Talanta 85 (2011) 245–251

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

On-line solid phase extraction of Ni and Pb using carbon nanotubes and modified carbon nanotubes coupled to ETAAS

Marianela Savio[a], Belén Parodi[b,c], Luis D. Martinez[a], Patricia Smichowski[d,e,**], Raúl A. Gil[a,*]

[a] Instituto de Química de San Luis (CCT-San Luis)-Área de Química Analítica, Facultad de Química Bioquímica y Farmacia Universidad Nacional de San Luis, Chacabuco y Pedernera, D5700B WQ-San Luis, Argentina
[b] Instituto Nacional de Tecnología Industrial (INTI), Centro de Investigación y Desarrollo en Mecánica, Colectora de Avenida General Paz 5445, B1650KNA-San Martín, Buenos Aires, Argentina
[c] Instituto de Investigación e Ingeniería Ambiental, Universidad de San Martín, Belgrano 3565, B1650KNA-San Martín, Argentina
[d] Comisión Nacional de Energía Atómica, Gerencia Química, Av. Gral Paz 1499, B1650KNA-San Martín, Buenos Aires, Argentina
[e] Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Rivadavia 1917, C1033AAJ-Ciudad de Buenos Aires, Argentina

ARTICLE INFO

Article history:
Received 15 February 2011
Received in revised form 15 March 2011
Accepted 23 March 2011
Available online 6 April 2011

Keywords:
Ni
Pb
FI-SPE-ETAAS
Carbon nanotubes
Oxidized carbon nanotubes
L-Alanine aminoacid

ABSTRACT

A study about the capabilities of three kinds of nanomaterials namely, carbon nanotubes (CNT), oxidized carbon nanotubes (ox-CNT) and L-alanine immobilized on carbon nanotubes (ala-CNT) to serve as sorbents for preconcentrating Ni and Pb using an on-line system coupled to electrothermal atomic absorption spectroscopy (ETAAS) technique, was accomplished. The solid phase extraction was performed in a conical minicolumn used as sorbent holder. After loading a fixed volume of the analytes, they were eluted with a discrete volume (50 μL) of nitric acid, placed directly into the platform of a L'Vov tube. After that, each analyte was determined individually. Ni and Pb retention was strongly influenced by pH but exhibiting different behaviors. The study demonstrated that the sorbent based on ox-CNTs was the one that exhibited the highest capacity and linearity for both analytes when compared with CNT or ala-CNT. The analytical performance was evaluated for the three sorbents to establish the best conditions regarding sensitivity, reproducibility and accuracy. The precision expressed as relative standard deviations ($n=6$) were 3.9 and 0.5% for Ni^{2+} and Pb^{2+}, respectively The limit of detection (LOD), calculated as the concentration required to yield a net peak equal to three times the standard deviation of the background signal (3σ) was 30 and 10 ng L^{-1} for Ni^{2+} and Pb^{2+} respectively. Alternatively, the limit of quantification (10σ) was calculated and resulted to be 0.79 and 0.07 μg L^{-1} for Ni^{2+} and Pb^{2+} respectively. After optimization, the method that involved the use of ox-CNT associated to an on-line preconcentration was tested in samples of relevant environmental importance. Accuracy was evaluated analyzing a certified reference material namely, Municipal Sludge (QC MUNICIPAL SLUDGE A) and a reference sample of Lake Sediment (TRAP-LRM from IJS).

1. Introduction

Lead and nickel can be released into the atmosphere from several industrial processes, including oil and coal burning power plants, trash incinerators, and metallurgy industry. Thus, the exposition to these elements may take place by air, soil, drinking water, food samples and mainly by skin contact [1–3]. Lead is classified as prevalent toxic metal, which constitutes a major environmental health problem [3,4]. Although nickel is considered an essential element, excessive Ni amount in the organism is reported as very toxic [1]. Exposure to nickel metal and soluble compounds should not exceed 0.05 mg/cm^3 in Ni equivalents per 40-h work week.

The determination of Ni and Pb at trace level is an important issue in the context of environmental protection, human health, food and agricultural chemistry as well as high purity materials [5–8]. They are normally present at low concentration, therefore sensitive, reproducible and accurate analytical methods are required for their determination. Many techniques have a significant drawback because their detection power is sometimes inadequate to comply with the requirements posed by the determination of Ni and Pb at trace levels in media such as environmental matrices [6]. Considering the spectroanalytical techniques, electrothermal atomic absorption spectrometry (ETAAS) remains a popular technique for trace element determinations in a variety

---

* Corresponding author at: Instituto de Química de San Luis (CCT-San Luis)-Área de Química Analítica, Facultad de Química Bioquímica y Farmacia Universidad Nacional de San Luis, Chacabuco y Pedernera, D5700B WQ-San Luis, Argentina.
** Corresponding author at: Comisión Nacional de Energía Atómica, Gerencia Química, Av. Gral Paz 1499, B1650KNA-San Martín, Buenos Aires, Argentina.
E-mail addresses: smichows@cnea.gov.ar (P. Smichowski), ragil@unsl.edu.ar (R.A. Gil).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.03.054

of samples as a consequence of its high sensitivity and superior detection power [4,8–11]. However, for ultra-trace determinations, ETAAS can be employed in conjunction with preconcentration methodologies to improve sensitivity and selectivity [8].

Nowadays, trace elemental determination has been performed in association with solid-phase extraction (SPE)/preconcentration techniques among others, basically aiming at the enrichment of metallic species and/or matrix separation with the advantage of easy coupling to flow injection systems (FI). Methods based on sorbent extraction have proven to be the most attractive ones due to their specificity and high preconcentration efficiency [6,11,12]. Additionally, systems based on FI-SPE-ETAAS increase sensitivity as well as sample throughput and sample/reagent consumption [13–15]. The choice of selective adsorbent is a critical factor to obtain full recovery and high enrichment factor. It should be based also on analyte, sample matrix and technique for final detection, whereas higher enrichment factors can be obtained using adequate experimental conditions (e.g., time of loading sample, sorbent mass, and volume of eluent) [6,16].

Carbon nanotubes (CNTs) have been proposed as a novel solid phase extractant for various inorganic and organic compounds/elements at trace levels [4,16–22], thus they have come under intense multidisciplinary study because of their unique physical and chemical properties and their possible applications. [4,6,23–26] Their large sorption capacity is linked to well develop internal pore structures, a large specific surface area, and the presence of a wide variety of surface functional groups [6–8]. The primary adsorption mechanism of metal ions to CNTs is perceived to be surface complexation with functional groups, so the performance is mainly determined by the nature and the concentration of these groups, which could be different due to the modification and functionalization of the graphitic surface [9,19–22]. Nowadays, work has progressed in developing diverse chemical varieties of CNTs which suggests a wide range of possible SPE materials (e.g. MWCNTs, SWCNTs, functionalized, non-functionalized, etc.) including different chemical possibilities and applications in SPE methods [6,9,23–25].

Taking into account the properties of the carbon nanotubes and the sensitivity of ETAAS coupled to FI, a study was undertaken to develop a method to determine Ni and Pb at ultra-trace levels. To this aim, a column-solid phase approach was evaluated using three kinds of nanomaterials i.e. carbon nanotubes (CNT), oxidized carbon nanotubes (ox-CNT) and alanine immobilized on carbon nanotubes (ala-CNT) in order to establish the best conditions regarding sensitivity, reproducibility and accuracy. The effect of several variables such as sample pH and flow rate, column capacity, eluent type concentration, and interference of foreign ions were studied. The method was adapted to the analysis of solid samples such as sediments and sludges.

2. Experimental

2.1. Standards and reagents

All solutions were prepared with Ultrapure water (18 MΩ cm) obtained from a Mili-Q, EASY pure RF (Barnsted, Iowa, USA). The acid used was HNO_3 from Fluka (Germany). To alkalinize solutions, NaOH (Merck, Germany), and NH_4OH (Cicarelli, Argentine) were used. All glasses and other lab materials were cleaned by soaking in 10% HNO_3 and rinsing with ultrapure water. Synthetic standard stock solutions (1000 mg L^{-1}) of Ni^{+2} and Pb^{+2} were from Fluka (Switzerland).

A certified reference material namely, Municipal Sludge (QC MUNICIPAL SLUDGE A) from DK-2970 Horsholm, Denmark and a reference sample of Lake Sediment (TRAP-LRM from IJS) from Ljubljana, Slovenia were employed for method validation.

Table 1
Instrumental operating conditions and furnace temperature program.

Parameter	Ni	Pb
Wavelength	221.47 nm	283.30 nm
Spectral bandpass	0.2 nm	0.2 nm
Lamp current	14 mA	14 mA
Background correction	Deuterium lamp	Deuterium lamp

Furnace program (Ni/Pb)

Stage	Temperature (°C)	Time (s)		Argon gas flow (L min^{-1})
		Ramp	Hold	
Drying	120/150	10/10	–	0.1
	250/250	5/5	–	1.0
Pyrolisis	800/800	10/10	10/10	1.0
	800/800	–	3/3	0.0 (read)
Atomization	2500/2500	–	5/2	0.0 (read)
	2600/2500	–	2/2	1.0

Multiwalled carbon nanotubes (MWCNTs) were purchased from Sun Nanotech Co. Ltd., Jiangxi, China.

All chemical (Merck) used for nanotubes functionalization (HNO_3, H_2SO_4, $SOCl_2$, DMF, THF, L-alanine) were of analytical reagent grade and were used without further purification.

2.2. Instrumentation

Measurements were performed with a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan) equipped with a deuterium background corrector, an EX7-GFA electrothermal atomizer and an ASC-6100 autosampler. L'vov graphite tubes (Shimadzu, Tokyo, Japan) were used in all experiments. Nickel and lead hollow-cathode lamps (Hamamatsu, Photonics K., Japan) were employed as the radiation sources. The wavelengths used were 221.47 nm and 217.00 nm for Ni and Pb, respectively. The ETAAS instrumental and operating conditions are listed in Table 1. A Minipulse 3 peristaltic pump Gilson (Villiers-Le-Bell, France) was also used. Sample injection was achieved using a Rheodyne (Cotati, CA, USA) Model 50, four-way and of six ports, two positions, rotary valves. The three conical minicolumns were prepared by placing 4 mg of each of the three nanomaterials i.e. carbon nanotubes (CNT), oxidized carbon nanotubes (ox-CNT) and alanine immobilized on carbon nanotubes (ala-CNT) into an empty conical tip using the dry packing method. To avoid filling losses when the sample solution passed through the conical minicolumn, a small amount of quartz wool was placed at both the ends. The column was then mounted on the furnace autosampler arm to form the preconcentration system. Prior to use, a 5% nitric acid solution was passed through the CNTs minicolumn. After that, the column was washed with ultra-pure water until reaching neutral pH. Tygon type pump tubing (Ismatec, Cole Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagents and eluent.

Microwave digestion was performed with a Milestone START D microwave furnace (Italy) and Milestone hermetically sealed 100 mL internal volume, 1 cm wall thickness polytetrafluoroethylene (PTFE) reactors.

2.3. Sample treatment

Aliquots of 0.25 g of a certified reference material (CRM) namely, Municipal Sludge were placed into PTFE vessels. Then, 4 mL of 65% HNO_3, 2 mL of 40% HF and 2 mL of 30% H_2O_2 were added and submitted to the temperature program showed in Table 2.

Table 2
Main steps of the MW digestion for Municipal Sludge and Lake Sediment (Section 2.3).

Stage		Municipal sludge		Lake sediment	
		Time (min)	Temperature (°C)[a]	Time (min)	Temperature (°C)[a]
1	Ramp	20	180	10	220
2	Step	20	180	20	220
3	–			10	Room temperature
4	Ramp			10	220
5	Step			20	220
Total time (min)	40			70	

[a] Threshold power applied = 0.5 KW.

In the case of Lake Sediment, 0.2 g of this reference sample was placed into PTFE vessels and two stages were required to reach its complete dissolution of the CRM. At first, 4 mL of 96% H_2SO_4 and 3 mL of 85% H_3PO_4 were added. Once it finished, the rotor was cooled by air until the solution reached room temperature. Then, vessels were opened and the second stage was carried out by adding 4 mL of 65% HNO_3, 2 mL 40% of HF and 2 mL of 30% H_2O_2. The digestion cycle adopted is detailed in Table 2.

Finally, all the vessels were opened and the solutions transferred to marked polyethylene flasks and made to a final volume of 50 mL with ultrapure water.

2.4. *Immobilization procedure*

Commercial mutiwalled CNTs were treated with a mixture of H_2SO_4:HNO_3 (3:1), used as oxidant agent, in two consecutively steps: 2 h in ultrasound bath followed by 7 h in a water bath at 55 °C. This procedure cleaned and eliminated possible residues present in CNTs due to the generation process. This method allowed the generation of –COOH and –OH groups on CNTs surface, improving their solubility. The reaction was easy to start at the end caps because of the heavy strain of the hexagon–heptagon pairs [25]. In this way, the end caps were quickly removed leaving open-ended tubes, functionalized with carboxylic acid (COOH) groups [26]. The oxidized CNTs (ox-CNTs) were filtered and washed repeatedly with ultrapure water until complete elimination of the residual acid. The resultant powder was dispersed in a solution of thionylchloride ($SOCl_2$); 2 ml of dimethylformamide (DMF) were added and stirred at 70 °C for 24 h. The resultant substrate (CNT-COCl) was centrifuged and the remaining solid was washed with tetrahydrofuran (THF). L-*Alanine* and CNT-COCl were mixed in THF at 45° for 4 days. The resultant solid was resuspended with ethanol, filtered and dried at room temperature.

Fig. 1 shows a scanning electron microscopy (SEM) photograph of CNTs previous and after the immobilization.

2.5. *Pre-concentration procedure and determination*

Aiming to optimize the overall analysis time, the discontinuous nature of the electrothermal atomizer must be synchronized with the continuous mode of the FI-SPE. A scheme of the pre-concentration manifold includes a six-port rotary valve containing the conical minicolumn (Fig. 2).

Before starting, the conical mini-column is conditioned for pre-concentration by passing some mL of a 5% HNO_3 solution, washed with ultra-pure water and finally conditioned at the correct pH value (valves V_1 in position B and V_2 in position a).

2.5.1. *Loading*

Analyte solutions were loaded separately on the minicolumns at a flow rate of 1.0 mL min^{-1} with valve V_1 in position S and valve V_2 in load position a (2 min).

2.5.2. *Injection*

After loading, the sample line (S) was emptied. The peristaltic pump (P) was stopped and the injection valve V_2 was switched to the injection position (b). Finally, the conical minicolumn, mounted in the arm of the furnace autosampler, was automatically moved into the dosing hole of the graphite tube, and the retained metal was eluted at a flow rate of 0.2 mL min^{-1} with 50 μL of 5% HNO_3 solution directly into the graphite furnace.

2.5.3. *Reading*

After injection (elution), the autosampler arm was moved back to the conditioning position and the temperature program was started. During this period, the minicolumn was washed with 5% HNO_3 solution, ultra-pure water and conditioned at the correct pH. The absorbance measurements (peak height) were proportional to the analyte concentration in the sample and were used for all measurements. The operating conditions were established and the determinations carried out.

3. Results and discussion

3.1. *pH studies*

The pH value plays an important role with respect to the adsorption of different ions on CNTs [5,19,25,27]. The surface charge depends on the pH of the surrounding electrolyte. The oxidation of CNTs with concentrated acids lead to the surface functionalization with oxygen-containing groups, and the isoelectric point (IEP) of MWNTs shifts to the lower pH values [5]. When the pH of the solution is higher than the IEP of the oxidized CNTs, the negative charge on the surface provides electrostatic attractions that are favorable for adsorbing cations. The decrease of pH leads to the neutralization of surface charge, so the adsorption of cations onto CNTs decreases quickly.

In order to evaluate the effect of pH, a series of sample solutions of Ni^{+2} and Pb^{+2} were adjusted to different pH values (between 1.0 and 9.0) and processed according to the recommended procedure (Section 2.4). Aliquots of 2 mL were loaded on the column at a flow rate of 1.0 mL min^{-1}. In order to optimize the sorption conditions for the retention of Ni^{+2} and Pb^{+2} on the different CNTs, the intensity of the analytes signal was recorded as a function of the pH. The effect of pH on Ni^{+2} and Pb^{+2} retentions are shown in Fig. 3a and b. As it can be seen, Ni^{2+} adsorption was achieved between pH 3.0 and 9.0 with the three sorbent tested. Lead started to be adsorbed at pH 3.0 as well, but a noticeably decreasing in the adsorption is advised at pH 8.0, probably due to hydrolysis of the metal ion.

Comparing the retention of both Ni^{2+} and Pb^{2+} on the different CNTs it can be synthesized as follows: ox-CNTs > ala-CNTs > non-modified CNTs. Under these dynamic conditions it is evident that the appearance of oxygen-containing groups on the CNTs surface is the main responsible for the retention of these two metal ions. Accordingly, pH 7 for Ni^{+2} and pH 3 for Pb^{+2} were selected for further experiments and ox-CNT were selected as the best alternative

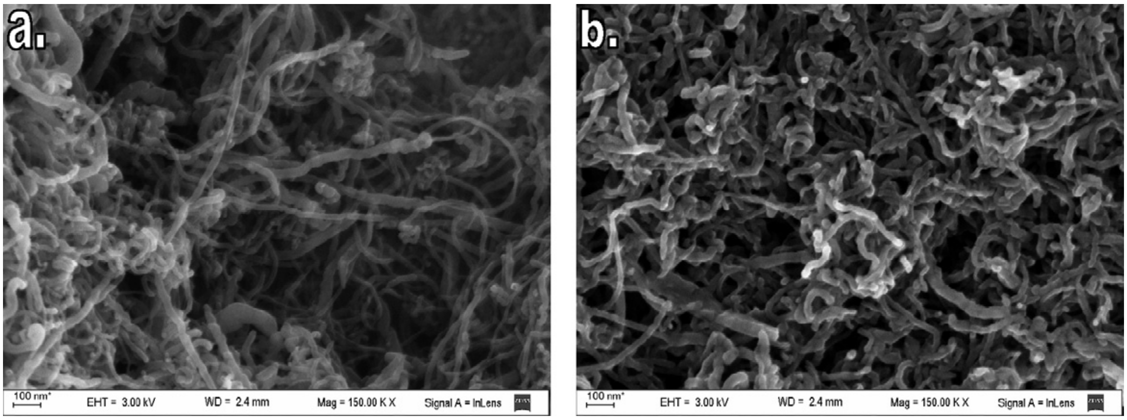

Fig. 1. A scanning electron microscopy (SEM) photographs of (a) CNTs previous immobilization and (b) after immobilization (L-ala CNTs).

for their superior adsorption capacity. All these studies were carried out with synthetic Ni^{+2} and Pb^{+2} solutions with a concentration of 20 μg L^{-1}.

3.2. Metals extraction and preconcentration performance

Parameters affecting Ni^{2+} and Pb^{2+} preconcentration were evaluated employing the proposed FI-SPE-ETAAS system. The analytical parameters studied were the following.

3.2.1. Loading flow rate

Beyond being one of the steps that controls the time of analysis, the rate of the sample through the minicolumn, it influences the time of contact between the analyte and the active sites (edges) and consequently the column capacity. In this study it was verified that the analytical signal diminished progressively when the loading flow rate was increased from 1.0 to 10.0 mL min^{-1}, whilst it remained constant at lower flow rates. This was carried out by comparing the signals from the mass expected from the metal stripped from the column with that of a directly injected sample. With the objective of avoiding tight packing of the filling material, with the consequent increasing of the back pressure, it was decided to work at a flow rate of 1.0 mL min^{-1} as optimum (Fig. 4).

3.2.2. Eluent

The elution step involves an exchange between analyte ions and H^+ [28]. A satisfactory eluent should effectively elute the analyte in a discrete volume in order to obtain the best analyte recovery. Nitric and hydrochloric acid have turned out to be good eluents in many on-line preconcentration systems. Both acids were tested at different concentrations in order to evaluate and compare the analytes recovery. Despite the fact that similar recoveries could be achieved with both of them, HNO_3 was preferable due to the better repetitively obtained in ETAAS measurements. In this way, different concentrations were tested and we verified that quantitative recoveries were obtained when Ni^{2+} and Pb^{2+} were retained on ox-CNT and eluted with 5% HNO_3. With the purpose of achieving the best analytical performance, this configuration was used in the application studies (Section 3.6).

As it is stated in Section 2.4, the elution of Ni^{2+} and Pb^{2+} is carried out with the column positioned in the dosing hole of the L'vov tube. This fact implies that the elution step is essentially the injection of the sample into the atomizer. Accordingly, the elution flow rate is a parameter of study for two main reasons: (1) the elution step is known to be an ionic exchange process that needs enough contact time to occur, and (2) the discrete volume of eluent should be properly deposited on the tube platform. In this sense, several eluent flow rates were tested and no significant changes were observed in the absorbance with flow rates up to 1.0 mL min^{-1}. However,

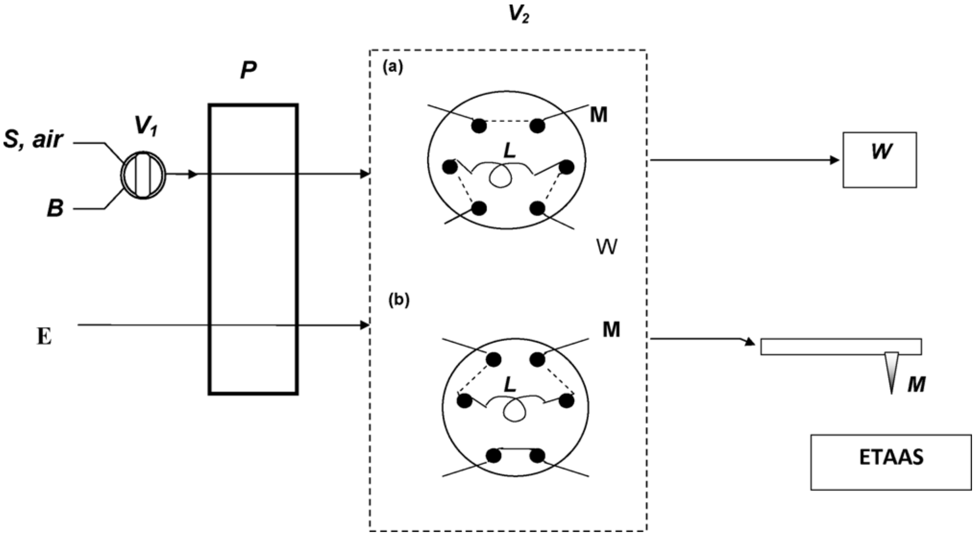

Fig. 2. Schematic diagram of the instrumental setup. Manifold of the FI-SPE-ETAAS method that include a selection valvlve (V_1), a two-way (a, load and b, injection) six-port rotary valve (V_2) with a fix-volume injection loop (L), an external 4-lines peristaltic pump (P), and a conical minicolumn (M).

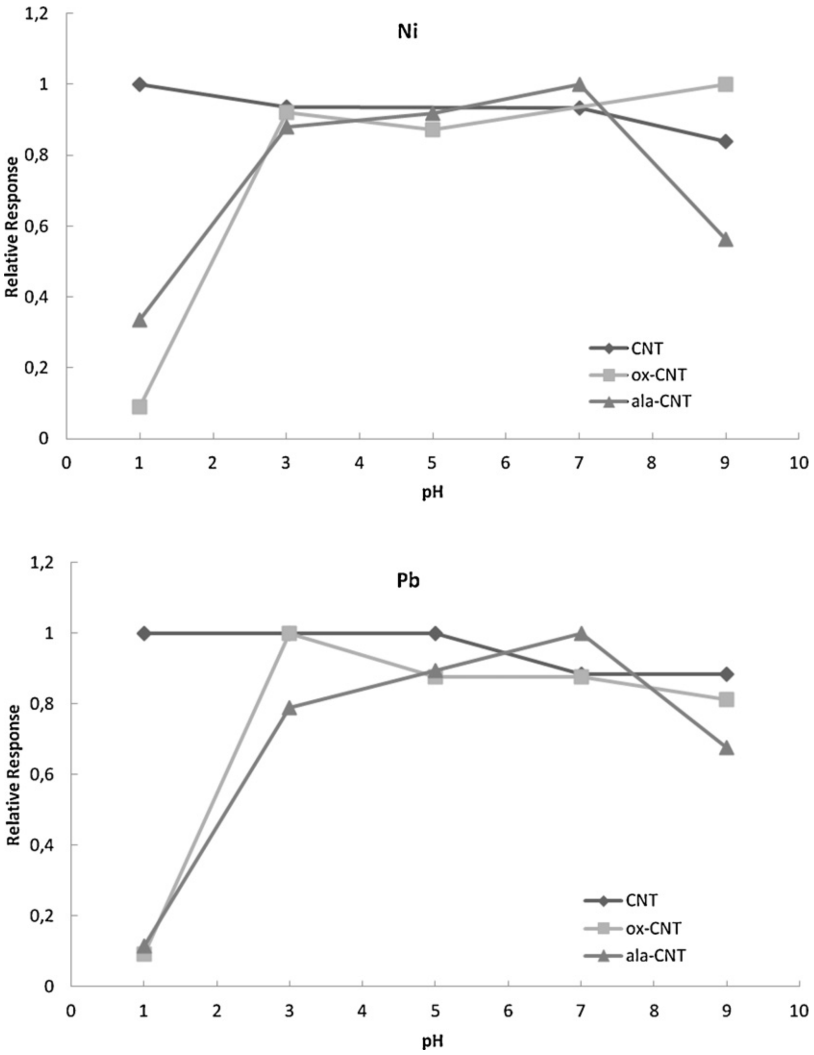

Fig. 3. Effect of the sample pH on analyte retention on the three diferents carbon nanotubes columns.

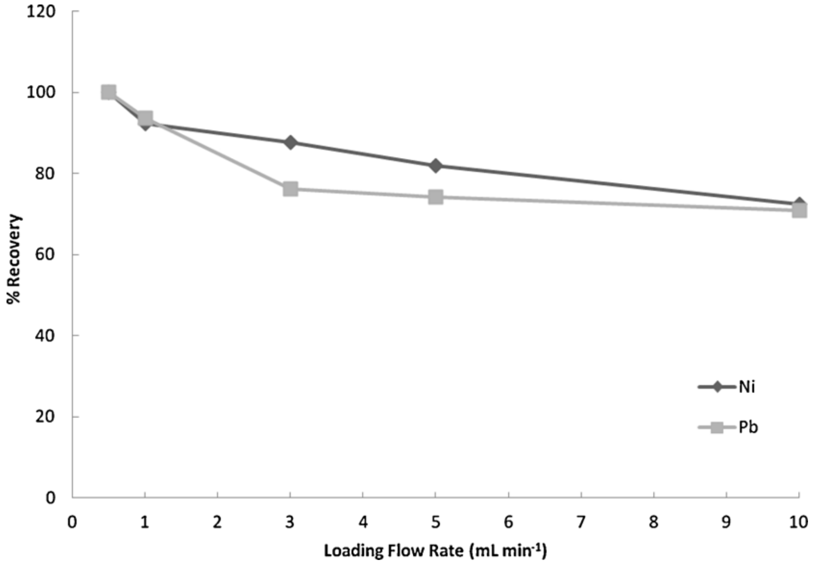

Fig. 4. Effect of the sample loading flow rate on the recovery of the analytes on ox-CNTs.

Table 3
Some commonly encountered ions were tested, and they were tolerated up to at least the levels specified down.

Coexisting	Tolerance (μg L^{-1})
Cd(II)	350
Co(II)	300
Cu(II)	900
Cr(III)	700
Fe(III)	8600
Hg(II)	150
K(I)	16,000
Sb(III)	400
Zn(II)	2100

working at high flow rates, the injection step was hardly reproduced and the uncertainty increased. Accordingly, a flow rate of 0.2 mL min^{-1} was selected, assuring repeatability of the elution and injection steps.

3.3. *Column re-use*

The stability and regeneration of the column were investigated. The column can be re-used after regeneration with 2 mL of 5% HNO_3 and then with a few milliliters of distilled water. The columns were stable up to 300 adsorption cycles without either deterioration or decrease in Ni^{2+} and Pb^{2+} species recovery.

3.4. *Analitycal performance*

The time required for the pre-concentration of 2.0 mL of sample (1.0 mL min^{-1}), elution/injection (0.2 mL min^{-1}), reading/data acquiring and conditioning was about 3 min, allowing 20 determinations per hour. The relative standard deviation (RSD) for six replicate measurements of solutions containing 20 μg L^{-1} of Ni^{2+} and Pb^{2+} was 3.9 and 0.5%, respectively. The pre-concentration factors, evaluated here as the ration between the slopes of the calibration plots made with solutions before and after pre-conentration were 38 and 40 for Ni and Pb respectively. The limit of detection (LOD), calculated as the concentration required to yield a net peak equal to three times the standard deviation of the background signal (3σ) was 30 and 10 ng L^{-1} for Ni^{2+} and Pb^{2+} respectively. Despite the fact that Ni was expected to have the lowest detection limits, the background in the line 221.47 nm line where high enough to diminish the detection capacity making the limit of detection a little bit higher than expected. Alternatively, the limit of quantification (10σ) was calculated and resulted to be 0.79 and 0.07 μg L^{-1} for Ni^{2+} and Pb^{2+} respectively. The calibration plot was linear from LOQ up to 5 and 2 μg L^{-1} for Ni^{2+} and Pb^{2+}, respectively.

3.5. *Interference studies*

The effects of potential interference ions at the concentration levels at which they may occur in the studied samples were tested. For this purpose, synthetic Ni^{2+} and Pb^{2+} solutions were prepared and the signal was monitored by the proposed method based on FI-SPE-ETAAS with the ox-CNTs minicolumn. The results (Table 3) indicate that samples could be analyzed without matrix effects due to cations, allowing calibration with simple aqueous standards.

3.6. *Application to environmental samples*

This FI-SPE-ETAAS method involving ox-CNT as sorbent material was employed to determine Ni^{2+} and Pb^{2+} in two environmental samples that had certified or reference values of Ni^{2+} and Pb^{2+} (i.e. QC MUNICIPAL SLUDGE A, and a lake sediment TRAP-LRM from IJS). The average concentrations of Ni^{2+} and Pb^{2+} found as well as the certified values are shown in Table 4. In all cases the calibration was run against aqueous standards solutions.

Table 4
Determination of Ni and Pb in environmental samples.

	Sample	Experimental values (mg kg^{-1})	Certified values (mg kg^{-1})
Ni	Municipal sludge	19.8 ± 0.8	21.5 ± 1.9
	Lake sediment	37.9 ± 1.3	39.8 ± 1.1
Pb	Municipal sludge	60.0 ± 1.5	61.7 ± 4.9
	Lake sediment	1401 ± 29.5	1373 ± 32.0

Confidence limits: $t_{(0.05;2)}s/n^{0.5}$.

4. Conclusion

The coupling FI-SPE-ETAAS exhibited ideal properties as a consequence of increasing the speed of preconcentration and the overall analysis process, reducing sample consumption and contamination risks. Furthermore, it is clear that the intimate contact between CNTs and liquid phases allows the direct extraction of metals from the samples. The evaluation of the retention capacity showed that oxidized carbon nanotubes (ox-CNTs) were the CNTs configuration with the highest adsorption capability being the best suitable substrate for preconcentration. The rapid uptake of both metals other than usually interfering cations, the almost instantaneous release of adsorbed analytes during the elution step and the possibility of column re-using for 300 cycles of retention/elution are ideal properties. In addition, the coupling used allows access to the limits of detection of ng L^{-1} levels overlapping to a certain extent that afforded by ICP–MS.

The methodology proposed has proved to be simple, reliable, sensitive, and reproducible, with a high sample throughput. Therefore, the method could be applied to the accurate determination of Ni^{2+} and Pb^{2+} in other samples with complex matrices.

Acknowledgements

The authors thank to Instituto de Química de San Luis from the Universidad Nacional de San Luis and Consejo Nacional de Investigaciones Científicas y Técnicas (UNSL-CONICET), and Agencia Nacional de Promoción Científica (FONCYT) for financial support.

References

[1] R.S. Amaisa, J.S. Ribeiro, M.G. Segatelli, I.V.P. Yoshida, P.O. Luccas, C.R.T. Tarley, Sep. Purif. Technol. 58 (2007) 122.
[2] M. Savio, R.A. Olsina, L.D. Martinez, P. Smichowski, R.A. Gil, Microchem. J. 96 (2010) 243.
[3] M. Tuzen, K.O. Saygi, M. Soylak, J. Hazard. Mater. 152 (2008) 632.
[4] Z. Zang, Z. Hu, Z. Li, Q. He, X. Chang, J. Hazard. Mater. 172 (2009) 958.
[5] K. Pyrzynska, TrAC Trends Anal. Chem. 29 (2010) 718.
[6] R.A. Gil, S.N. Goyanes, G. Polla, P. Smichowski, R.A. Olsina, L.D. Martinez, J. Anal. At. Spectrom. 22 (2007) 1290.
[7] L.M. Ravelo-Pérez, A.V. Herrera-Herrera, J. Hernández-Borges, M.A. Rodríguez-Delgado, J. Chromatogr. A 1217 (2010) 2618.
[8] A. Duran, M. Tuzen, M. Soylak, J. Hazard. Mater. 169 (2009) 466.
[9] T. Shamspur, A. Mostafavi, J. Hazard. Mater. 168 (2009) 1548.
[10] P.H. Pacheco, P. Smichowski, G. Polla, L.D. Martinez, Talanta 79 (2009) 249.
[11] Z. Fang, Flow Injection Separation and Preconcentration, VCH Publishers, Inc., New York, 1993.
[12] M. Burguera, J.L. Burguera, P. Carrero, C. Rondón, Talanta 58 (2002) 1157.
[13] J.L. Burguera, M. Burguera, Spectrochim. Acta Part B 56 (2001) 1801.
[14] C.F. Poole, Trends Anal. Chem. 22 (2003) 362.
[15] S. Iiijima, T. Ichihasi, Nature 363 (1993) 603.
[16] S. Iiijima, Nature 354 (1993) 56.
[17] P.H. Pacheco, R.A. Gil, P. Smichowski, G. Polla, L.D. Martinez, Anal. Chim. Acta 656 (2009) 36.
[18] K. Pyrzynska, M. Bystrzejewski, Colloids Surf. A 362 (2010) 102.
[19] M. Tuzen, K.O. Saygi, C. Usta, M. Soylak, Bioresour. Technol. 99 (2008) 1563.
[20] M. Tuzen, M. Soylak, J. Hazard. Mater. 147 (2007) 219.

[21] K. Pyrzynska, Anal. Sci. 23 (2007) 631.
[22] M. Valcarcel, S. Cardenes, B.M. Simonet, Y. Moliner-Martinez, R. Lucena, Trends Anal. Chem. 27 (2008) 34.
[23] J. Muñoz, M. Gallego, M. Valcarcel, Anal. Chem. 77 (2005) 5389.
[24] F. Avilés, J.V. Cauich-Rodríguez, L. Moto-Tah, A. May-Pat, R. Vargas-Coronado, Carbon 47 (2009) 2970.
[25] J. Zhang, H. Zou, Q. Qing, Y. Yang, Q. Li, Z. Liu, X. Guo, Z. Du, J. Phys. Chem. B 107 (2003) 3712.
[26] J. Shen, W. Huang, L. Wu, Y. Hu, M. Ye, Mater. Sci. Eng. A 464 (2007) 151.
[27] P. Liang, Y. Liu, L. Guo, J. Zeng, H. Lu, J. Anal. At. Spectrom. 19 (2004) 1489.
[28] P.H. Pacheco, R.A. Olsina, P. Smichowski, L.D. Martinez, Microchem. J. 91 (2009) 159.