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Use of carbon nanotubes and electrothermal atomic absorption spectrometry for the speciation of very low amounts of arsenic and antimony in waters

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ABSTRACT

A procedure for the determination of inorganic arsenic (III, V) and antimony (III, V) in water samples by using a miniaturized solid-phase extraction with carbon nanotubes followed by electrothermal atomic absorption measurement is proposed. The trivalent species are first complexed with ammonium pyrrolidinedithiocarbamate, next retained in a mini-column containing nanotubes and then eluted by means of a plug of an ammonia solution. The atomizer is impregnated with a tungsten salt which acts as an effective chemical modifier during the heating cycle. Total inorganic arsenic and antimony are determined after the reduction of the pentavalent forms with an ammonium iodide solution. Pentavalent arsenic and antimony are calculated by difference. When using 50 mL sample solutions, the limits of detection are 0.02 and 0.05 $\mu g\,L^{-1}$ for As and Sb, respectively, and the enrichment factor is 250. The relative standard deviations calculated for five determinations at the 1 $\mu g\,L^{-1}$ level are below 4%.

1. Introduction

Arsenic and antimony are present in waters at very low concentrations as inorganic compounds, and their determination is a subject of practical relevance. In addition, and because of the different toxicity of the trivalent and pentavalent forms, the convenience of a reliable, relatively simple procedure allowing the speciation of the two oxidation degrees is evident. The goal can be achieved by using chromatographic techniques coupled to specific detectors, but non-chromatographic procedures [1] represent an interesting alternative choice without the need of expensive instrumentation. In any case, and due to the extremely low concentrations to be measured, a preconcentration stage is commonly used.

Solid-phase extraction (SPE) has repeatedly proven to be a suitable way for preconcentrating analytes, and the use of carbon nanotubes (CNTs) for SPE purposes has aroused increasing interest as has been shown in recent reviews [2–6]. Most of the applications refer to organic analytes [7–13] but CNTs can also be applied for the case of inorganic ions [14,15]. For this purpose, in some of the procedures up-to-date reported, CNTs are first functionalised by treatment with oxidizing agents [16–18], while some authors have suggested functionalization by means of organic reagents [19–24] or mixing with other sorbents [25]. After the preconcentration stage, inductively coupled plasma mass spectrometry (ICP-MS) is a suitable technique for the final measurement of inorganic species [18,24,26]. Atomic fluorescence spectrometry (AFS) has also been proposed for the determination of bismuth [27], lead [28] and mercury [29], while electrothermal atomic absorption spectrometry (ETAAS) has been used for the determination of tin [30], chromium [31], copper [32], thallium [33], vanadium [34] and cobalt [35]. In the particular case of arsenic and antimony, CNTs have been used for preconcentration purposes as a previous stage for AFS [19,36] or ICP-MS measurement [37]. The determination of arsenic in waters by means of its extraction with an ammonium pyrrolidinedithiocarbamate (APDC)-modified activated carbon mini-column followed by ETAAS measurement has also been reported [38].

In this work, a procedure allowing inorganic arsenic and antimony to be speciated in waters is reported. The procedure uses APDC as the complexing agent in order to the trivalent complexes be retained in a CNTs-containing mini-column, and is based on our previous work [39] that proved the advantages of using a permanent chemical modifier when dealing with the ETAAS determination of arsenic and antimony.

2. Experimental

2.1. Instrumentation

A model 800 atomic absorption spectrometer (Perkin-Elmer, Shelton, USA) equipped with a Zeeman-effect background correction device, a transversely heated graphite tube atomizer (THGA)

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Table 1
Instrumental parameters.

Instrumental parameters	Arsenic	Antimony
Lamp current, mA	380 (EDL)	20 (HCL)
Wavelength, nm	193.7	217.6
Bandwitdth, nm	0.7	
Atomizer type	Platform	
Injected sample volume, μL	20	
Chemical modifier	W (permanent modifier)	
Background correction	Zeeman	
Furnace heating program		

Step	Temperature, °C	Ramp, s	Hold, s
1: Dry	80	1	30
2: Pyrolysis	400	15	20
3: Atomization[a,b]	2000	0	4

[a] Flow of argon stopped.
[b] Reading step.

and an AS-800 autosampler were used. Pyrolytic graphite platforms inserted into pyrolytically coated tubes were obtained from the same manufacturer (part number B050-4033). Argon was the inert gas, the flow rate being 250 mL min^{-1} during all the stages except for atomization, when the flow was stopped. Measurements were carried out using an arsenic electrodeless discharge lamp and an antimony hollow cathode lamp (Perkin–Elmer) as the radiation sources. The instrumental parameters are summarized in Table 1.

2.2. Reagents

All the solutions were prepared with pure water (18 MΩ cm) obtained with a Millipore system (Millipore, Bedford, MA, USA). To decrease the risk of contamination, no glassware was used, and plastic (polypropylene) vessels were used exclusively. The plasticware was washed with 1% (v/v) concentrated nitric acid solution and then rinsed with water before use. The arsenic (III) and (V) standard solutions (1 g L^{-1}) were prepared from As_2O_3 and $Na_3AsO_4\cdot 12H_2O$ (Fluka, Buchs SG, Switzerland), respectively. The antimony (III) and (V) standard solutions (1 g L^{-1}) were prepared by dissolving in water appropriate amounts of potassium antimonyl tartrate and potassium pyroantimonate (Fluka), respectively. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. The 0.1 mol L^{-1} ammonium pyrrolidine dithiocarbamate (APDC) solution was prepared by dissolving the compound (Sigma-Aldrich Chemie GmbH, Germany) in high purity methanol. Other chemicals used were obtained from Fluka. A 0.1% (m/V) ammonium iodide aqueous solution was used for reducing pentavalent arsenic and antimony. The multiwalled carbon nanotubes (CNTs) were obtained of Nanocyl, Belgium (reference Nanocyl NC 7000).

2.3. Impregnation of the pyrolytic material with a tungsten salt

Impregnation was carried out as indicated elsewhere [39,40]. Both tubes and platforms were immersed in a solution containing 1 g L^{-1} $Na_2WO_4\cdot 2H_2O$ and left at atmospheric pressure overnight. Next, they were dried in an oven at 120 °C for 4 h and, finally, submitted to a simple temperature programme (Table 2).

2.4. Preparation of the CNTs minicolumns

20 mg CNTs were suspended in ethanol and submitted to a mild ultrasound treatment (10 min in a 50 W ultrasonic bath) to help disaggregation. Then, by means of a peristaltic pump, the suspension was passed through a glass minicolumn (20 mm length, 2 mm internal diameter) at 2 mL min^{-1}, with a small amount of quartz wool placed at the end. Once the CNTs were retained inside the column, the other end was also closed by means of a small amount of quartz wool. The column was pre-conditioned by passing first 10 mL of a 0.1 mol L^{-1} nitric acid solution, and then pure water until no traces of acid were detected in the liquid emerging of the column.

Table 2
Temperature programme for conditioning the graphite atomizers after the treatment with sodium tungstate.

Step	Temperature, °C	Ramp, s	Hold, s
1	120	1	120
2	200	5	120
3	1200	5	30
4[a]	2400	1	6

[a] Flow of argon stopped.

2.5. Procedure

For maximum sensitivity, 50 mL sample aliquots containing up to 30 ng arsenic and/or 50 ng antimony were used. Nitric acid was incorporated to give a 0.01 mol L^{-1} solution, and 500 μL of a 0.1 mol L^{-1} APDC solution were also added. The resulting solution was passed through the column at 1.5 mL min^{-1} by using a peristaltic pump. Once air was passed for 2 min to remove sample residues, the trivalent arsenic and antimony complexes with APDC were eluted by means of a 200 μL plug of a 1 mol L^{-1} ammonia solution, the liquid being collected in a vial for ETAAS measurement. The heating programme recommended is given in Table 1. The minicolumn can repeatedly be used once it is regenerated by passing diluted (0.01 mol L^{-1}) nitric acid solution, and then water. If an extreme sensitivity is not required, a 15 mL sample volume is recommended because of the considerable saving of time.

For determining total inorganic arsenic and antimony concentrations, 0.1% m/V ammonium iodide was incorporated to the sample and left for 15 min before adding the APDC solution. The procedure was repeated, and new ETAAS measurements were carried out which allowed As(V) and Sb(V) to be calculated by difference.

3. Results and discussion

3.1. Selection of the type of carbon nanotubes

CNTs were obtained of several dealers (Table 3), and a large number of preliminary experiments were devoted to select the most appropriate for the purpose here discussed. The literature is controversial as regards the need of the CNTs to be functionalised with –OH or –COOH groups for retaining inorganic species [14]. The treatment with acid solutions allows CNTs to be functionalised mainly with –OH groups. The percentage of carboxylic acid groups increases when the treatment includes, in addition, hydrogen peroxide or potassium permanganate [41]. However, such an energetic treatment may result in a serious damage to the nanoparticles [42], and a milder acid oxidation treatment with the help of ultrasounds has been recommended to avoid CNTs deterioration.

With this in mind, a large number of experiments were carried out using the materials indicated in Table 3 as received, as well as others resulting of functionalizing the MWCNTs provided by NANOCYL. The retention of the analyte was in each case calculated after passing standard solutions through a minicolumn filled with the absorbent being tested. No significant differences among the different materials were noted, being in all cases the percentage of analyte retained within the 90–97% range. On the other hand, it was experimentally verified that, when using functionalised CNTs, the elution stage required a more acidic solution than for the case of normal CNTs. All these experiments showed that the most suitable

Table 3
Types of nanotubes used in this work.

Trademark	Web	Type	Information
BAYER	http://www.baytubes.com/	MWCNTs	
MER	http://www.mercorp.com/mercorp/	MWCNTs	
NTP	http://www.nanotubes.com.cn/	SWCNTs	<2 nm[a]
		MWCNs	10–30 nm[a]
			40–60 nm[a]
CHEAPTUBES	http://www.cheaptubesinc.com/	MWCNTs	Normal
			–OH
			–COOH
NANOCYL	http://www.nanocyl.com/	MWCNTs	
MICROPHASE	http://www.microphase.jp/e_index.html	MWCNTs	
ALDRICH	http://www.sigma-aldrich.com/	MWCNTs	
		Fullerene C_{60}	

[a] Outer diameter.

material for the purpose here considered were non-functionalised MWCNTs (NANOCYL), and so these were used throughout the rest of the work.

3.2. Effect of pH

The literature shows that there is a strong dependence of the surface charge of the CNTs, and so of its absorbent properties, with the pH of the solution [43]. For the case of non-functionalised materials, previous reports indicate that, when metallic ions are involved, the retention increases above pH 4, and is maximal at pH 7 or even higher [44]. However, when complexes are involved, the effect of the pH is different since the stability of the ligand:metal compounds plays a relevant role [45].

Trivalent arsenic originates stable complexes with APDC within a wide pH range [46], while pentavalent arsenic is not complexed. For the case of Sb(III), stable complexes are formed at pH values in the 0.2–6 pH range, and Sb(V) originates stable compounds even in a 1 mol L^{-1} hydrochloric acid medium. Since these values are approximate, and depends on the APDC concentration used [47,48], a study was carried out in the presence of 0.001 mol L^{-1} APDC. As can be seen in Fig. 1, both As(III) and Sb(III) complexes were retained in the CNTs mini-column even at low pHs. The results showed in the graph indicate that it is possible to determine As(III) in the presence of As(V). Consequently, speciation can be carried out by reducing As(V) and repeating the measurement. In this way, the amount of total inorganic arsenic is obtained, and the concentration of As(V) calculated. The same reasoning applies for the Sb(V)/Sb(III) couple. For the rest of the experiments, a pH close to 2 was used without the need of a buffer solution by incorporating 0.01 mol L^{-1} hydrochloric acid to the sample solution.

3.3. Effect of other experimental variables

The effect of the APDC concentration was studied and the results are summarized in Fig. 2. To obtain these graphs, solutions containing 1 μg L^{-1} As(III) or 2 μg L^{-1} antimony (as the trivalent or pentavalent form) were used. No data for As(V) are shown since, as indicated, this species is not retained. A 0.001 mol L^{-1} APDC concentration was selected as suitable.

The nature and volume of the solution to be used for the elution stage is important in order a high preconcentration factor to be achieved. The procedures recommended in the literature for eluting APDC complexes of several metals retained in CNTs or extracted in organic solvents use solutions containing at least 1 mol L^{-1} nitric acid. Such a high acid concentration would result in a decreased lifetime of the pyrolytic material in the final ETAAS stage. To avoid this, other less aggressive solutions were tested as the eluents, and some of the results found for the case of As(III) are shown in Fig. 3. It is noteworthy that even using pure water the complex could be eluted. This partial elution (graph a) means a practical difficulty since, once the sample solution is passed through the column, pure water cannot be used as a washing solution and, for this reason, air is recommended to remove the residues of the sample solution remaining inside the column before elution. As can be seen in Fig. 3, 200 μl of a 1 mol L^{-1} ammonia solution allowed As(III) to be completely eluted of the column. Similar results were found for the case of the Sb(III) compound.

On the other hand, experiments were carried out using volumes of sample in the 10–100 mL range, and it was found that retention (for a 0.3 μg L^{-1} sample solution) was maximum until a 50 mL volume, and then decreased for higher volumes. Additional experiments were devoted to calculate the retention capacity of the CNTs for the purpose here studied. To this effect, 0.1 g CNTs were added

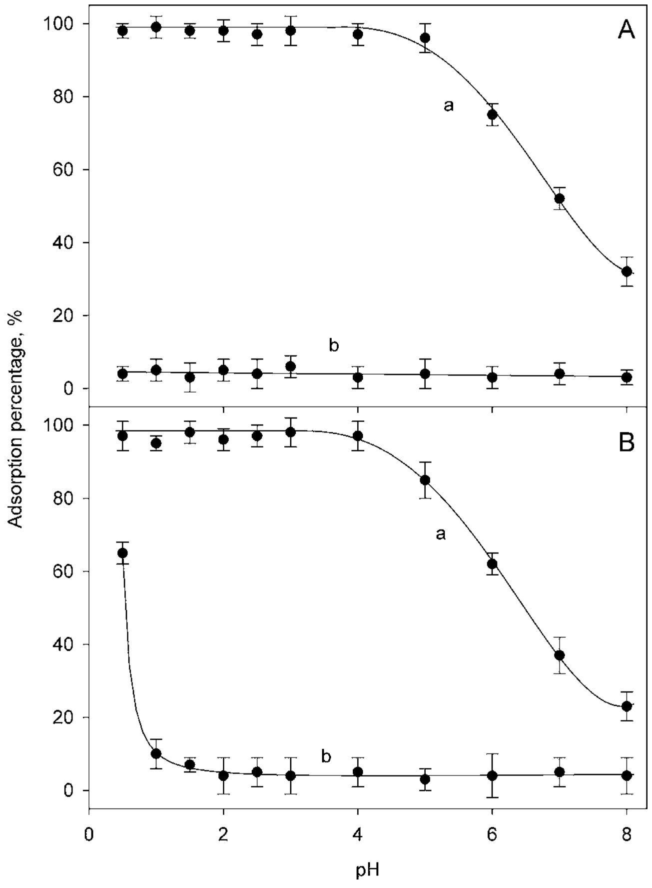

Fig. 1. Effect of pH on the adsorption percentage of arsenic (graph A) and antimony (graph B). Lines a and b correspond to the trivalent and pentavalent forms, respectively. Vertical bars show the standard deviation for three experiments.

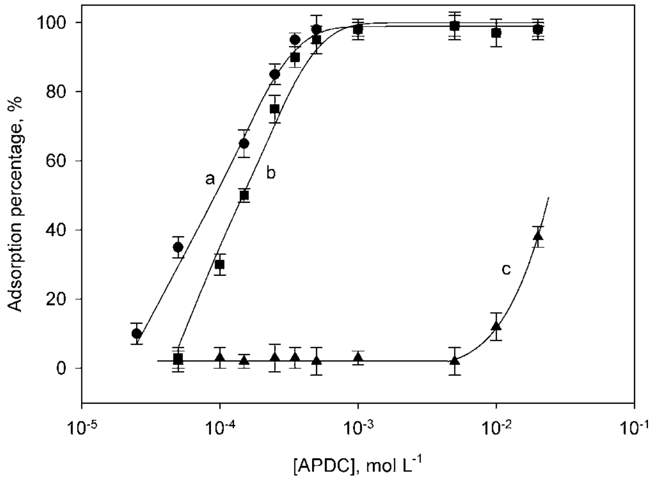

Fig. 2. Effect of the APDC concentration. Curves a, b, and c correspond to As(III), Sb(III) and Sb(V), respectively.

to 50 mL of a 0.01 mol L^{-1} APDC solution at pH 2 containing 1 mg As(III). After stirring magnetically for 30 min, the mixture was filtered and the As(III) remaining in the liquid phase was measured after a suitable dilution. The maximum retention capacity was calculated to be 9.1 mg As(III) per gram of CNTs. The experiments were repeated replacing As(III) by Sb(III) and, in this case, the retention capacity was calculated to be 8.95 mg per gram.

The optimal flow-rates to be used for both the retention and elution processes were also studied. The effect of the sample flow-rate through the column was varied in the 0.5–4 mL min^{-1} range, and the retention for both As(III) and Sb(III) proved independent of this variable up to 1.5 mL min^{-1}. This relatively high value is recommended in order to pass the maximum volume of sample through the column in a minimum time, and so to improve the preconcentration efficiency. Only a small volume (200 µL) is required for the elution stage, and so the flow-rate can be decreased until 0.5 mL min^{-1} to ensure maximum recovery of the analyte. The practical significance of these data is noteworthy. In the case of using 50 mL sample, a preconcentration factor of 250 can be achieved, but this requires more than 30 min for the retention stage. From a practical point of view, since such a high preconcentration factor would rarely be required, the use of 15–20 mL sample aliquots is recommended. Because of in all cases the final volume collected from the column is 200 µL, this means that preconcentration factors ranging 75–100 are obtained spending a more reasonable period of time. In addition, as indicated below, when the preconcentration factor increases, the detection limit does not decrease at the same extent due to the worsening in reproducibility.

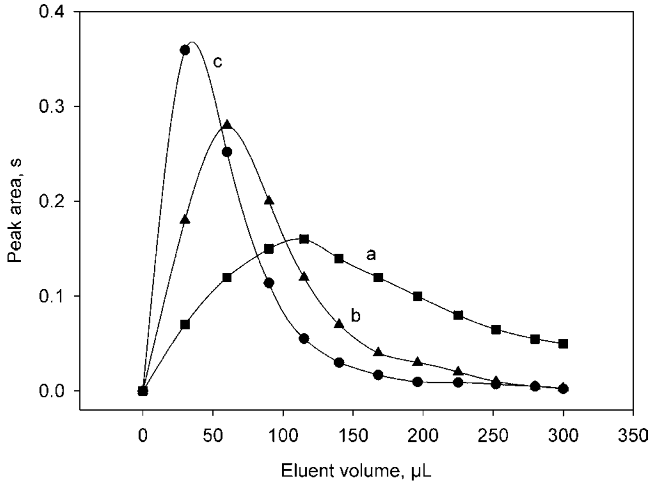

Fig. 3. Elution profiles obtained when 30 mL of a 1 µg L^{-1} As(III) solution were passed through the mini-column and then eluted with: pure water, acetic/acetate buffer or ammonia solution (lines a, b, and c, respectively).

Table 4
Results (mean ± sd, $n = 5$) for the determination of As(III,V) and Sb(III,V) in aqueous solutions.

Added, µg L^{-1}		Found, µg L^{-1}		Calculated, µg L^{-1}
As(III)	As(V)	As(III)	As(III) + As(V)	As(V)
2	0	1.99 ± 0.03	2.02 ± 0.04	0.03 ± 0.05
1	1	0.96 ± 0.04	2.01 ± 0.03	1.05 ± 0.05
0.5	1.5	0.52 ± 0.02	2.00 ± 0.02	1.48 ± 0.03
0	2	0.02 ± 0.02	1.97 ± 0.04	1.95 ± 0.04
Sb(III)	Sb(V)	Sb(III)	Sb(III) + Sb(V)	Sb(V)
4	0	3.98 ± 0.05	4.02 ± 0.05	0.04 ± 0.07
2	2	2.01 ± 0.04	3.97 ± 0.06	1.96 ± 0.07
1	3	0.99 ± 0.04	3.98 ± 0.04	2.99 ± 0.06
0	4	0.02 ± 0.03	4.01 ± 0.06	3.99 ± 0.07

3.4. *Determination of pentavalent species*

Since As(V) and Sb(V) do not react with APDC, total inorganic arsenic and antimony could be determined after reducing these species to the trivalent form. The addition of sodium thiosulphate [39] was found to be inappropriate because of the formation of elemental sulphur, that has a deleterious effect on the APDC complexes. Other reducing agents were tested, and ammonium iodide proved suitable. The effect of this chemical was studied, and it was verified that when a 0.1% m/V concentration was used, a 20-min reaction time allowed the pentavalent forms to be completely reduced. To verify the reliability of the speciation, several solutions containing mixtures of both oxidation states were prepared and submitted to the procedure recommended. The results, summarized in Table 4, showed that speciation at very low levels was possible. A statistical study of the data by means of the non-parametric Wilcoxon test [49] showed the absence of significant differences at the 95% confidence level between the amounts of analyte added and those found.

All the above described experiments were carried out using a tungsten salt as a permanent modifier for the final ETAAS measurement, as has already been recommended [39]. For comparison and verification purposes, additional experiments were made by using conventional chemical modification with a palladium salt instead of the impregnation with sodium tungstate, and the advantages of the latter were confirmed. The heating cycle to be applied was studied in the usual way, and the optimized programme was that given in Table 1.

3.5. *Analytical figures of merit*

As indicated above, the preconcentration factor achieved is a compromise between extreme sensitivity and sampling frequency. Calibration graphs were obtained for both analytes by using two different volumes of the sample solution, namely 50 and 15 mL. This means preconcentration factors of 250 and 75, respectively, and the main analytical figures of merit are summarized in Table 5. As can be seen, the detection limit, calculated on the basis of the analyte concentration providing a signal equivalent to three times the standard error of the regression line, only decreased from 0.03 to 0.02 µg L^{-1} when the preconcentration factor changed from 75 to 250, respectively. This is due to the decrease in reproducibility when using large volumes of sample.

The possible interference caused by some ions commonly present in waters was also studied. No deleterious effects were

Table 5
Main figures of merit.

Characteristic	As(III)	Sb(III)
Enhancement factor	250/75	250/75
Sample consumption, mL	50/15	50/15
Eluent volume, mL	0.2	0.2
Working range, $\mu g\,L^{-1}$	0.03–0.6/0.1–2	0.05–1.0/0.2–4
Limit of detection, $\mu g\,L^{-1}$	0.02/0.03	0.05/0.06
Precision (RSD, $n = 5$), %	3.5/3.1	3.7/3.5
Calibration function (5 standards, $n = 3$, $\mu g\,L^{-1}$)	$A_{int} = 0.003 + 0.702\,C_{As}/A_{int} = 0.002 + 0.213\,C_{As}$	$A_{int} = 0.002 + 0.365\,C_{As}/A_{int} = 0.003 + 0.162\,C_{As}$
Correlation coefficient	0.9987/0.9991	0.9980/0.9986

Table 6
Determination of inorganic As and Sb species in water samples.

Specie	Added, $\mu g\,L^{-1}$	BMW[a]		TW[b]		TWDIOS[c]		RW[d]		SpW[e]		SW[f]	
		Found[g], $\mu g\,L^{-1}$	R, %	Found[g], $\mu g\,L^{-1}$	R, %	Found[g], $\mu g\,L^{-1}$	R, %	Found[g], $\mu g\,L^{-1}$	R, %	Found[g], $\mu g\,L^{-1}$	R, %	Found[g], $\mu g\,L^{-1}$	R, %
As(III)	0	<LOD	–	<LOD	–	<LOD	–	0.68 ± 0.04	–	<LOD	–	<LOD	–
	0.5	0.48 ± 0.03	96	0.49 ± 0.03	98	0.49 ± 0.03	98	1.21 ± 0.05	106	0.52 ± 0.03	104	0.47 ± 0.03	94
As(V)	0	0.41 ± 0.04	–	<LOD	–	<LOD	–	0.79 ± 0.04	–	<LOD	–	0.65 ± 0.04	–
	0.5	0.92 ± 0.05	102	0.51 ± 0.02	102	0.52 ± 0.04	104	1.32 ± 0.05	106	0.49 ± 0.02	98	1.17 ± 0.05	104
Sb(III)	0	<LOD	–	<LOD	–	<LOD	–	0.18 ± 0.02	–	0.16 ± 0.02	–	<LOD	–
	1.0	0.94 ± 0.02	94	1.01 ± 0.04	101	0.98 ± 0.03	98	1.15 ± 0.04	97	1.18 ± 0.03	102	0.96 ± 0.03	96
Sb(V)	0	0.21 ± 0.03	–	<LOD	–	<LOD	–	0.26 ± 0.03	–	0.12 ± 0.02	–	<LOD	–
	1.0	1.19 ± 0.04	98	1.03 ± 0.03	103	1.02 ± 0.04	102	1.24 ± 0.04	98	1.15 ± 0.04	103	1.01 ± 0.04	101

[a] Bottled mineral water.
[b] Tap water.
[c] Tap water treated with domestic inverse osmosis system.
[d] River water.
[e] Spring water.
[f] Sea water.
[g] Mean ± standard deviation, $n = 5$.

Table 7
Comparison of some reported procedures.

Sorbent	Analyte	Detector	EF[a]	LOD, $ng\,L^{-1}$	Reference
Carbon nanotubes	As, Sb	FI-HG-AFS	25, 24	4, 2	[36]
Eggshell	As	HG-AFS	33.3	1	[50]
Modified activated carbon	As	ETAAS	50	50	[38]
MnO_2	As	HPLC-HG-QFAAS, ETAAS	17	20	[51]
Modified Sepabeads SP 70	As	HG-AAS	36	13	[52]
Ionic exchanger	As	NAA	–	1–16	[53]
TiO_2	As	ETAAS	–	20	[54]
Modified SiO_2	As	ICP-OES	100	50	[55]
Cigarette filter	As	HG-AFS	25	1	[56]
C_{18}	As, Sb	ICP-MS	50	1–6	[57]
Immobilised aminoacid	Sb	ICP-OES	11	90	[58]
Modified TiO_2	As, Sb	ICP-OES	10	530–710	[59]
Carbon nanotubes	As, Sb	ETAAS	250	20	This work

[a] Enrichment factor.

noted for chloride, sulphate, calcium, magnesium, sodium and potassium even at $1\,g\,L^{-1}$ concentrations. However, the analytical signals decreased when Fe(III), Al(III) or Cr(VI) were present at concentrations above $2\,mg\,L^{-1}$. It should be noted this means interferent/analyte ratios largely exceeding 1000. Consequently, when dealing with contaminated waters, and thanks to the high sensitivity of the procedure, the interference can be overcome simply by diluting the sample solution.

A number of water samples were submitted to the recommended procedure. Due to the very low concentrations involved, the direct comparison of the results with those found by means of an alternative procedure was considered unreliable and, for checking validity, standard additions were used instead (Table 6). The recovery values were in the 94–104% range. In addition, the slopes of the standard addition graphs were the same than the slopes of the calibration graphs obtained with aqueous standards, in this way proving the absence of a matrix effect for all the samples considered. A comparison of the main characteristics of the present procedure with others reported in the literature, and based in a solid-phase separation, is given in Table 7. The detection limit achieved for the procedure here reported is similar or better than those reported by other procedures based in ETAAS or ICP optical emission spectrometry.

4. Conclusion

Carbon nanotubes are shown to be excellent sorbents for the APDC complexes of As(III) and Sb(III), which allows these analytes to be preconcentrated. The conjunction of a high preconcentration effect with a sensitive analytical technique as ETAAS results in a highly sensitive and reliable procedure for the speciation of low amounts of arsenic and antimony in waters. In addition to extend the wide range of analytical possibilities offered by carbon nanotubes, the procedure here studied represents a relatively simple, economical and easy-to-perform alternative to other procedures based in chromatographic techniques followed by ICP-MS measurements.

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References

[1] A. Gonzalvez, M.L. Cervera, S. Armenta, M. de la Guardia, Anal. Chim. Acta 636 (2009) 129.
[2] M. Valcárcel, S. Cárdenas, B.M. Simonet, TrAC Trends Anal. Chem. 27 (2008) 34.
[3] L.M. Ravelo-Pérez, A.V. Herrera-Herrera, J. Hernández-Borges, M.A. Rodríguez-Delgado, J. Chromatogr. A 1217 (2010) 2618.
[4] K. Pyrzynska, Chemosphere 83 (2011) 1407.
[5] R. Lucena, B.M. Simonet, S. Cárdenas, M. Valcárcel, J. Chromatogr. A 1218 (2011) 620.
[6] F. Augusto, E. Carasek, R.G.C. Silva, S.R. Rivellino, J. Chromatogr. A 1217 (2010) 2533.
[7] S. Guan, Z. Yu, H. Yu, C. Song, Z. Song, Z. Qin, Chromatographia 73 (2011) 33.
[8] Z. Es'haghi, Z. Rezaeifar, G.H. Rounaghi, Z.A. Nezhadi, M.A. Golsefidi, Anal. Chim. Acta 689 (2011) 122.
[9] L. Chen, W. Chen, C. Ma, D. Du, X. Chen, Talanta 82 (2011) 104.
[10] Y. Sun, W.Y. Zhang, J. Xing, C.M. Wang, Microchim. Acta 173 (2011) 223.
[11] F. Wu, W. Lu, J. Cheng, W. Liu, L. Zhang, Talanta 82 (2010) 1038.
[12] J. Ma, R. Xiao, J. Li, J. Yu, Y. Zhang, L. Chen, J. Chromatogr. A 1217 (2010) 546.
[13] M. Cruz-Vera, R. Lucena, S. Cárdenas, M. Valcárcel, Anal. Bioanal. Chem. 391 (2008) 1139.
[14] K. Pyrzynska, TrAC. Trends Anal. Chem. 29 (2010) 718.
[15] M. Soylak, Y.E. Unsal, Food Chem. Toxicol. 48 (2010) 1511.
[16] Q. Zhou, H. Bai, J. Xiao, At. Spectrom. 28 (2007) 150.
[17] C.R. Teixeira-Tarley, A.F. Barbosa, M. Gava-Segatelli, E. Costa-Figueiredo, P. Orival-Luccas, J. Anal. At. Spectrom. 21 (2006) 1305.
[18] S. Chen, C. Liu, M. Yang, D. Lu, L. Zhu, Z. Wang, J. Hazard. Mater 170 (2009) 247.
[19] L. Li, Y.M. Huang, Y. Wang, Anal. Chim. Acta 631 (2009) 182.
[20] D. Afzali, A. Mostafavi, Anal. Sci. 24 (2008) 1135.
[21] T. Shamspur, A. Mostafavi, J. Hazard. Mater. 168 (2009) 1548.
[22] Y. Liu, Y. Li, Z.Q. Wu, X.P. Yan, Talanta 79 (2009) 1464.
[23] Z. Zang, Z. Hu, Z. Li, Q. He, X. Chang, J. Hazard. Mater. 186 (2011) 1985.
[24] J. Wang, X. Ma, G. Fan, M. Pan, X. Ye, S. Wang, J. Hazard. Mater. 172 (2009) 958.
[25] Z. Es'haghi, M. Khalili, A. Khazaeifar, G.H. Rounaghi, Electrochim. Acta 56 (2011) 3139.
[26] K.X. Yang, M.E. Kitto, J.P. Orsini, K. Swami, S.E. Beach, J. Anal. At. Spectrom. 25 (2010) 1290.
[27] H. Wu, X.C. Wang, C.L. Xu, J.S. Lu, J.Y. Tian, J. Ma, At. Spectrosc. 31 (2010) 14.
[28] H. Wu, H.Y. Wen, B.P. Han, B.X. Du, J.S. Lu, J.Y. Tian, Microchim. Acta 166 (2009) 41.
[29] X.H. Shang, At. Spectrosc. 28 (2007) 35.
[30] H.H.V. Costa, G.D. Lima, L.R. Nacano, C.R.T. Tarley, Water Air Soil Pollut. 217 (2011) 557.
[31] X. Zhang, M.L. Chen, Y.L. Yu, T. Yang, J.H. Wang, Anal. Methods 3 (2011) 457.
[32] L. Zhao, Q.J. Gong, H. Sun, B.W. Yang, Y. Zhu, At. Spectrosc. 31 (2010) 201.
[33] P.H. Pacheco, R.A. Gil, P. Smichowski, G. Polla, L.D. Martínez, Anal. Chim. Acta 656 (2009) 36.
[34] R.A. Gil, S.N. Goyanes, G. Polla, P. Smichowski, R.A. Olsina, L.D. Martínez, J. Anal. At. Spectrom. 22 (2007) 1290.
[35] J.M.O. Souza, C.R.T. Tarley, Int. J. Environ. Anal. Chem. 89 (2009) 489.
[36] H. Wu, X. Wang, B. Liu, Y. Liu, S. Li, J. Lu, et al., Spectrochim. Acta B 66 (2011) 74.
[37] Z. Li, S. Chen, D. Lu, X. Cheng, At. Spectrosc. 30 (2009) 218.
[38] Y. Jiang, Y. Wu, J. Liu, X. Xia, D. Wang, Microchim. Acta 161 (2008) 137.
[39] R.E. Rivas, I. López-García, M. Hernández-Córdoba, Spectrochim. Acta B 64 (2009) 329.
[40] H. Fritzsche, W. Wegscheider, G. Knapp, H.M. Ortner, Talanta 26 (1979) 219.
[41] K. Yang, L.Z. Zhu, B.S. Xing, Environ. Sci. Technol. 40 (2006) 1855.
[42] P.X. Hou, C. Liu, H.M. Cheng, Carbon 46 (2008) 2003.
[43] J. Hu, C. Chen, X. Zhu, X. Wang, J. Hazard. Mater. 162 (2009) 1542.
[44] A.H. El-Sheikh, J.A. Sweileh, Y.S. Al-Degs, Anal. Chim. Acta 604 (2007) 119.
[45] M. Tuzen, M. Soylak, J. Hazard. Mater. 147 (2007) 219.
[46] A. Eaton, H.C. Wang, J. Northington, Analytical Chemistry of Arsenic in Drinking Water, AWWA Research Foundation and American Water Works Association, Denver, CO, USA, 1998, p. 25.
[47] K.S. Subramanian, J.C. Meranger, Anal. Chim. Acta 124 (1981) 131.
[48] W.M. Mok, C.M. Wai, Anal. Chem. 59 (1987) 233.
[49] J.N. Miller, J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, 6th ed., Pearson Ed. Ltd, 2010, 163.
[50] Y. Zhang, W. Wang, L. Yi, Y. Huang, J. Cao, Talanta 80 (2010) 1907.
[51] Y. Tian, M.L. Chen, X.W. Chen, J.H. Wang, Y. Hirano, H. Sakamoto, et al., J. Anal. At. Spectrom. 26 (2011) 133.
[52] O.D. Uluozlu, M. Tuzen, D. Mendil, M. Soylak, Food Chem. Toxicol. 48 (2010) 1393.
[53] W.M. Sánchez, B. Zwicker, A. Chatt, J. Radioanal. Nucl. Chem. 282 (2009) 133.
[54] J.A. Baig, T.G. Kazi, A.Q. Shah, M.B. Arain, H.I. Afridi, G.A. Kandhro, et al., Anal. Chim. Acta 651 (2009) 57.
[55] D. Chen, C. Huang, M. He, B. Hu, J. Hazard. Mater. 164 (2009) 1146.
[56] N. Li, G. Fang, H. Zhu, Z. Gao, S. Wang, Microchim. Acta 165 (2009) 135.
[57] M. Mulugeta, G. Wibetoe, C.J. Engelsen, W. Lund, J. Anal. At. Spectrom. 25 (2010) 169.
[58] A.A. Menegário, P. Smichowski, P.S. Tonello, G. Polla, E.P. Oliveira, R.E. Santelli, Anal. Chim. Acta 625 (2008) 131.
[59] C. Huang, B. Hu, Z. Jiang, Spectrochim. Acta B 62 (2007) 454.