On-line solid phase extraction of bismuth by FI–HG–AAS using L-proline immobilised on carbon nanotubes combined with factorial design

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ABSTRACT

This study explores further the analytical capabilities of functionalised multiwalled carbon nanotubes with L-proline (pro-MWCNTs) for the reliable preconcentration and determination of Bi(III) in waters using an on-line flow injection hydride generation atomic absorption spectrometry (FI–HG–AAS) system. To avoid carbon nanoparticles aggregation, the preconcentration was carried out on a microcolumn filled with functionalised pro-MWCNTs and a low molecular weight polyethylene. The optimisation was performed by employing a full factorial design. The factors related to the optimisation process were the concentration of eluent and pH of the sample. The best performance was achieved packing the substrate in a microcolumn of 2.3 mm (i.d) × 25 mm (pro-MWCNTs net length: 10 mm), the pH was 7.0 and the concentration of the eluent (HCl) was 10% (v/v). Under optimal conditions, the adsorption capacity of the substrate was found to be 0.1 mg g^{-1} reaching a preconcentration factor (PF) of 160. A detection limit (3σ) of 0.7 ng L^{-1} was achieved, when using only 3.0 mg of substrate. Interferences affecting Bi(III) signal were carefully studied. Precision, expressed as relative standard deviation (RSD) turned to be 1.5% at the 0.1 μg L^{-1} level (n = 10). Accuracy 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 Bi(III) in different categories of waters.

1. Introduction

Bismuth is a naturally occurring element that is found at low levels (127 ng g^{-1}) in the upper continental crust [1]. It can exist in four oxidations states. Among them, Bi(V) is a powerful oxidant in aqueous solution in contrast to other elements of Group 15 namely, As and Sb for which the pentavalent state is the most abundant. Bismuth is found as Bi(III) in environmental biological and geological samples [2]. According to Filella [2] Bi is toxic to some prokaryotes, and Bi compounds have been used for more than 200 years to treat aliments resulting from bacterial infections. Other authors reported that the use of this metalloid is increasing, even though it is known to be toxic for humans, animals and plants [3].

Even when Bi and its compounds are used in a variety of industrial and pharmaceutical products, this metalloid has much less studied in

comparison to other elements and consequently, to gain information on its ecotoxicology, behaviour and transport in natural waters is necessary. In an excellent critical review, Filella [2] attributes this lack of information to: (i) the low concentration of Bi in environmental systems, often justified on the grounds of the insolubility of its compounds and (ii) the renowned low toxicity of the element to humans.

Electroanalytical techniques such as adsorptive stripping voltammetry (ASV) [4], and stripping voltammetry [5] have been, and still are, very used for Bi determination. In these studies, limits of detection of 20 μg L^{-1} were reported. Atomic spectrometric and plasma-based techniques, in many cases including hydride generation (HG) for increasing detection power, represent another group of techniques successfully used for Bi determination at trace and ultra-traces in water samples [6,7]. An analytical methodology was developed by Calvo Fornieles et al. [8] to provide information on Sb, Bi and Sn content in sea waters samples using a preconcentration system and ICP–MS with HG for detection. The authors reported a LOD of 2.0 ng L^{-1}. Atomic fluorescence spectrometry (AFS) was also a suitable technique for Bi determination reaching a LOD of 0.2 μg L^{-1} [7].

Because of the expected levels of Bi(III) in natural waters and matrices of environmental interest (~ng L^{-1} or below) many analytical

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techniques are far below to directly achieve the detection power required. This situation can be improved be adding a preconcentration step. In this direction, the use of different substrates has been reported such as: octadecyl bonded silica cartridges modified with cyanex 301 in conjunction with graphite furnace atomic absorption spectrometry (GFAAS) [9], Lewatit TP-207 chelating resin and flame atomic absorption for detection [10]. More recently modified multiwalled carbon nanotubes (MWCNTs) have been tested as a selective sorbent for Bi(III) preconcentration [11]. For many years, our group has been studying the capabilities of biosorption for elemental solid phase extraction using amino acids immobilised on controlled pore glass [12–14]. More recently, amino acids such as L-tyrosine were immobilised on MWCNTs for the selective determination of Tl [15]. The detection limit reported for total Tl by STPF-ETAAS was 150 ng L^{-1} while for Tl(III), employing the separation system a much lower value was obtained (3 ng L^{-1}). As regards Co, the LOD was 50 ng L^{-1} [16]. L-Alanine was another amino acid successfully used for Ni, Pb [17] and Cd [18] preconcentration. In conclusion, solid phase extraction methods are rapid, simple and sensitive and can be considered as a low cost alternative in comparison with other techniques such as ICP–MS.

In this study, it was deemed of interest to further investigate the capabilities of multiwalled carbon nanotubes with L-proline (pro-MWCNTs) as a new substrate for Bi(III) determination using an on-line solid phase extraction (SPE) procedure involving its coupling to flow injection–hydride generation–atomic absorption spectrometry (FI–HG–AAS). The optimisation was performed using a factorial design. The conditions were established and Bi(III) determination in different kinds of waters was successfully carried out reaching a high preconcentration factor.

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 Bi(III) determination. The gas–liquid separator (Perkin–Elmer) 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 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 Bi(III) is depicted in Fig. 1.

A bismuth electrodeless discharge lamp (PerkinElmer) operated at a current of 370 mA and a wavelength of 223.1 nm with a spectral band pass of 1.8 nm was used. Instrumental details and operating conditions are summarised 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 Bi was not detected within the working range. Commercially available 1000 mg L^{-1} standard solutions (Merck) of Bi(III) were used. Diluted working solutions were prepared daily by serial dilutions of the stock solution. Sodium tetrahydridoborate(III) solution (0.4% w/v) was prepared daily by dissolving NaBH$_4$ (Merck, Darmstadt, Germany) in deionised water, stabilizing in 0.2% (w/v) NaOH and filtering through Whatman N° 42 filter–paper to eliminate turbidity. The resulting solution was stored in polyethylene flask at 4 °C. The cation solutions used in the study of interferences were prepared from analytical-reagents grade chemicals. Buffers solutions tested were: 2-(N-morpholino) ethanesulfonic acid (MES) (AppliChem GmbH, Darmstadt, Germany), tris(hydroxymethyl)aminomethane (TRIS) (AppliChem GmbH, Darmstadt, Germany), Na$_2$HPO$_4$.12H$_2$O and NaH$_2$PO$_4$.H$_2$O (Carlo Erba, Milan, Italy), potassium phthalate monobasic (Sigma-Aldrich, St. Louis, MO, USA). Hydrochloric acid solutions were prepared by step-wise dilution of the concentrated acid (Merck).

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 chemical (Merck) used for MWCNTs functionalisation (HNO$_3$, H$_2$SO$_4$, SOCl$_2$, DMF, THF, L-proline) were of analytical reagent grade and were used without further purification.

2.2. Sample collection, treatment and preconcentration procedure

Water samples were collected in different sites in Argentina. They include: tap water, river water, sea water, effluents from mining
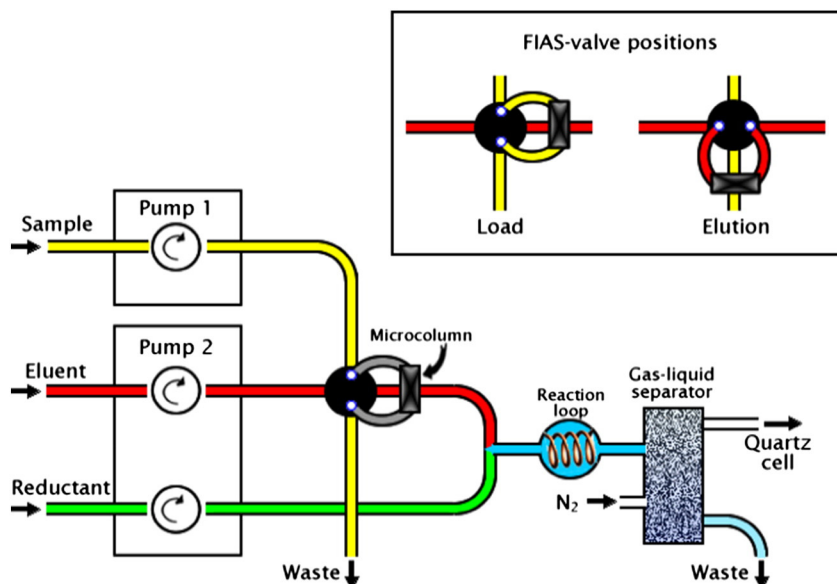

Fig. 1. Operational diagram of the FI-HG-AAS system used for Bi(III) preconcentration.

Instrument	PerkinElmer AAnalyst 200
Cell temperature	940 °C
EDL lamp current	370 mA
Measurement mode	Peak area
Slit width	1.8 nm
Wavelength	223.1 nm
Hydride generation	
$NaBH_4$ concentration	0.4% (w/v); NaOH 0.2% (w/v)
Reductant flow rate	4.4 mL min^{-1}
Eluent (HCl) flow rate	8.8 mL min^{-1}
HCl concentration	10% (v/v)
Carrier gas (N_2) flow rate	30 mL min^{-1}

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 (62°14′18″S, 58°40′0″W).

Collected samples were placed in poly(ethylene terephthalate) PET bottles previously cleaned with 10% (v/v) 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 tap water, sea water, river water, well water, thermal water and effluent samples were filtered through a 0.45 μm polyvinyldifluoride syringe filter (Minisart-Sartorius, Göttingen, Germany). As in a previous study [19] Teflon® and PET bottles were used for sampling and storage of waters.

Before starting the experiments, the microcolumn was conditioned for preconcentration by passing one mL of a 10% (v/v) HCl solution, washed with 2.5 mL of DDW. Then, 5.0 mL of analyte solutions were loaded on the microcolumn at a flow rate of 3.2 mL min^{-1}. For stripping Bi from the column, a 10% (v/v) HCl solution was passed and Bi was injected in the on-line system. The absorbance measurements (peak area) were proportional to the analyte concentration in the sample and were used for measurements. Samples were analysed as soon as it was possible.

2.3. Immobilisation procedure

Firstly, oxidation of MWCNTs was carried out in a mixture of H$_2$SO$_4$: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 (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.

2.4. Characteristics of the column and the sorbent material

The preparation and dimension of the microcolumn is a key topic when nanoparticles are used as the filler material. The characteristics of the sorbent and the column geometry greatly influence the analyte retention. According to previous experiences [19], to avoid aggregation and an unacceptable higher back-pressure due the tight packing of the filling material we adopted to fill the column 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.

We performed a careful evaluation of the optimum dimensions of the microcolumn. These tests demonstrated that to reach an efficient Bi(III) preconcentration as well as higher and thinner peaks, a good compromise was: (i) using a small home-made microcolumn of 2.3 mm (i.d) × 25 mm (pro-MWCNTs net length: 10 mm and a nominal microcolumn capacity ~42 μL), and (ii) carefully assess the filler material and the way of packing it.

The microcolumn was filled with a mixture of pro-MWCNTs and Epolene®. According to our experiments, the optimal proportion was ~90% of Epolene® and ~10% of pro-MWCNTs. In addition to the lack of aggregation, microcolumns resulted to be even better in terms of peak sharpness.

In this study a mixture of ~3.0 mg of pro-MWCNTs and 30 mg of Epolene® was used to fill the microcolumn using the dry packing method. 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 system was washed with 1 mL of a 10% (v/v) HCl solution and then with 2.5 mL of DDW.

To check that Bi(III) was not retained by the low molecular weight polyethylene wax, a test microcolumn was filled only with ~30 mg of this material and inserted in the preconcentration system. No Bi(III) retention was observed which evidenced that Bi(III) was retained by pro-MWCNTs and not by Epolene®.

Scanning electron micrographs of particles of Epolene® with pro-MWCNTs showed a significant dispersion of the nanotubes on the particles with the preservation of their backbone after 690 cycles of Bi(III) preconcentration.

2.5. Optimization strategy

Screening studies showed that sample and elution flow rates have no statistical significant influence on Bi retention (see next Section). The optimisation step was carried out considering two factors such as (i) eluent acid concentration and (ii) sample pH using a four levels factorial design. A simple response was analysed as peak area. All experiments were performed in triplicate with a random order to minimize the effects of uncontrolled factors that may introduce bias in the measurements.

3. Results and discussion

3.1. Sampling and elution flow rates

Sampling flow rate (SFR) was evaluated between 2.3–4.1 mL min^{-1} while the effect of elution flow rate (EFR) was studied between 7–10.5 mL min^{-1}. Statistical significance of the effects was checked by analysis of variance (ANOVA) and using p-value significance levels less than 0.05. Sampling flow rate and elution flow rate had no significant effects with p-values of 0.704 and 0.082, respectively. SFR was optimised at 3.2 mL min^{-1} and EFR at 8.8 mL min^{-1}.

3.2. Factorial design

A two factors (acid concentration and pH) factorial design at four levels with 16 runs (by triplicate) was developed in order to determine the influence of the two factors and its interaction on the system.

Table 2
Factors and levels used in the factorial design.

Variable	Minimum (−)	Maximum (+)
Acid concentration (%v/v)	10	20
pH	3	9

Minimum and maximum levels of each factor (Table 2) were chosen according to data from previous experiments. The factorial design was evaluated using the analytical signal (peak area). Significance of the effects was checked by ANOVA and using p-value significance levels (0.05).

Fig. 2 shows the surface response of Bi(III) retention as a function of pH and acid concentration. From observation and evaluation of the surface graphic, the acid concentration does not affect the system, which was demonstrated by the ANOVA test ($p = 0.5710$). On the other hand, the pH statistically affects the on-line preconcentration system ($p < 0.0001$). Besides, the interaction (pH × acid concentration) has not shown statistically significant ($p = 0.5090$).

The sample pH optimised value was 7 and acid concentration for stripping Bi(III) from the column was left to the minimum value, 10% (v/v) HCl, in order to prevent microcolumn detriment. Then, when these parameters were fixed, buffers solutions in the range of optimised pH, were prepared and tested in order to improve the adjustment of sample pH for Bi(III) retention and find a reaction medium that can control the interferences at which Bi(III) is expected to be affected. A preliminary study of the effect of selected potential interferences on Bi(III) signal showed the necessity of doing this. To this end, four buffer solutions were prepared as follows: MES (pH range: 5.2–7.2), TRIS (pH range: 7.0–9.0), sodium phosphate (6.2–8.2) and potassium phthalate (pH range: 4.4–6.4) at 0.01 mol L^{-1} concentration. Results are shown and discussed in the next Section.

3.3. Interference study

The determination of Bi(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 Cd, Cu, Fe, Mn, Mo, Ni and Zn on the generation of BiH$_3$ 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 Groups 14, 15 and 16).

As stated before, it was necessary to select an appropriate sample reaction media to better control the interferences on Bi signal. In this direction, several buffer solutions were tested. The best performance in terms of Bi signal was obtained in 0.01 mol L^{-1} phthalate buffer but
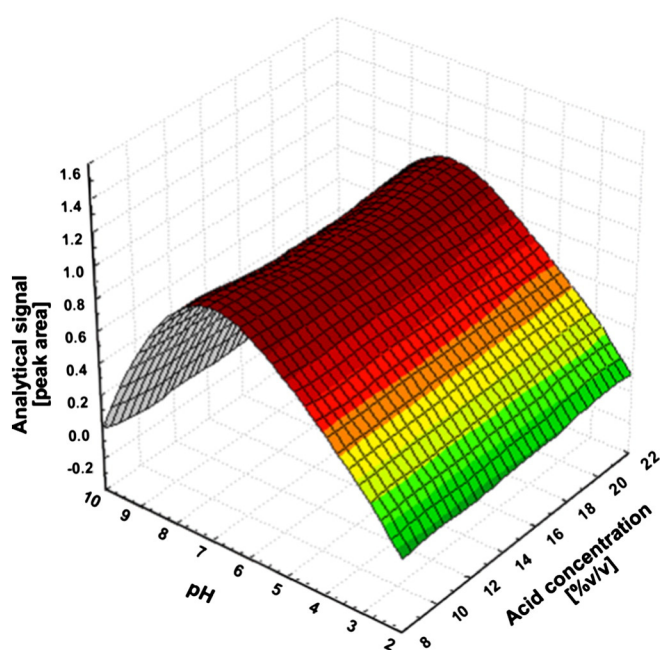
the interferences were not completely controlled. When higher concentrations of this buffer were assessed we observed a significant reduction of the interferences for most elements. The best results were obtained with 0.1 mol L^{-1} potassium phthalate and it was selected as the best alternative for further work. Interference studies under the optimised working conditions were investigated and Table 3 summarises the results obtained. Variations over $\pm 5\%$ in the analytical signal of Bi(III) in the presence of other elements were taken as an interference. All samples analysed contained 5.0 µg L^{-1} Bi and the results are the average of three measurements. Enhancing effects were observed only for As (11.1 and 9.5%) and Sn (8.5 and 10.9%) while Cd, Ge, Pb and Te produced a slight depression on Bi signal (<12% in all cases).

3.4. Analytical performance and method accuracy

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 for Bi(III) retention resulted as follows: the repeatability, expressed as relative standard deviation (RSD) was 1.5% 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 0.7 ng L^{-1}. The limit of quantification (10σ) resulted to be 2.3 ng L^{-1}. The calibration curve was linear from levels close to the LOD up to 75 ng L^{-1}. A good correlation coefficient has been obtained with $R^2 = 0.997$.

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 sample at 3.2 mL min^{-1} using an elution flow rate of 8.8 mL min^{-1} reading/data acquiring and conditioning was ~3 min resulting in a sample throughput of 20 samples per hour. An enrichment factor (EF) of 160 for a sample volume

Table 3
Interferences of heavy metals and hydride forming elements in the determination of Bi(III). Results are percentage change in Bi signal (5 µg Bi L^{-1}).

Interferent	Interferent concentration [µg L^{-1}]	Phosphate 0.01 M	MES 0.01 M	TRIS 0.01 M	Phthalate 0.01 M	Phthalate 0.1 M
As	10	0	−44.3	0	18.3	8.9
As	100	0	−34.0	0	17.4	10.0
Cd	10	−6.8	−33.2	−22.1	0	−6.7
Cd	100	−15.3	−20.2	−12.6	0	−7.7
Co	10	−18.2	−44.6	−29.0	0	0
Co	100	−12.6	−36.2	−20.2	−9.6	0
Cr	10	−53.9	−66.4	−27.4	−44.5	0
Cr	100	−56.1	−54.1	−13.1	−22.6	0
Cu	10	−20.1	−34.9	−19.1	−11.0	0
Cu	100	−34.6	−31.1	−18.7	−36.1	0
Fe	10	−66.4	−32.1	−31.7	−22.1	0
Fe	100	−69.2	−28.7	−52.6	−24.4	0
Ge	10	−18.2	−11.2	−28.7	−11.4	−7.0
Ge	100	−14.0	−6.8	−35.5	−7.9	−6.1
Hg	10	−25.1	−44.1	0	−8.2	0
Hg	100	−17.3	−31.9	0	−15.4	0
Mn	10	−13.4	−43.2	−19.9	−10.1	0
Mn	100	−11.6	−30.3	−17.7	−9.1	0
Ni	10	−7.9	−44.1	−14.0	−9.7	0
Ni	100	−14.9	−38.1	−10.0	−18.3	0
Pb	10	−20.6	−32.3	−11.6	−9.9	−9.4
Pb	100	−39.1	−22.2	−8.1	−11.3	−8.2
Sb	10	0	−12.7	−9.0	0	0
Sb	100	−11.6	−33.2	−8.9	−6.4	0
Se	10	−8.0	−39.6	−18.8	−7.5	0
Se	100	−14.2	−34.4	−14.9	−9.2	0
Sn	10	−9.4	−45.2	−9.0	−8.0	8.5
Sn	100	−15.3	−38.5	−8.9	−23.2	10.9
Te	10	−11.9	−39.1	−11.8	−15.3	−11.9
Te	100	−17.1	−34.4	−10.8	−16.2	−11.0
Zn	10	−27.8	−38.4	0	−17.4	0
Zn	100	−21.5	−29.3	0	−14.6	0

Fig. 2. Surface response of Bi(III) retention as a function of pH and acid concentration.

of 160 mL was obtained with respect to the Bi determination by FI–HG–AAS without preconcentration.

Accuracy test for the entire analytical procedure was performed by means of the Standard Reference Material (SRM) NIST 1643e (trace elements in water). Our results were in good agreement with the certified values as follows: 14.09 ± 0.15 μg L^{-1} Bi (certified) vs 13.77 ± 0.66 μg L^{-1} Bi (found).

3.5. Bismuth in different kind of waters

Information on Bi(III) levels in natural waters is scarce and with much dispersion in the data published. In this context, it is difficult to establish a range of typical concentrations in natural waters for comparative purposes. Table 4 summarises the results of this study for different categories of waters.

Bismuth was not detected in sea water. Even with discrepancies, compiled data stated a concentration of Bi(III) in sea water from different origins ranging from 10 to 30 ng L^{-1} [2]. Respect to tap water analysis, the situation is repeated and nor is it possible to find a probably range of concentrations. While in our study, Bi(III) was not detected in samples collected in two different sites; other authors reported levels significantly high. Using a chemically modified electrode for Bi(III) preconcentration prior to its quantification by voltammetry, Dong et al. [20] informed a mean concentration of Bi(III) in tap water of 48 nM (equivalent to 16,500 ng L^{-1}).

River waters collected in Mendoza province showed concentrations between <LOD and 178 ± 8 ng L^{-1} Bi. A wide range of levels of Bi(III) in river water was reported in the literature and concentrations up to 12,000 ng L^{-1} were informed for waters collected in Japan [21]. Also in Japan, in Takahashi river, a significant much lower concentration of 2.08 ng L^{-1} Bi was measured by ICP–MS and sample preconcentration [22].

Antarctic water collected at Carlino Station exhibited a concentration of 166 ± 8 ng L^{-1}. This level appears to be high if we take into account the concentrations described above. However, Boswell and co-workers [23] determined several elements in high-saline Antarctic waters by a combined spectrochemical and solvent extraction procedure and reported concentrations of Bi(III) varying from <200 to 7100 ng L^{-1}.

In mine effluents we found low Bi(III) concentrations, up to 81.0 ± 2.4 ng L^{-1}. Very few studies considered the determination of this element in mining effluents and again it is difficult to establish a range of concentrations for the comparison of results. In the vicinity of a Cu–W mine in Korea, Jung et al. [24] determined Bi(III) by ICP–OES with hydride generation in different environmental compartments.

Stream water samples contained concentrations varying from 300 to 8400 ng L^{-1} Bi.

To the best of our knowledge, for thermal waters the information is limited to one publication where waters and sediments from Santorini hydrothermal field, Greece were analysed in the framework of a geochemical study [25]. Even when Bi(III) was quantified by ICP–OES, concentrations <800 ng L^{-1} were informed. In our study, we found a concentration of Bi(III) in thermal waters from the province of Entre Rios of 38.1 ± 1.9 ng L^{-1}.

4. Conclusions

The on-line combination of pro-MWCNTs and FI–HG–AAS is fully able to determine bismuth at ng L^{-1} levels. The detection power afforded by this analytical approach is completely adequate to comply with the concentrations of Bi usually expected in different kind of waters. Unfortunately, the detection limits of many studies reported in the literature are well above those required for Bi(III) determination in natural waters.

The mixture of pro-MWCNTs with a low molecular weight polyethylene wax (with no need for substrate immobilisation) avoided agglomerations and overpressures in the on-line system. The pro-MWCNTs microcolumn featured excellent chemical stability and retention efficiency without appreciating Bi(III) breakthrough for sample volumes of 250 mL, and with a long lifetime of up to 690 sorption/elution cycles.

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

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Table 4
Bismuth concentrations (expressed in ng L^{-1}) in different kind of waters.

Sample	Bi concentration
Tap water (Córdoba)	<LOD
Tap water (Buenos Aires province)	<LOD
Sea water (Mar del Plata)	<LOD
Well water 1 (Buenos Aires province)	23.5 ± 1.1
Well water 2 (Buenos Aires province)	28.2 ± 1.1
River water 1 (Mendoza)	178 ± 8
River water 2 (Mendoza)	<LOD
Thermal water (Entre Ríos)	38.1 ± 1.9
Antarctic water (Carlini Station)	166 ± 8
Mine effluent 1 (Córdoba)	25.4 ± 1.2
Mine effluent 2 (Córdoba)	2.58 ± 0.09
Mine effluent 3 (San Luis)	3.12 ± 0.09
Mine effluent 4 (San Luis)	<LOD
Mine effluent 5 (San Luis)	81.0 ± 2.4
Mine effluent 6 (Córdoba)	226 ± 12
Mine effluent 7 (Córdoba)	226 ± 12
Effluent water (Buenos Aires province)	62.6 ± 3.0
Treatment plant (Buenos Aires province)	1580 ± 71

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