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Article

On Site Stripping Voltammetric Determination of Zn(II), Cd(II) and Pb(II) in Water Samples of the Cananéia-Iguape Estuarine-Lagoon Complex in São Paulo State, Brazil

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Os sistemas estuarinos desempenham um importante papel na retenção de elementos traços devido à afinidade destes com algumas partículas dissolvidas em água. Nesse trabalho, apresenta-se o uso de um sensor voltamétrico para monitorar as concentrações de Zn (II), Cd(II) e Pb (II) na região do Sistema Estuarino Lagunar de Cananéia-Iguape (estado de São Paulo). No setor sul, (Cananéia) obteve-se menores valores de concentração, e no setor norte (Iguape) os valores foram maiores devido às atividades antrópicas, com ênfase à introdução prévia de resíduos de mineração e insumos de efluentes agrícolas, industriais e domésticos. O método proposto é viável, barato e rápido, e permite a determinação dos íons metálicos simultaneamente. Além disso, o dispositivo portátil é simples e pode ser facilmente utilizado para medições de campo a bordo de navios oceanográficos.

Estuarine systems play an important role in the retention of toxic trace elements owing to the affinity of these elements with particles dissolved in water. This work presents the use of a voltammetric sensor to monitor heavy metal (Zn (II), Cd(II) and Pb (II)) concentrations in the Cananéia-Iguape Estuarine-Lagoon region (São Paulo State, Brazil). Lower concentrations were found in the Southern estuarine system (Cananéia City) and increased concentrations observed in the Northern sector (Iguape City) were promoted by anthropogenic activities, with particular influence from the historical introduction of mining wastes and inputs from agricultural, industrial and domestic effluents. The proposed method is reliable, inexpensive and fast, can simultaneously provide information on the concentration of these metallic ions and can be easily used for field measurements aboard oceanographic ships.

Keywords: zinc, cadmium, lead, stripping voltammetry, estuary.

Introduction

Estuarine systems play an important role in the retention of heavy metals owing to the affinity of these elements to the muddy particulate matter transported from rivers to estuarine waters. The dissolved metal phases constitute an important basis for the bioaccumulation process in organisms, as once in the food chain, they can develop a toxic role. The fast and precise measurement of metals in water (without the need for pre-concentration processes) represents an efficient tool for the evaluation of water quality.

The Cananéia-Iguape Estuarine-Lagoon complex (São Paulo State, Brazil) is a biosphere reserve established by UNESCO[1] due to the conservation status of the ecosystem. The Ribeira de Iguape River reaches the Northern part of the system, and the Valo Grande Channel was constructed in the 19th century to decrease the distance from the river to the estuarine port. This channel is 300 m wide and transports fresh water to the system. The Ribeira de Iguape River comes from the Alto do Ribeira region, which is characterized by intense agricultural activities and an inactive lead-mining industry whose residues are still found in the environment. The Southern part of the system is still preserved, and contains mangrove vegetation that functions as an important nursery for water life.[2]

The concentration of toxic elements such as zinc, cadmium and lead in this environment has increased mainly owing to anthropogenic activities associated with industrial pollution, mining, water sports, agriculture (fertilizers) and domestic sewage. Zinc acts as an essential micronutrient for microorganisms, vegetables and animals, but is toxic

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to the environment at high concentrations and can cause vomiting, diarrhea, cramps, changes in the nervous system, mutagenesis and carcinogenesis in humans.[3,4] Cadmium has a diverse range of toxicity levels, including nephrotoxicity and carcinogenicity, and acts in the collapse of the skeleton.[5] Lead in the environment has received much research attention owing to its high toxicity, as its accumulation in the body has serious deleterious effects on humans. In particular, lead strongly affects the mental and physical development of children, and can cause poisoning in adults, inducing severe damage to the liver, brain, kidneys, reproductive system and central nervous system.

In oceanic systems, the natural levels of cadmium, lead and zinc ions are in the order of nmol L^{-1} or pmol L^{-1}, whereas in most coastal systems, the values may be slightly enhanced because of continental inputs.[4] Estuaries and coastal regions often receive the discharge of urban and industrial effluents, leading to contamination of waters and marine life. In estuaries, the concentration of these metallic ions can reach critical levels, which have led to the formulation of strategies to reduce the impact on ecosystems that sustain most of the marine biodiversity and the main fishing resources.

Sensitive analytical techniques are required to monitor the concentration of metallic ions in order to assess the environmental quality of estuarine compartments. Spectroscopic techniques are routinely used in environmental studies, but sometimes do not allow the determination of trace concentrations. Hence, pre-concentration procedures are needed and require large volume water samples that are difficult to handle aboard research and oceanographic vessels. Alternatively, electroanalytical techniques are capable of low limits of detection, and enhanced sensitivity can be gained by the application of pre-concentration steps such as those explored in stripping voltammetry.[6-8] For instance, the use of stripping voltammetric methods for the determination of various toxic metallic ions in seawater has been reported.[9-12] Mercury-based electrodes have been used in stripping techniques because of their high area reproducibility, but the use of bismuth films presents an attractive alternative to the mercury films owing to their environmentally friendly nature, as well as their easy preparation, high sensitivity, well-defined and undistorted stripping signals, and excellent neighboring peak resolution.[13-20]

Additional sensitivity is obtained if electroanalytical determinations are performed with microelectrodes. These have unique properties, such as reduced ohmic drop, capacitive effects, and improved material flux owing to the radial diffusion; hence, much lower limits of detection are obtained.[21] Moreover, the response of microelectrodes is not greatly affected by solution stirring, which is very convenient for on site measurements.

In this work, we report on the design, characterization, optimization and field deployment of a remote sensor for on site monitoring of trace metals in an estuarine-lagoon region. Data were collected from sediments and water bodies that have an influx of heavy metals from mining activities, as well as from agricultural, industrial and domestic effluents from the Ribeira de Iguape River.

Experimental

Chemicals and materials

All solid reagents were of analytical grade and were used without further purification. Solutions were prepared by dissolving the reagents in distilled, deionized water processed through a water purification system (Nanopure Infinity water purification system, Barnstead, Dubuque, IA). The zinc sulfate, cadmium nitrate and lead nitrate solutions were prepared by dissolving the salts in a 0.1 mol L^{-1} acetate buffer, pH ca. 4.5. The Bi(III) solution was prepared by dissolving the $Bi(NO_3)_3.5H_2O$ salt in a 10% (v/v) nitric acid solution, followed by further adjustment to the desired volume with deionized water. The acetate buffer solution was prepared by mixing suitable amounts of sodium acetate and acetic acid solutions. All reagents used were supplied by Merck (Darmstadt, Germany), except for sodium acetate (Synth, São Paulo, Brazil). The estuarine water reference material for trace metals (SLEW-3, salinity 15 and acidified to pH 1.6) used in this study was obtained from the National Research Council of Canada, Institute for National Measurement Standards (Ottawa, Canada).

Electrodes and instrumentation

A PalmSens portable electrochemical analyzer (PalmSens BV, Houten, Netherlands) was used to carry out the electrochemical experiments. Voltammograms were recorded in an electrochemical cell containing three electrodes: a carbon fiber microelectrode (radius of 3 µm), a homemade Ag/AgCl saturated KCl reference electrode and a platinum electrode (Metrohm).

Carbon fiber microelectrode fabrication

A carbon fiber rod (radius of 3 µm) was connected to a Ni/Cr wire with silver paste (Joint Metal Comercio Ltda, São Paulo, Brazil) and inserted into a glass capillary whose tip was insulated with epoxy resin. The microelectrode was left to dry for about 3 h, and then, its surface was polished with sandpaper and alumina, this was followed by copious washing with distilled water. The radius of the microelectrode was calculated by measuring the limiting diffusion current in a $K_3Fe(CN)_6$ solution of known concentration using KCl as the supporting electrolyte.

Fabrication of bismuth film microelectrodes (BiFME) and square wave anodic stripping voltammetric (SWASV) measurements

In situ bismuth films were prepared by first spiking the samples with a 1 mmol L^{-1} Bi(III) solution (final concentration of 10 µmol L^{-1}). Bi and the metals were then simultaneously electrodeposited on the surface of the microelectrode at −1.6 V under quiescent conditions for a determined period of time, followed by a 10 s rest period. The voltammogram was then recorded between −1.6 and 0.2 V by applying a square waveform. The residual metals and bismuth film were cleaned from the electrode for 30 s at 0.3 V prior to each experiment. SWASV measurements were performed in quiescent solutions at an optimized pH of 5.5, unless otherwise stated. The instrumental parameters are shown in Table 1 and were selected taking into account the best sensitivity. The limit of detection was calculated as the concentration that gives a current response three times the standard deviation of the background signal and the values for Cd(II), Zn(II) and Pb(II) were found to be 0.03, 0.8 and 0.02 nmol L^{-1}, as already reported in a previous study.[22]

Table 1. Optimized voltammetric parameters used in the determination of Cd(II), Zn(II) and Pb(II) by SWASV

Parameter	Studied range	Optimum value
E_{dep} / V	–1.2 to –1.8	–1.6
E_{step} / mV	2.5 to 30	10
$E_{amplitude}$ / mV	5 to 50	25
$E_{cleaning}$ / V	0.1 to 0.7	0.3
Frequency / Hz	5 to 50	30
t_{dep} / s	200 to 120	800
$t_{cleaning}$ / s	10 to 60	30

Water sampling

Water sampling was carried out in summer 2010 along of the Cananéia-Iguape Estuarine-Lagoon complex on the Southeastern coast of São Paulo State (24°00' S; 46°21' W), Brazil. The water samples were collected using Nansen Hydrobios® bottles washed with 10% HNO_3 solution and rinsed with Milli-Q water aboard RV Albacora from the Oceanographic Institute of São Paulo University. Analyses were performed at eleven points (stations) distributed along the estuary (Figure 1). The water temperature was measured using a protected reversion thermometer with a precision of ± 0.02 °C. The water salinity was determined using a Beckman RS10 inductive salinometer, using a seawater standard as reference, with a precision of ± 0.01. The pH value was measured using an Orion pHmeter with a precision of ± 0.01. The samples were maintained at 4 °C unless otherwise stated.

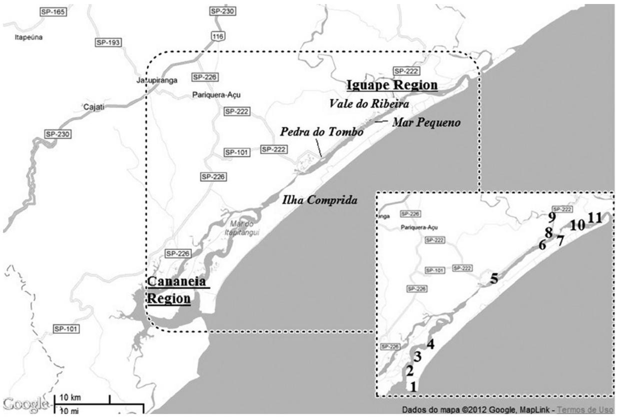

Figure 1. Location of the sample stations in the Cananéia-Iguape Estuarine-Lagoon complex (São Paulo State, Brazil).

Results and Discussion

Method validation

The performance characteristics of the proposed method were investigated in an attempt to demonstrate its compliance with the intended analytical application requirements. The analytical parameters evaluated for the method validation were the recovery of a certified material.

The concentrations of Cd(II), Pb(II) and Zn(II) in natural samples were determined using the standard addition method. Figure 2 shows a typical stripping voltammogram recorded with an estuarine water sample, and the peak responses at −1.1, –0.7 and –0.4 V correspond to the anodic oxidations of Zn (a), Cd (b) and Pb (c), respectively. As expected, the addition of known amounts of the metallic ions to the water sample caused an increase in the peak current.

The accuracy of the proposed electrochemical procedure was also examined by using the SLEW-3 Certified Reference Material. Table 2 presents typical results from such tests, which were in good agreement with the certified values. The results obtained for recovery tests (ranging from 90 to 105%, Table 3) were within the

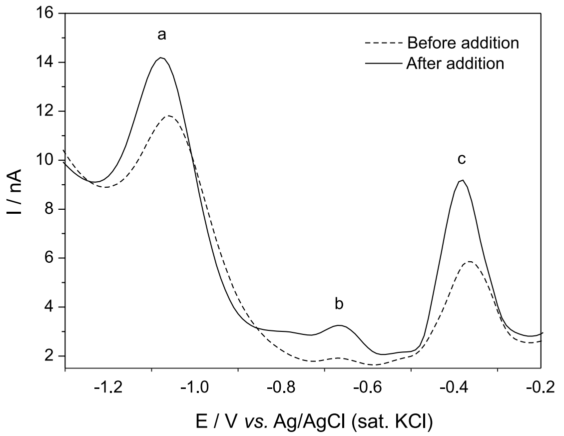

Figure 2. Stripping voltammograms obtained with a BiFME in an estuarine water sample (adjusted to pH ca. 5.5) before and after addition of Zn(II), Cd(II) and Pb(II) to give a final concentration of 1 nmol L^{-1}.

acceptable range for samples with concentrations in the nmol L^{-1} range.[23] It is concluded that the developed method can be used for the determination of Zn(II), Cd(II) and Pb(II) ions in brackish water.

Table 2. Data obtained by the determination of metals in certified estuarine water (SLEW-3)

Ions	Certified sample / (nmol L^{-1})	Mean value / (nmol L^{-1})	Recovery / %
Zn(II)	3.0	3.4 ± 0.2	113 ± 7
Cd(II)	0.40	0.40 ± 0.06	100 ± 15
Pb(II)	0.043	0.049 ± 0.004	114 ± 9

Environmental application

Temperature, salinity and pH values are presented in Figure 3. Temperature data were in agreement with those corresponding to the summer period, with an average of 26.17 °C. The salinity values from the Northern and Southern parts of the system differ significantly, as previously reported.[2] This is explained by the important freshwater input from the Ribeira de Iguape River across

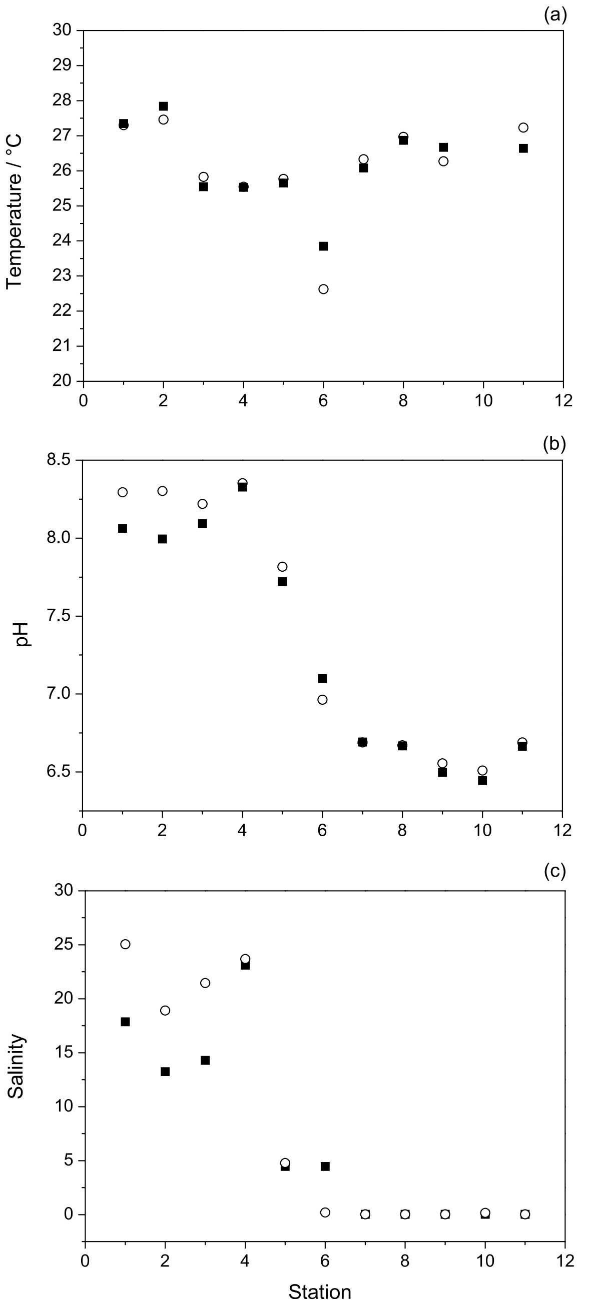

Figure 3. Distribution of (a) temperature, (b) salinity and (c) pH in the Cananéia-Iguape Estuarine-Lagoon complex (■ 0 and ○ 5 m).

Table 3. Results of determination of Pb(II), Cd(II) and Zn(II) in the samples (n = 3)

	Ions	Concentration / (nmol L^{-1})			Recovery / %
		Found	Added	Found after spiking	
Sample (1)	Zn(II)	2.40 ± 0.05	2.0	4.40 ± 0.08	100 ± 2
	Cd(II)	0.050 ± 0.004	0.050	0.095 ± 0.009	90 ± 14
	Pb(II)	0.20 ± 0.03	0.20	0.39 ± 0.03	95 ± 10
Sample (10)	Zn(II)	2.0 ± 0.1	2.0	3.8 ± 0.2	90 ± 10
	Cd(II)	0.110 ± 0.005	0.100	0.22 ± 0.01	105 ± 4
	Pb(II)	0.47 ± 0.06	0.40	0.90 ± 0.02	103 ± 3

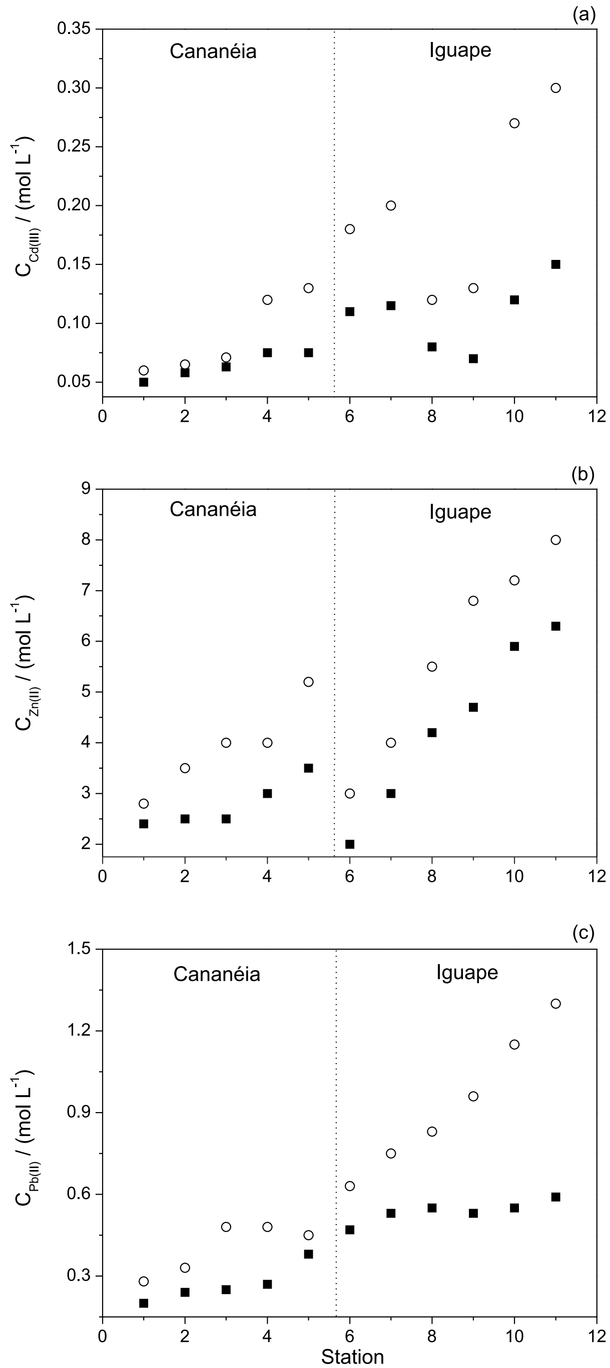

Figure 4. Concentrations of Zn(II) (A), Cd(II) (B) and Pb(II) (C) in the Cananéia-Iguape Estuarine-Lagoon complex (■ 0 and ○ 5 m).

the Valo Grande Channel. Samples from the Southern part (Cananéia City) exhibited salinities from 4.46 to 25.46 and higher pH values (7.72-8.35), as a consequence of seawater input from the movement of the tide. In contrast, samples from the Northern part (Iguape City) had low salinities (0.02-0.20) and lower pH values (6.45-7.10), and they are classified as fresh water, according to Resolution No. 357/2005 of the Brazilian National Environmental Council (CONAMA).[24]

The established SWASV method using the BiFME was applied to measure the concentrations of Cd(II), Zn(II) and Pb(II) in water samples collected at different stations along the system. Figure 4 shows the determined values at the surface (0 m) and at the bottom (5 m) and presents four main issues to be addressed:

(*i*) The metallic ion concentration considerably changes over the course of the estuary. For all three metallic ions, the concentration increases from Cananéia to Iguape as a consequence of anthropogenic activities in the Iguape region, including mining, agriculture, industrialization and urbanization.

(*ii*) The concentration of ions in bottom water is higher than in superficial water, and this trend is probably explained by metal accumulation in the sediments and resuspension/redissolution processes.

(*iii*) There is a noticeable decrease in Zn(II) and Pb(II) concentrations in bottom waters around the fifth station. This observation can be justified by taking into account mixing processes and general circulation in the Cananéia-Iguape Estuarine system, which is governed by the tide and river discharges. Waters coming from Iguape and Cananéia during the flood tide near the Pedra do Tombo form the mixing zone at station 5, which may explain the decrease in Zn(II) and Pb(II) concentrations at this sample point.

It is well recognized that metal ions are present in seawater in various forms, depending on their interaction with other compounds. In stripping methods, only species that are in a labile form can be electrodeposited and yield an analytical response owing to the anodic oxidation step. Whether a particular species is present in a labile or inert form depends mainly on the dissociation kinetics of the complex. In order to obtain information on the total metal concentration, the complete conversion to labile forms is usually performed by treating the water sample with HCl down to a pH of 2.[11]

A simplified, three-fraction scheme has been recently proposed[11] and includes the following: (*i*) the water-soluble fraction, (*ii*) the insoluble/dilute-acid-extractable fraction and (*iii*) the insoluble/residual fraction. The first fraction contains free ions and soluble salts such as chlorides, sulfates, nitrates and acetates. The second consists mainly of carbonate without any significant loss of iron oxides, while the third fraction includes that bound to oxides, silicates and organic matter. In an attempt to measure both the water-soluble fraction and the acid-soluble fraction (considered potentially bioavailable) in the Cananéia-Iguape Estuary, experiments were carried out with the BiFME before and after extraction with HCl solution at pH 2, and the results are presented in Table 4. The increase in concentrations after acidification of the samples (total concentration) can be interpreted as an increase in the analytical response caused by a shift to active metal from inert complex species.

Table 4. Data obtained in the determination of free (labile fraction) and total ions (after extraction) in sample waters of the Cananéia-Iguape estuary

Station of sample collection	Íons	Concentration / (nmol L^{-1})		
		Zn(II)	Cd(II)	Pb(II)
1	free	2.4	0.050	0.20
	total	2.9	0.063	0.28
2	free	2.5	0.058	0.24
	total	3.2	0.079	0.39
3	free	2.5	0.063	0.25
	total	3.5	0.078	0.37

The difference between the total and free concentrations corresponds to the weak-acid-soluble fraction. Hence, the acid-soluble fraction of the metallic ions was calculated as the ratio of the acid-soluble concentration to the total concentration, and values of 30, 29 and 50% were found for Zn(II), Cd(II), and Pb(II), respectively. These values are consistent with those obtained by Annibaldi *et al.*,[11] who found that ions complexed with organic matter became soluble by adding hydrochloric acid.

Onboard stripping voltammetric experiment

Onboard field measurements were also performed to demonstrate the versatility of the electrochemical sensor developed. Sample handling is reduced to a minimum for labile metal analysis (as only Bi(III) is added), and the elimination of the stirring and of the degassing steps renders an easily portable instrumentation. Figure 5 shows a typical voltammogram recorded with the BiFME in a water sample obtained from station 9. The experiment was performed just after sample collection. Peaks at −1.05 and −0.50 V are well defined and readily resolved from the background, and correspond to the anodic oxidation of electroplated Zn and Pb, respectively. No peak attributable to cadmium was found in this voltammogram. This may be explained by the fact that the pH was not adjusted in this experiment, and hence, free Cd(II) was not detected under this experimental condition.

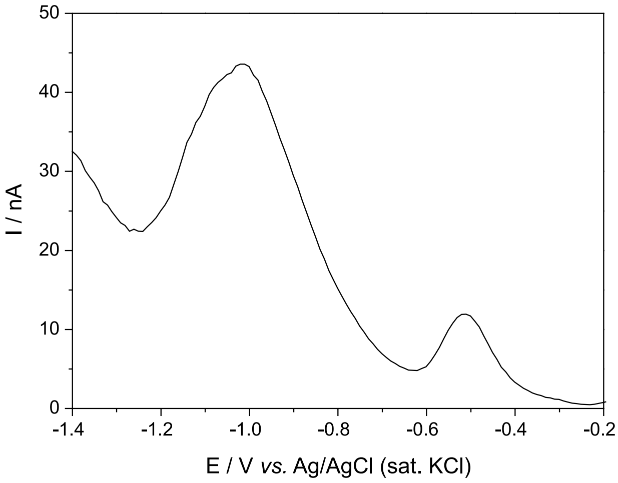

Figure 5. Onboard stripping voltammogram recorded with the BiFME in a water sample from near station 9.

Conclusions

A sensitive SWASV method with a BiFME for the determination of zinc, cadmium and lead concentrations in estuarine waters was developed. The analytical features of the proposed method make it suitable for monitoring these metallic ions at very low levels, in the nmol L^{-1} concentration range. The method is reliable, inexpensive, and fast, and can provide simultaneous information on the concentration of a number of metallic ions. Moreover, the apparatus is simple and portable, hence, can be easily used for field measurements on oceanographic vessels. The environmental data showed the expected lower metal concentration values in the Southern sector of the estuarine system, which is normally diluted by seawater movement. Increased values were found in the Northern sector, because of anthropogenic disturbances generated by the input from different sources, particularly effluent from mining activities. These materials are incorporated into the sediment and organic matter in the river and are then transported to the estuarine-lagoon system.

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