



Simultaneous determination of zinc, cadmium and lead in environmental water samples by potentiometric stripping analysis (PSA) using multiwalled carbon nanotube electrode

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ABSTRACT

The present paper has focused on the potential application of multiwalled carbon nanotube for the development of a new, simple and highly selective electrochemical method for simultaneous Zn (II), Cd (II) and Pb (II) monitoring in water samples (lake and effluent waters), by using potentiometric stripping analysis (PSA). The electrochemical method is based on simultaneous preconcentration/reduction of metal ions onto a multiwall carbon nanotube electrode at -1.3 V (versus $\text{Ag}/\text{AgCl}_{\text{sat}}$) in 0.3 mol L^{-1} acetate solution containing 15 mg L^{-1} Hg (II) ions during 180 s, followed by subsequent chemical stripping. The analytical curve for all analytes covered the linear range varying from 58.4 up to $646.2\text{ }\mu\text{g L}^{-1}$ with correlation coefficients higher than 0.981 . The limits of detection for Zn (II), Cd (II) and Pb (II) were found to be 28.0 , 8.4 and $6.6\text{ }\mu\text{g L}^{-1}$, while the relative standard deviation (RSD) at $352\text{ }\mu\text{g L}^{-1}$ was 5.6 , 7.1 and 5.6% ($n=5$), respectively. The behavior of the simultaneous determination in the presence of following ions Co (II), Cr (III) and Cu (II) was affected by using the analyte:interferent ratio $1:10$. Therefore, by using standard addition method, Zn (II), Cd (II) and Pb (II) ions in lake and effluent water samples were determined after the spiking procedure and the results were successfully compared with those obtained by atomic absorption spectrometry (AAS). The obtained results suggest that the proposed method can be applied as a simple and efficient alternative for the simultaneous monitoring of heavy metals in water samples, according to those established requirements from environmental organizations. In addition, this method demonstrates the powerful application of carbon nanotubes in the field of potentiometric stripping analysis.

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1. Introduction

In recent years, the determination of potentially toxic metal ions in environmental samples, mainly in water bodies, has been a common concern for several researchers and extensively discussed. Despite the efforts of the scientific community to develop alternative forms to reduce the disposal of metal ions in water bodies, including different treatment effluents such as precipitation, membrane filtration, ion exchange and adsorption [1], the levels of toxic metals disposed into water bodies are still rising, mainly in aqueous effluents discharged into lake waters [2]. Owing to their potential danger to aquatic life, especially at high levels, there is a growing need for simultaneous monitoring of metal ions, such as zinc, cadmium and lead in different kind of water samples. The maximum levels of zinc, cadmium and lead established

by National Council for the Environment in Brazil (CONAMA) [3] for effluent discharge in water bodies are 5.0 , 0.2 and 0.5 mg L^{-1} , respectively. In addition, the maximum contaminant levels in drinking water allowed by EPA are 5.0 , 5.0 and $15.0\text{ }\mu\text{g L}^{-1}$ [4]. Thus, the metal ions monitoring can provide both important aspects in water quality and controlling the industrial processes [5]. Atomic absorption spectrometry (AAS) techniques have been accepted as the standard technique for metals determination since they offers satisfactory sensitivity and fairly low acquisition cost [6]. However, the majority of equipments can measure only one element at a time. Inductively coupled plasma optical emission spectrometry (ICP OES), on the other hand, offers multi-element analysis [7], but this technique is not yet extensively used in underdeveloped countries due to their high implementation and maintenance costs. These constraints justify the search for improved methods and suggest that the electrochemical analytical method for metal ions is still indispensable. Some advantages of electroanalytical methods can be pointed out for the analysis of metal ions such as high sensitivity, selectivity, simultaneous determination, simplicity

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and relatively low cost [8]. Indeed, electroanalytical techniques of stripping, including anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) and stripping potentiometry have received very much attention for metal ions determination owing to their intrinsic sensitivity and selectivity [9–11]. It occurs because in stripping analysis, a preconcentration step is combined with a stripping step, thereby enhancing sensitivity and selectivity. During the preconcentration step, the metal of interest is collected onto a working electrode and during the stripping step the collected metal is stripped out into solution [12]. The basic difference between potentiometric stripping analysis (PSA) and stripping voltammetry is that in PSA the redox processes on working electrode during stripping are spontaneous. Thus, according to Jagner and Graneli [13] it makes the technique insensitive to interferences from electroactive substances such as organic compounds present in complex environmental samples. In the voltammetric stripping analysis, such substances give rise to background currents that overlap the current stripping peak. Moreover, the time is the physical parameter measured in potentiometric stripping that can be measured with higher accuracy, precision and resolution than currents used in voltammetric methods [14]. In recent years, some researchers have shown that PSA can be successfully applied to simultaneous metal ions determination in a variety of matrices such as tap water [15], sediment sludge [16], blood sample [17] and seawater [18]. However, it is important to emphasize that these previous studies are based on the use of gold and mercury electrodes, while attempts have been devoted to the development of new electrodes, such as carbon pastes or glassy carbon electrode plated with mercury or bismuth film, and composites based on epoxy-graphite [19–22]. Considering that in PSA a deposition step is carried out, the electrode must comprise excellent specific surface area. In this sense, owing to the strong sorption properties of carbon nanotubes (CNTs) and their advantages in electrochemical measurements, this nanostructured material has allowed some novel methods of stripping analysis to be developed [23], but at the best of our knowledge this application has been limited to voltammetric methods, which makes use of carbon nanotubes film-coated glassy carbon electrode. CNTs have also been exploited for their interactions with metal ions and the possibilities generated for separation techniques coupled to spectroanalytical techniques [24–26].

In this context, the development of a reliable potentiometric stripping method for simultaneous determination of zinc, cadmium and lead in lake water and aqueous effluent using a multiwalled carbon nanotube paste electrode was described in the paper.

2. Experimental

2.1. Apparatus

All electrochemical experiments were performed using a potentiostat/galvanostat Autolab® PGSTAT-12 (Eco Chemie B.V., The Netherlands). Experiments were performed in a conventional three-electrode cell at room temperature, with a Ag/AgCl electrode as reference, a platinum wire as counter and carbon nanotube paste electrode as working electrode.

The accuracy of the method was tested by comparing the results obtained from the water samples spiked with known amounts of zinc, cadmium and lead with those obtained from flame atomic absorption spectrometry (FAAS) and/or graphite furnace atomic absorption spectrometry (GF AAS). A Shimadzu AA-6800 flame atomic absorption spectrometer (Shimadzu, Tokyo, Japan), equipped with hollow cathode lamps for zinc and cadmium with a deuterium lamp for background correction, was used. For measurements of lead ions a Graphite Furnace Atomic Absorption Spectrometer (GF AAS) (Zeiss AA55, Germany) equipped with deu-

terium lamp for background correction and a hollow cathode lamp as radiation source for lead was used. All operation conditions of FAAS and GF AAS were employed according to manufacturer instructions.

2.2. Reagents and solutions

The solutions were prepared with analytical grade chemical reagents as well as with water obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA). In order to prevent metal contamination from laboratory glassware, it was kept overnight in a 10% (v/v) HNO₃ solution from Vetec (Rio de Janeiro, Brazil). A solution of 0.3 mol L⁻¹ buffer acetate was prepared daily by dissolving a mass of 2.46 g of sodium acetate from Merck in 100 mL volumetric flask. The pH was adjusted with solution of concentrated nitric acid from Merck (Darmstadt, Germany).

Multiwalled carbon nanotubes (MWCNT) were supplied by CNT Co., Ltd. (Yeonsu-Gu, Incheon, Korea) with >93% purity, diameter between 10–40 nm and length of 5–20 μm and mineral oil from Sigma (St. Louis, MO, USA). Graphite powder (purity 99.9%) was supplied by Sigma.

All metal solutions were prepared daily by appropriate dilution of 1000 mg L⁻¹ stock standard solution from Merck.

2.3. Preparation of paste electrode

The carbon nanotube paste electrodes were prepared by mixing MWCNT with mineral oil at 2.7:7.3 (w/w), weight to weight ratio, in a mortar ground during 30 min. After this step, the resulting paste was carefully forced into a cavity (3 mm diameter; 1 mm depth) at the end of a glass tube. The electrical connection was provided by a copper wire connected to the paste in the inner hole of the tube. The surface of the paste electrode was smoothed and rinsed carefully with Milli-Q water. Afterwards, the carbon nanotube paste electrode was immersed into a 10% (v/v) nitric acid solution during 5 min. Finally, prior to the electrochemical measurements, the carbon nanotube electrode was submitted to electrochemical activation, carried out by cyclic voltammetry in the potential window from -1.0 to 1.0 V (18 cycles) using a scan rate of 100 mV s⁻¹ in a 0.3 mol L⁻¹ acetate buffer solution, pH 3.6 [27].

2.4. Sample preparation

Lake water samples were collected in polypropylene bottles from Lake Furnas, Minas Gerais State, Brazil. In order to preserve the sample, three drops of concentrated nitric acid were added for each 100 mL of water. Afterwards, the samples were filtered under vacuum using 0.45 μm cellulose acetate membranes and 10.0 mL of sample was added into the electrochemical cell and the volume was made up to 10.75 mL after adding 750 μL of 4.0 mol L⁻¹ acetate buffer solution at pH 3.6. Aqueous effluent samples were collected from a textile industry located at Alfenas, Minas Gerais State, Brazil. Aliquots of 100 mL of samples were collected in polypropylene bottles at the outlet of the Parshall Gutter from the effluent treatment plant. A total of 10 aliquots were taken in order to guarantee the representation of the samples. These collected samples were acidified, stored in a freezer and analysed in similar way to lake water, but without the filtering procedure.

2.5. Analytical procedure

Potentiometric responses were recorded at an electrochemical cell 15 mL capacity containing the working electrode (carbon nanotubes paste electrode), Ag/AgCl (3.0 mol L⁻¹) reference electrode and platinum as counter electrode. Aliquots of stock solution of zinc,

cadmium and lead were added into the electrochemical cell containing 0.3 mol L^{-1} acetate buffer solution (pH 3.6) and Hg (II) ions at 15.0 mg L^{-1} . In these experiments, the potential was first held at -1.3 V for 180 s at stirred solution, where the metal ions were electrochemically deposited onto the working electrode surface. After a 20 s rest the chemical stripping step was carried out from -1.3 V up to -0.35 V at unstirred solution and the corresponding transients analytical signals (dt/dE) (s/V) versus E (V) were recorded. All experiments were carried out without oxygen removal.

3. Results and discussion

3.1. Composition of carbon nanotube paste electrode

Electrodes based on carbon nanotube paste prepared by a mixture of multiwalled carbon nanotube powder and a mineral oil was adopted in this work because they are easily obtained with minimal costs, simplicity and is especially suitable for several electroanalytical techniques. However, their electrochemical characteristics depend on the proportion of the conducting MWCNT powder and the pasting liquid. Therefore, the first study was carried out to establish the best composition of carbon nanotube paste electrode. For this task, the assays were performed at a medium containing 0.1 mol L^{-1} of acetate buffer solution (pH 3.6) in the presence of Hg (II) ions at 12.0 mg L^{-1} concentration, while the concentrations of zinc, cadmium and lead were fixed at $650 \mu\text{g L}^{-1}$. A constant potential of -1.3 V was applied during 300 s at stirred solution and after a 20 s rest the chemical stripping step was carried out from -1.3 V up to -0.35 V at unstirred solution. Fig. 1 shows the effects of different proportion MWCNT:mineral oil on the potentiometric response. As can be observed, the best results were obtained using paste containing 73.0% (w/w) mineral oil. This result demonstrates that even using high insulator amount, the excellent conductivity of MWCNT led to the magnification of analytical signal. In addition, it is worth emphasizing the high homogeneity of the paste in the presence of high amount of mineral oil, which facilitates the handling of the paste as well as promoting an electrode surface smoother than those other electrodes tested. Thus, the proportion 2.7:7.3 (w/w) for MWCNT and mineral oil was used for further experiments. A comparative study with graphite paste electrode also was performed to emphasise the great advantage of MWCNT electrode. As can be seen from Fig. 1, the use of MWCNT leads to improvement of sensitivity of method in relation to use of graphite paste, thus justifying the use

of this nanostructured material. Moreover, as the peak for Cd (II) is practically overlapped in the presence of Pb (II) their simultaneous determination would not be possible for analytical purposes.

3.2. Effect of deposition potential

It is well known that in stripping analysis, the application of adequate deposition potential is very important to achieve the best sensitivity and sensibility. Thus, the influence of this parameter on analytical response is shown in Fig. 2. The potential range varied from -0.7 V up to -1.5 V and as observed, when a deposition potential more negative than -1.3 V was employed, an insignificant variation on the response was observed for cadmium and lead; however, a significant decrease in the zinc peak was observed. It seems that owing to a higher affinity of cadmium and lead ions than of zinc ions towards MWCNT surface, a competitive electrostatic attraction occurs between the analytes for those sites of MWCNT. Moreover, it is important to note that under the negative potential higher than -0.9 V mercury ions suffer electrolysis onto electrodes based on carbon substrate [28]. Hence, it would imply in a more pronounced competition, but previous studies carried out in the absence of mercury ions showed very small analytical signal for the analytes. For this study the stripping step was carried out by using constant current at $25 \mu\text{A}$. Based on these results, we can conclude that mercury ions act not only as chemical oxidant in the stripping step, but also play an important role in the deposition step by forming a metallic film onto carbon nanotube paste electrode surface. The enhancement of deposition efficiency is partially attributed to the metal-amalgam formation with mercury film. Thus, according to the aforementioned the deposition potential of -1.3 V was chosen as the best value to avoid codeposits of other metal ions from analysis of real samples.

3.3. Effect of sample pH

The influence of sample pH on the potentiometric response was investigated from pH 1.4 up to 7.8 (Fig. 3). For the extremely acid medium (pH 1.4) the measurements were made in the presence of hydrochloric acid as supporting electrolyte, while for the other pH values sodium acetate solutions were used at 0.1 mol L^{-1} concentration. As shown, the analytical signal for the metal ions increased with increasing pH up to 3.6, which suggests that the deposition mechanism also takes place by electrostatic attraction due to high affinity of metals for those sites of MWCNT surface, which con-

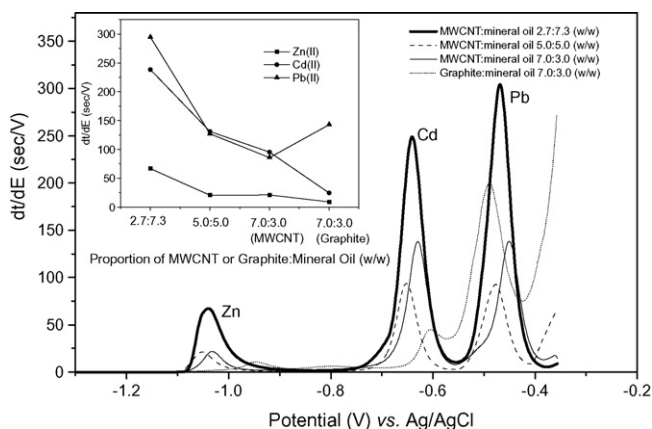


Fig. 1. Comparisons of the stripping potentiometric signal for zinc, cadmium and lead at four different working electrodes built with MWCNT and graphite powder. The experiment was performed in a medium containing 0.1 mol L^{-1} acetate buffer (pH 3.6) in the presence of 12 mg L^{-1} Hg (II) ions with deposition time of 300 s. The concentration of each analyte was $650 \mu\text{g L}^{-1}$ and the deposition potential was -1.3 V .

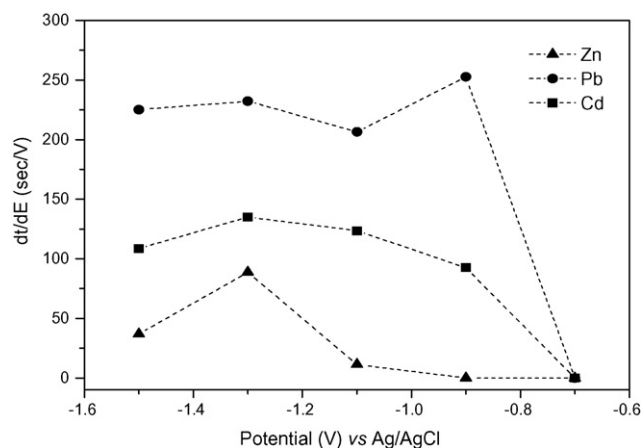


Fig. 2. Influence of deposition potential on the potentiometric response for zinc, cadmium and lead. The experiment was performed in a medium containing 0.1 mol L^{-1} acetate buffer (pH 3.6) in the presence of 12 mg L^{-1} Hg (II) ions with deposition time of 300 s. The concentration of each analyte was $1000 \mu\text{g L}^{-1}$.

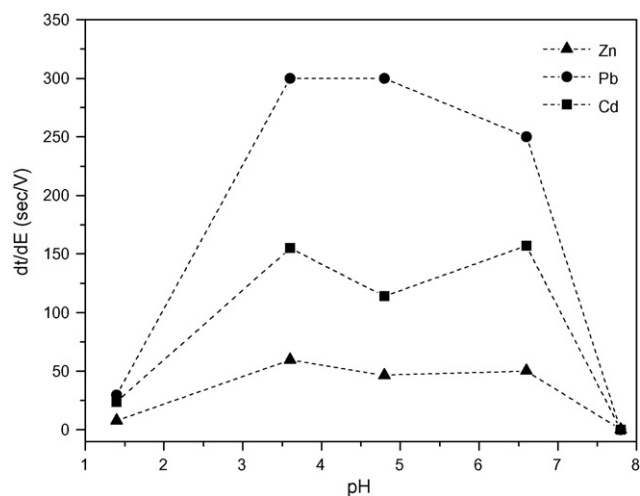


Fig. 3. Influence of pH medium on the potentiometric response for zinc, cadmium and lead. The experiment was performed in the presence of 12 mg L^{-1} Hg (II) ions with deposition time of 300 s. The concentration of each analyte was $1000 \mu\text{g L}^{-1}$ and the deposition potential was -1.3 V .

tain carboxylic and hydroxyl groups that probably have pK_a values ranging from 3 to 5 [29]. The presence of these functional groups is common in MWCNT, once mineral acid washing is made in the material to remove the metallic catalysts. It is also interesting to note that the analytical signal significantly decreased at pH 7.8, which was due to hydrolysis of metal ions. Therefore, pH 3.6 in acetate medium was selected for stripping measurements.

3.4. Effect of ionic strength

The effect of changing the ionic strength on the potentiometric response was examined under the range varying from 0.01 to 0.8 mol L^{-1} (Fig. 4). From the results, changes in ionic strength seriously change the analytical response with the best value at 0.3 mol L^{-1} . The low analytical responses obtained at lower ionic strength than 0.3 mol L^{-1} clearly indicate that with decreasing the ionic strength, the insufficient amount of support electrolytes lead to a decrease in the electrical current conduction during deposition step. Using high ionic strength naturally makes the formation

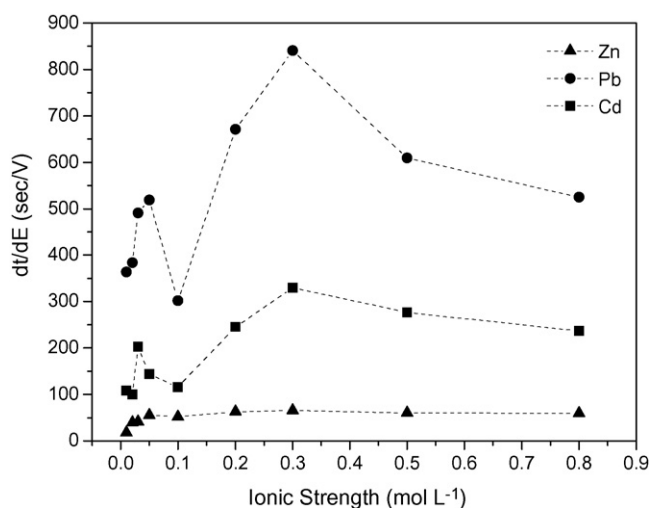


Fig. 4. Influence of ionic strength on the potentiometric response for zinc, cadmium and lead. The experiment was performed at pH 3.6 in the presence of 12 mg L^{-1} Hg (II) ions with deposition time of 300 s. The concentration of each analyte was $1000 \mu\text{g L}^{-1}$ and the deposition potential was -1.3 V .

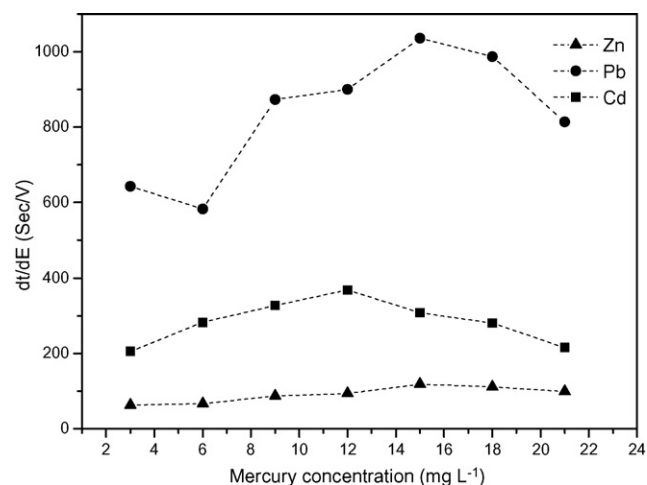


Fig. 5. Influence of mercury concentration on the potentiometric response for zinc, cadmium and lead. The experiment was performed in a medium containing 0.3 mol L^{-1} acetate buffer (pH 3.6). The concentration of each analyte was $1000 \mu\text{g L}^{-1}$ and the deposition potential was -1.3 V .

of electrical double layer of zinc, cadmium and lead with MWCNT surface difficult, and as a consequence, the deposition efficiency. In addition, high ionic strength also makes the diffusion of analytes towards the solution bulk difficult during stripping step, thus corroborating to those experimental data showed in Fig. 4. Therefore, 0.3 mol L^{-1} acetate buffer concentration was established as the best value in this study.

3.5. Effect of mercury concentration

The stripping step in potentiometric stripping analysis can be performed by analyte oxidation using chemical oxidation caused by oxidants present in the sample or by means of an applied current. This later alternative was not employed in this study since the analytical signal of zinc, cadmium and lead were very small, thus demonstrating that oxidation by mercury ions exert significant influence on the stripping step. Moreover, as mentioned before from pH studies, during the deposition step the metals can be deposited in both mercury film by amalgam formation and carbon nanotubes

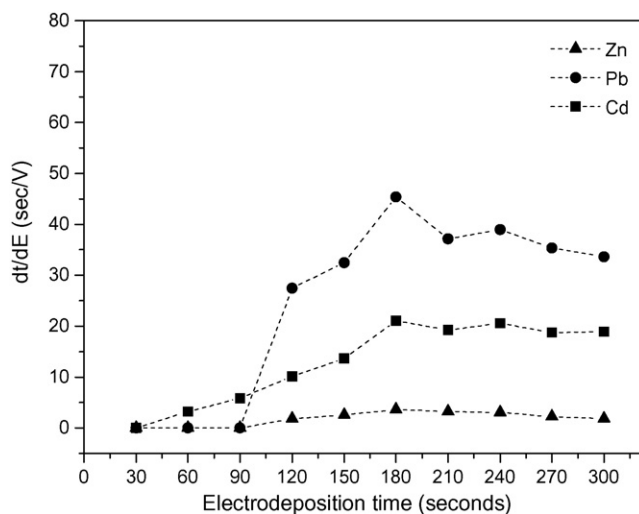


Fig. 6. Influence of electrodeposition time on the potentiometric response for zinc, cadmium and lead. The experiment was performed in a medium containing 0.3 mol L^{-1} acetate buffer (pH 3.6). The concentration of each analyte was $60 \mu\text{g L}^{-1}$ and the deposition potential was -1.3 V .

Table 1
Influence of foreign ions in the potentiometric response of metal ions (Zn, Cd and Pb).

Foreign ions	Ratio analyte/foreign ions	Recovery of analytical signal (%)
Al (III)	1:1	92.5
	1:10	104.5
Mg (II)	1:1	97.3
	1:10	98.5
Fe (III)	1:1	96.2
	1:10	99.8
Ni (II)	1:1	98.7
	1:10	93.2
Co (II)	1:1	56.5
	1:10	17.3
Cr (III)	1:1	90.7
	1:10	33.6
Cu (II)	1:1	95.6
	1:10	37.9
Sb (III)	1:1	92.7
	1:10	90.8

surface. Therefore, the effect of mercury concentration on analytical signal was investigated from 3 up to 21 mg L⁻¹. As observed from Fig. 5, the best mercury concentration was found to be 15 mg L⁻¹ being this value chosen in this study. At low mercury concentration there is not enough mercury ions to create the film as well as to chemically strip off metal ions. When measurements are carried out at mercury concentration higher than 15 mg L⁻¹, a decrease of analytical signal is observed due to competition between metals and mercury ions on the surface of the carbon nanotubes.

3.6. Effect of deposition time

The deposition time must be carefully controlled since this parameter can significantly influence the sensitivity of the determination. Fig. 6 shows a plot of potentiometric response versus deposition time varying from 30 up to 300 s. As observed, we achieved the best results by increasing the deposition time, but the potentiometric response for metal ions leveled off after 180 s, presumably due to surface saturation. Hence, a further deposition time increase beyond 180 s practically does not improve the ana-

Table 2

Validation of the method for simultaneous determination of zinc, cadmium and lead in spiked lake waters and aqueous effluent.

Samples	Analytes	Concentration of metals added ($\mu\text{g L}^{-1}$)	Concentration of metals found ^a ($\mu\text{g L}^{-1}$)			$t_{\text{calculate}}$
			Proposed method	GFAAS	FAAS	
Lake water	Zn (II)	100.7	92.6 ± 3.2		94.6 ± 7.1	0.71
		330.5	318.3 ± 0.8		318.9 ± 1.6	0.90
		536.5	563.3 ± 3.0		552.2 ± 11.6	2.63
	Cd (II)	100.7	95.9 ± 1.1		93.5 ± 5.0	1.30
		330.5	324.9 ± 1.5		320.7 ± 2.4	2.10
		536.5	550.0 ± 1.0		546.6 ± 6.0	1.56
	Pb (II)	58.4	56.2 ± 0.9	56.9 ± 2.4		1.54
		330.5	325.5 ± 1.4	324.6 ± 2.0		1.09
		536.5	543.9 ± 1.4	543.0 ± 2.3		0.06
Textile industry effluent	Zn (II)	100.7	93.5 ± 0.1		94.8 ± 1.0	3.48
		330.5	319.3 ± 2.0		321.2 ± 0.9	2.42
		536.5	528.3 ± 2.8		526.1 ± 4.0	1.23
	Cd (II)	100.7	93.9 ± 1.0		94.6 ± 0.7	1.75
		330.5	319.5 ± 1.1		321.9 ± 1.7	3.30
		536.5	537.3 ± 4.0		536.1 ± 3.7	0.58
	Pb (II)	58.4	55.3 ± 3.9	56.2 ± 2.0		0.59
		330.5	325.9 ± 2.9	326.1 ± 1.8		0.19
		536.5	532.1 ± 1.4	534.0 ± 0.8		3.46

Confidence interval, 95%. ($n - 1$) = 2; $t_{\text{tabled}} = 4.303$. GF AAS, graphite furnace atomic absorption spectrometry; FAAS, flame atomic absorption spectrometry.

^a The results are expressed as mean value ± S.D. based on three replicates ($n = 3$) determinations.

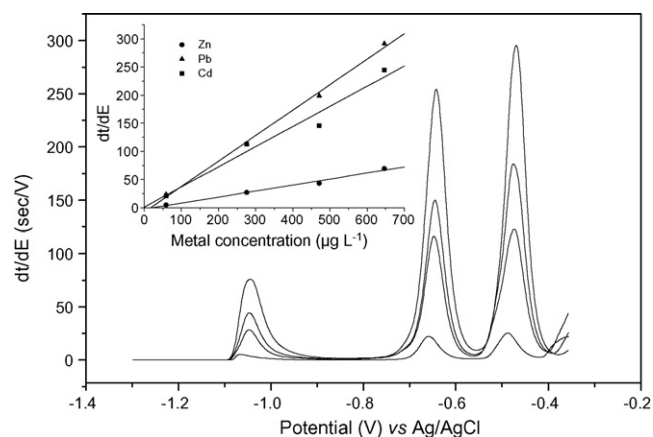


Fig. 7. Analytical curves (inset) for zinc, cadmium and lead. Linearity covering the range of concentration from 58.4 up to 646.2 $\mu\text{g L}^{-1}$.

lytical signal. Thus, the optimum deposition time of 180 s was fixed for further studies. This value is similar [30,31] or smaller [21,11] than those results previously published in the literature.

3.7. Effect of foreign ions as potential interferences

The effect of foreign ions on the simultaneous determination of 60 $\mu\text{g L}^{-1}$ each of zinc, cadmium and lead was studied under the optimized method. For this task, the elements Al (III), Mg (II), Fe (III), Ni (II), Co (II), Cr (III), Cu (II) and Sb (III) were investigated in the ratio analyte:interferent 1:1 and 1:10. The results of analytical response recovery of solution containing only zinc, cadmium and lead were compared with those in the presence of potential interferences (Table 1). The foreign ion was considered as interferent when it caused a negative change at ca. 10% as regards the response of analytes signals alone. As verified, the interference was observed only for the ratios analyte:interferent 1:1 and 1:10 for Co (II), 1:10 for Cr (III) and Cu (II). The interferences possibly come from two aspects: one derives from the competition between analytes and interferent ions for those sites of MWCNT and the other from the intermetallic compound formation. Despite the interference, for practical analysis, applying standard addition method in simultaneous determination of Zn (II), Cd (II) and Pb (II) can elimi-

nate the interference of Co (II), Cr (III) and Cu (II) as will be further demonstrated from successful analysis of real sample (lake water and aqueous effluent).

3.8. Features of the method and analytical application

Under the optimized chemical and electrochemical variables for the proposed method, the calibration curves for zinc, cadmium and lead were built from 58.4 up to 646.2 $\mu\text{g L}^{-1}$. The typical records of potentiometric stripping analysis of zinc, cadmium and lead at increasing concentrations are displayed in Fig. 7 (inset the dt/dE versus metal concentration curve) with respective correlation coefficient of 0.993, 0.982, 0.998. The limits of detection (LD) and quantification (LQ) were calculated according to IUPAC [32] and were based, respectively, on 3 and 10 times the standard deviation of 10 measurements of the blank solution. The results obtained for LD were found to be 28.0, 8.4 and 6.6 $\mu\text{g L}^{-1}$, while for LQ were 93.6, 28.0 and 22.1 $\mu\text{g L}^{-1}$ for zinc, cadmium and lead, respectively. Such values are sufficient for monitoring these metals in aqueous effluents based on acceptable levels established by CONAMA [3]. The precision assessed as relative standard deviation (RSD) in terms of reproducibility for five authentic replicate determination of 352 $\mu\text{g L}^{-1}$ for zinc, cadmium and lead was 5.6, 7.1 and 5.6%.

The proposed method was successfully applied to the simultaneous determination of zinc, cadmium and lead in spiked lake water samples and aqueous effluent from a textile industry (Table 2) using standard addition method. The accuracy of the method was checked by means of comparison with those data obtained from atomic absorption spectrometry (AAS). The assessment by Student's *t*-test did not show a statistical significant difference between the methods used (95%), thus confirming the accuracy.

4. Conclusions

In the present study, it was reported the first time the combination of PSA with the unique properties of MWCNT for the development of a new electroanalytical method for simultaneous determination of zinc, cadmium and lead. Few applications of MWCNT have been reported to construct carbon nanotube electrode and has been devoted especially to voltammetric methods. The chemical and electrochemical parameters that exert influence on deposition and stripping of metal ions, such as deposition potential, deposition time, sample pH, ionic strength, composition of carbon nanotube paste electrode and oxidant concentration were carefully studied. Unlike the majority of the PSA methods, in which a mercury film is first placed onto the working electrode previous to the analytical measurements, in the present work this electrode treatment was not necessary. In addition, other features in this work were observed, such as: satisfactory application of the method without severe interference even in complex environmental water samples; sufficient sensitivity for simultaneous metal ions monitoring in aqueous effluent according to CONAMA, being an effective replacement to those methods based on AAS; simplicity in the building of the electrode; excellent reproducibility of measurements; reduced time of analysis compared to other electrochemical stripping methods and low operation cost. Finally, it could be shown that with the present work a more expanded application of MWCNT in stripping analysis is described, thus contributing for the new analytical investigation for this nanostructured material.

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