpness. To check that Hg(II) was not retained by the low molecular weight polyethylene wax, a test microcolumn was filled only with ~10 mg of this material and inserted in the preconcentration system. No Hg(II) retention was observed which evidenced that Hg(II) was retained by ox-CNTs and not by Epolene®.

Epolene® is a substrate with some interesting characteristics: about 75% of the particles have a particles size of ~800 µm with a significant dispersion in particles size and shape which contributes to avoid ox-CNTs aggregation. Particle size distribution of Epolene® was studied by laser diffraction using a Malver Mastersizer 2000® instrument (Malvern Instruments Limited, Malvern, UK). Five consecutive measurements were made of two samples and the results averaged to produce the overall size distribution. In Fig. 2 it is shown the percentage of particles, by volume, between 1-2000 µm. No particles < 1µm were detected in the sample analyzed of Epolene®. The scanning electron micrograph of Epolene® (Fig. 3-a) exhibits a typical morphology of the polymer. Figures 3-b and 3-c show the distribution of ox-CNTs onto one particle of Epolene® at two magnifications. It is important to emphasise the significant dispersion of the nanotubes on the particle with the preservation of their backbone after 450 cycles of Hg(II) preconcentration.

The selection of the chemical and physical parameters influencing Hg(II) retention was studied in order to achieve appropriate sensitivity, selectivity and precision for the subsequent mercury determination at low concentration in water samples.

Influence of pH on Hg(II) retention on ox-CNTs

The pH value of the sample solution plays a crucial role in sorption of different ions on ox-CNTs.[16,17] The sorption of metal ions on ox-CNTs increases as pH increases because the ox-CNTs surface becomes more deprotonated, causing electrostatic interactions between metal ions and oxygen functional groups (–COO- and -O-). In this context, the isoelectric point (IEP) of ox-CNTs shifts to the lower pH values. When the pH of the solution is higher than the IEP of the ox-CNTs, the negative charge on the surface provides electrostatic attractions that are favourable for adsorbing cations. The decrease of pH leads to the neutralisation of surface charge, so the adsorption of cations onto ox-CNTs decreases quickly.

In order to evaluate the effect of pH, a series of sample solutions of Hg(II) of 0.5 μg L^{-1} were adjusted to different pH values (between 1.0 and 9.0) and the preconcentration/elution was carried out. Aliquots of Hg(II) solutions of 1.0 mL were loaded on the microcolumn at a flow rate of 1.7 mL min^{-1}. In order to optimise the sorption conditions for the retention of Hg(II) on the sorbent, peak area was recorded as a function of the pH. Mercury was retained in all the wide range of pHs tested and retention was maximum at pH 5. Beyond this pH a noticeably decreasing in the adsorption is advised. At pHs higher than 8, the decrease of Hg(II) adsorption may be attributed to metal hydrolysis. Accordingly to these findings, pH 5 was selected for further experiments.

Eluent type and concentration

Hydrochloric acid was tested as eluent to promote Hg(II) desorption from the sorbent material. The elution step involves an exchange between analyte ions and H^+. In addition chloride ions could remove mercury ions by forming $HgCl_2$.[18]

Hydrochloric acid was examined within a wide range of concentrations ranging from 1.0 to 20% (v/v). Maximum absorbance readouts for Hg were recorded at a concentration of 15 % (v/v). A transient signal was obtained and the peak area was proportional to Hg(II) concentration in the loaded solution.

Influence of sample volume

The effect of sample volume was also investigated on the recorded Hg signal. To this end, the mass of analyte was kept constant but increasing sample volume (2 mL-200 mL) was examined. This test showed that no influence of sample volume on Hg signal in the range of concentrations examined.

Loading and elution flow rate

In flow sorptive on-line preconcentration systems, loading flow rate and loading time are crucial variables to which the sensitivity of the method and the preconcentration factor are directly related to. Beyond being one of the steps that controls the time of analysis, the rate of the sample through the microcolumn, it influences the time of contact between the analyte and the active sites (edges) and consequently the microcolumn capacity. The effect of loading flow rate on Hg absorbance was studied in the range of 0.5-2.7 mL min^{-1} and the elution flow rate was kept constant at 10 mL min^{-1}. Experimental results revealed that the analytical signal increased continuously given a maximum at 1.75 mL min^{-1} and then diminished progressively. An almost linear increase of the absorbance within the assayed range reveals a very fast mass transfer onto the ox-CNTs that ensures quantitative uptake of the analyte. This is without doubts an advantage because elevated enrichment factors are expected to be obtained in high-throughput assays. A flow rate of 1.75 mL min^{-1} sufficed for obtaining reasonable low sample consumption. It was not necessary to work at lower loading flow rates because no increasing of the back pressure was observed.

The influence of the stripping flow rate upon desorption and detection of mercury was also examined within the range of 6.5–10 mL min^{-1}. No significant differences were observed in the range of flow rates examined. A flow rate of 10 mL min^{-1} was adopted for further work.

Microcolumn re-use studies

The stability and regeneration of the microcolumn were also investigated. The microcolumn can be re-used after regeneration with 10 mL of 15% HCl and then with ultrapure water. The microcolumn was stable without either deterioration or decrease in Hg(II) recovery. This study comprised at least 450 preconcentration cycles and no decrease in capacity of the microcolumn was observed.

Interference study

The determination of Hg 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 Cd, Cu, Fe, Mn, Mo, Ni and Zn on the generation of Hg vapour were considered because these elements compete with the analyte for reduction and catalyse $NaBH_4$ decomposition. Another group of typical interferents are volatile hydrides elements (Periodic Group 14, 15 and 16).

Interference studies under the optimised working conditions were investigated. Variations over ±5% in the analytical signal of Hg in the presence of other elements were taken as interference. All samples analysed contained 2.5 μg L^{-1} Hg(II) and the results are the average of three measurements. Results are summarised in Table 2 Enhancing effects were observed for Bi and Mn while As, Al, Fe, Mo and Sb produced a depression on Hg signal (< 11.5 in all cases).

Analytical performance and method accuracy

Under the selected physical and chemical variables detailed in the foregoing sections, the analytical performance of the FI–SPE–CV–AAS method using ox-CNTs for Hg(II) retention resulted as follows: the repeatability, expressed as relative standard deviation (RSD), was 1.6% for ten replicate measurements. The limit of detection (LOD), calculated as the concentration associated with three times the standard deviation of 10 independent measurements of the procedural blank (3σ criterion) was 1.9 ng L^{-1}. The limit of quantification (10σ) resulted to be 6.3 ng L^{-1}. The calibration curve was linear from levels close to the limit of quantification (LOQ) up to 500 μg L^{-1}. A good correlation coefficient has been obtained with $R^2 = 0.998$.

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 4 mL of sample at 1.75 mL min^{-1}, using an elution flow rate of 10 mL min^{-1}, reading/data acquiring and conditioning was about 3 min, resulting in a sample throughput of 20 samples per hour. An enrichment factor (EF) of 150 for a sample volume of 200 mL was obtained with respect to the Hg determination by FI–CV–AAS without preconcentration.

The Certified Reference Material (CRM) SLRS-5 (River water Reference Material for Trace Metals (NRCC, Ottawa, Canada) available in our laboratory does not report neither certified nor informative values for Hg. Consequently, to obtain at least recovery data, known amounts of Hg(II) standards were added to the different real water samples. An aliquot of 10 ml of the spiked samples was preconcentrated in the FI system and a plot of the recovered concentrations versus added concentrations was obtained (three replicates of each concentration were analysed). Although they cannot replace accuracy test, some information is gained about the good performance of the effective control of phenomena of contamination, absorption, losses on the FI-tubing walls. The average recoveries obtained ranged from 96 to 103 %. Table 3 shows the results of the recovery test for samples spiked with different Hg(II) concentrations.

Mercury concentrations in different kind of waters

Different categories of water samples were collected from different places in Argentina and were analysed by means of the proposed preconcentration system by following the procedure already described in the Experimental section. In most water samples Hg(II) levels were below the detection limit. The analytical results obtained for three real water samples containing Hg(II) are (in ng L^{-1}) as follows: (1) Sea water: 330±8 (Mar del Plata); (2) River water (Buenos Aires): 85.0±1.5; (3) Municipal effluent: 342±8 (Buenos Aires province), and (4) Effluent from mining activities: 514±10 (Córdoba province). Mercury concentration values for the real samples were obtained by a standard addition technique (three replicates).

Conclusions

On the basis of the findings of this study, the preconcentration of Hg(II) using ox-CNTs in combination with FI–CV–AAS resulted to be a fully adequate method of determining mercury in water samples at ng L^{-1} levels. Taking into account the extremely low levels of mercury in water samples, a preconcentration step is necessary when a technique such as CV–AAS, available in most laboratories, is used for detection.

The mixture of ox-CNTs with a low molecular weight polyethylene wax (with no need for substrate immobilization) avoided agglomerations and overpressures in the on-line system. The ox-CNTs microcolumn featured excellent chemical stability and retention efficiency without appreciate Hg(II) breakthrough for sample volumes of 200 mL, and with a long lifetime of up to 450 sorption/elution cycles.

This method is rapid, simple and sensitive and can be considered as a low cost alternative, in comparison with other techniques such as ICP-MS, to analyse waters with complex matrices such as sea water and effluents.

Research work in our lab is underway to expanding the proposed preconcentration method to other nanomaterials or composites and analytes/species for the determination of key pollutants in environmental matrices.

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To surmount particles agglomeration when columns filled with CNTs are used in flow sorptive systems we propose to mixture CNTs with a low molecular weight polyethylene.

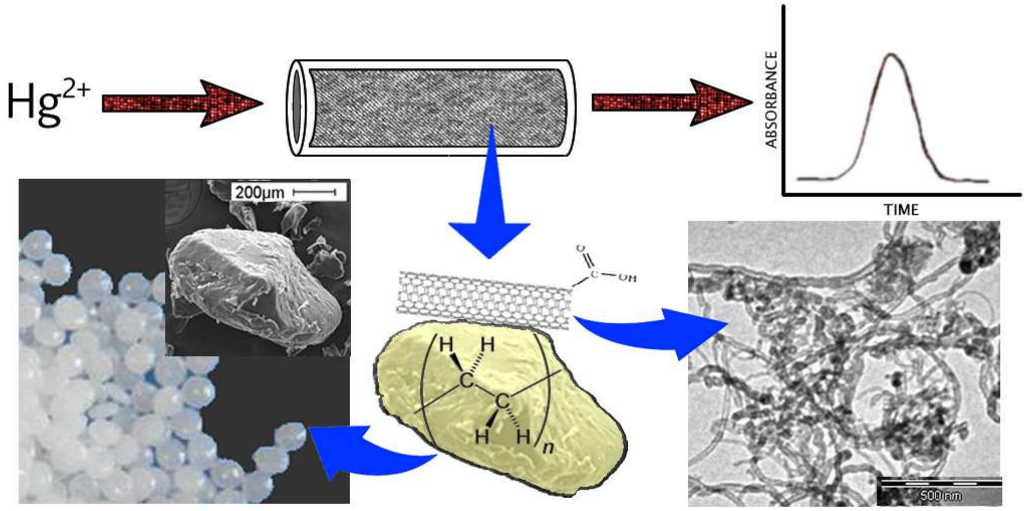


Table 1 Characteristics of the FI-CV-AAS system for determination of Hg

Instrument characteristics and settings	
Cell temperature	110 ºC
EDL lamp current	190 mA
Measurement mode	Peak area
Slit width	0.7 nm
Wavelength	253.7 nm
Cold vapour generation	
$NaBH_4$ concentration	0.2% (w/v); NaOH 0.1% (w/v)
Reductant flow rate	5.5 mL min^{-1}
Hydrochloric acid flow rate	10 mL min^{-1}
Hydrochloric acid concentration	15% (v/v)
Carrier gas (N_2) flow rate	30 mL min^{-1}

Table 2 Interferences of heavy metals and hydride forming elements in the determination of Hg(II) by CV AAS. Results are percentage change in Hg signal (Hg: 2.5 µg L^{-1}; $NaBH_4$: 0.2%).

Species	Interferent concentration (mg L^{-1})	% variation
Al (III)	10	-11.0
As (III)	5	-10.4
Bi (III)	5	11
Cd (II)	5	0
Cu (II)	10	0
Fe (III)	10	-11.0
Mn (II)	10	9.7
Mo (VI)	5	-11.1
Ni (II)	5	0
Pb (II)	5	0
Sb (III)	10	-10.2
Se (IV)	10	0
Sn (II)	10	0
Zn (II)	10	0

Table 3 Recovery test for different kinds of waters. Concentrations are expressed in μg L^{-1}.

Sample	Hg added	Hg found	Recovery (%)
CRM SLRS-5	2.0	1.94±0.03	97
Tap water (Buenos Aires)	1.5	1.52±0.02	101
Well water (Córdoba)	1.2	1.22±0.02	101
Well water 1 (Buenos Aires province)	1.0	1.05±0.02	105
Well water 2 (Buenos Aires province)	2.0	1.92±0.03	96
Antarctic water (Carlini Station)	1.5	1.54±0.03	103

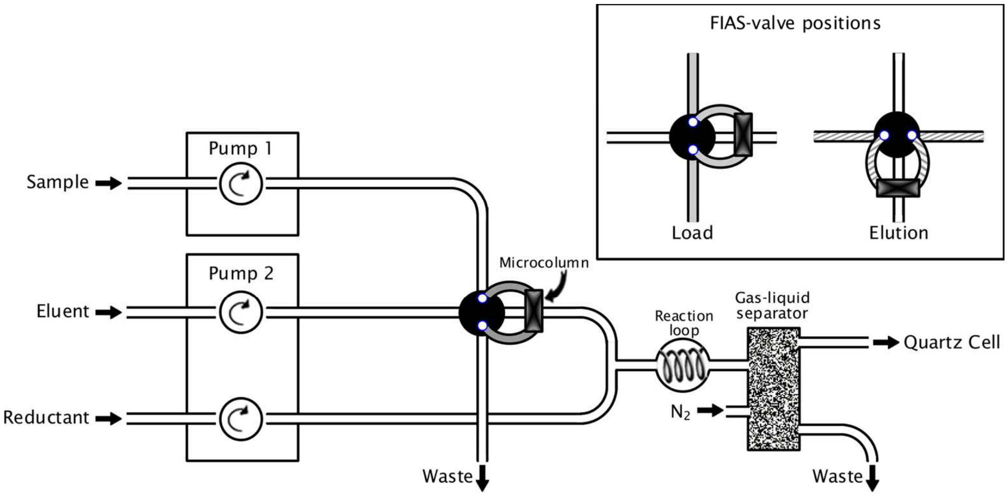
Figure captions

Fig. 1: Operational scheme of the FI-CV-AAS system used for Hg preconcentration

Fig. 2: Average particle size distribution of Epolene®

Fig. 3-a: Scanning electron micrograph of Epolene®

Fig. 3-b and 3-c: Scanning electron micrograph of one particle of Epolene® with ox-CNTs after 450 cycles of Hg preconcentration (3-b: 20000x and 3-c:40000x).



Operational scheme of the FI-CV-AAS system used for Hg preconcentration
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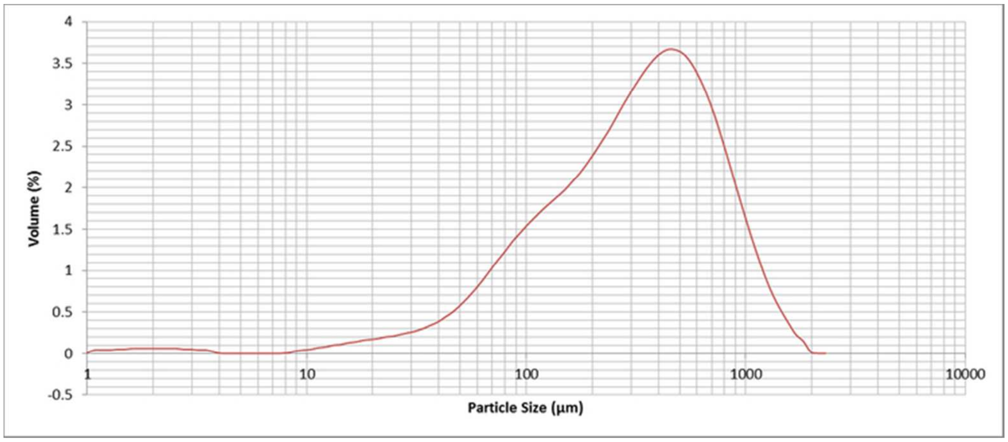
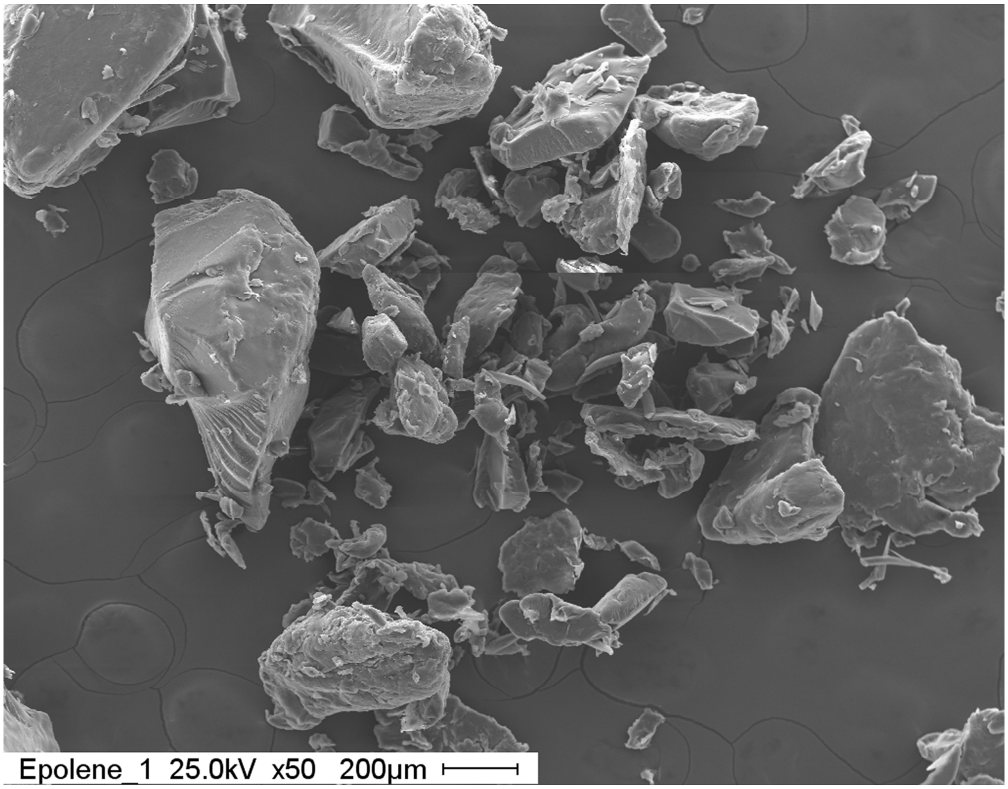
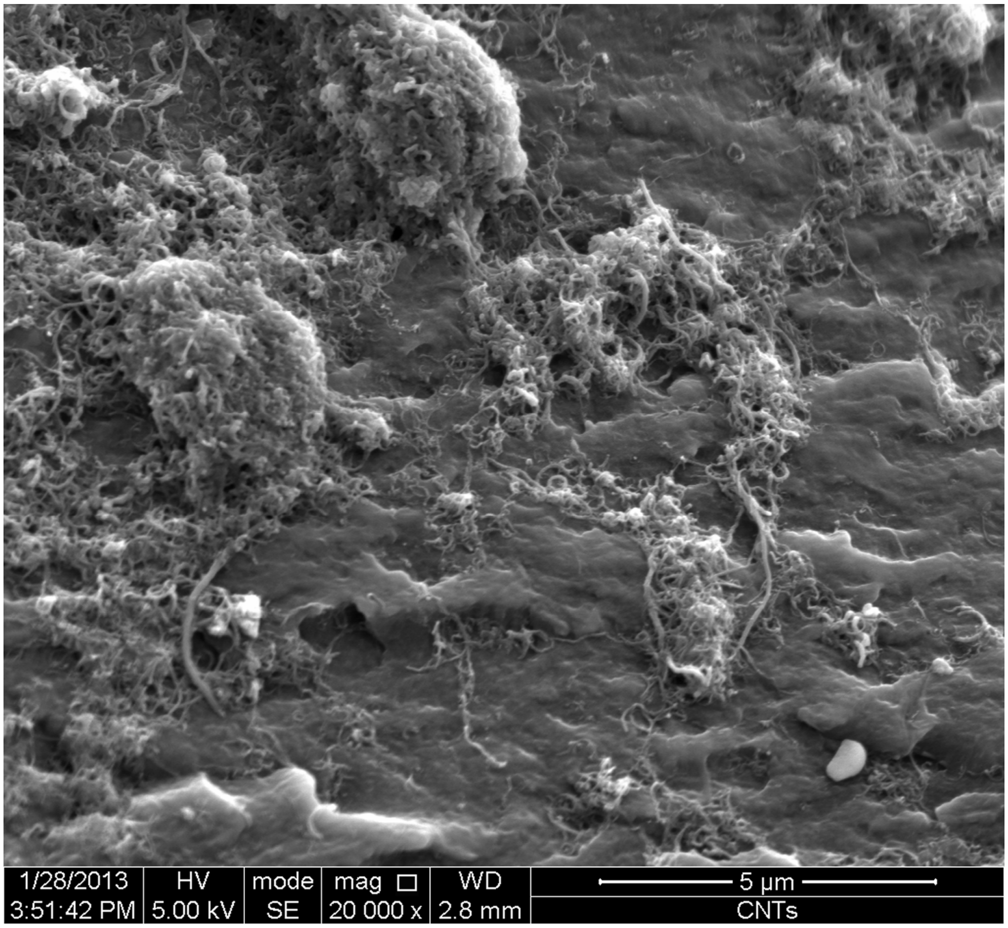


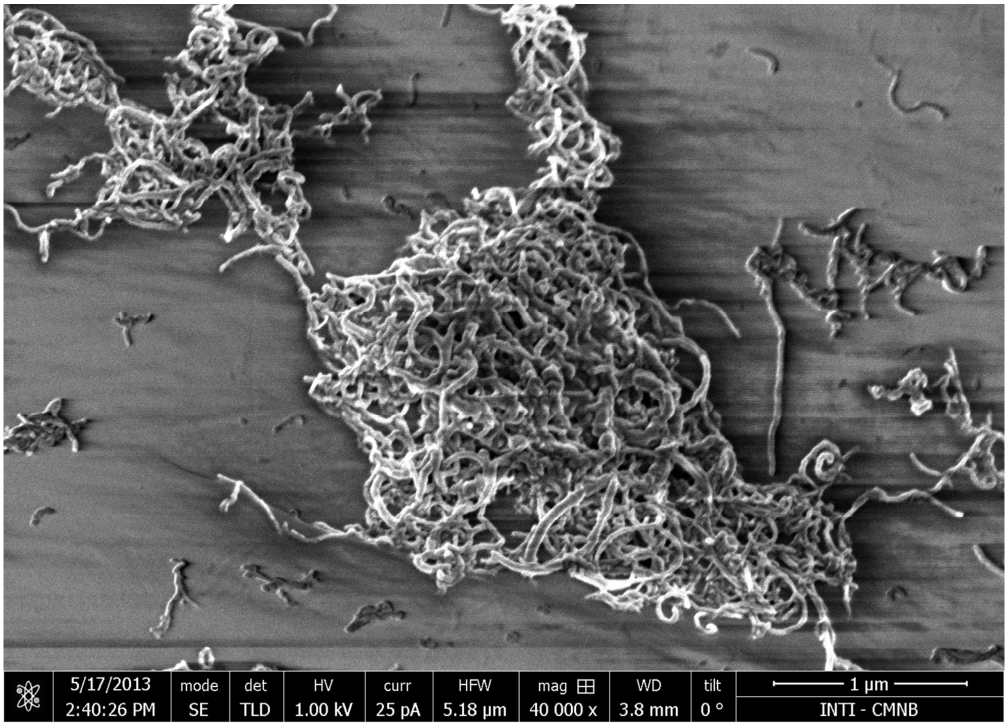
Average particle size distribution of Epolene®
62x27mm (300 x 300 DPI)



Scanning electron micrograph of Epolene®
260x203mm (300 x 300 DPI)



Scanning electron micrograph of one particle of Epolene® with ox-CNTs after 450 cycles of Hg preconcentration (3-b: 20000x and 3-c:40000x).
313x288mm (300 x 300 DPI)



Scanning electron micrograph of one particle of Epolene® with ox-CNTs after 450 cycles of Hg preconcentration (3-b: 20000x and 3-c:40000x).
210x151mm (300 x 300 DPI)