

Analysis of Trace Metals Cu²⁺, Pb²⁺ and Zn²⁺ in Coastal Marine Water Samples from Florianópolis, Santa Catarina State, Brazil

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A determinação de metais traço é um indicador importante da toxicidade dessas espécies no ambiente marinho. As técnicas de redissolução são freqüentemente utilizadas, devido a sua sensibilidade e seletividade. Nesta investigação foram determinados parâmetros eletroquímicos para a detecção da concentração dos íons de metais chumbo, zinco e cobre, em águas costeiras, empregando as técnicas de voltametria de redissolução anódica de pulso diferencial (DPASV) e voltametria de redissolução catódica adsorptiva de pulso diferencial (DPACSV). Para a determinação do limite de detecção dos íons de metais foram utilizadas amostras sintéticas, em pH 2 para chumbo e zinco e em pH 9 para cobre. Na etapa de validação das metodologias realizada em amostra de água de mar costeira certificada (CASS-4) encontrou-se a concentração de 10,3 nmol L⁻¹ para o íon Cu(II). Utilizou-se o procedimento de enriquecimento e recuperação para os metais analisados sendo obtidos os seguintes percentuais de recuperação: 95±10 (Pb²⁺), 110±11 (Zn²⁺) e 95±8 (Cu²⁺). Os valores de concentrações de metal total foram considerados baixos, quando comparados aos índices estabelecidos pelo CONAMA, principalmente para chumbo e zinco. Para o íon cobre a maior concentração pode ser atribuída ao uso de tintas antiincrustantes e de processos industriais.

The determination of trace metal concentrations is an important indicator of toxicity toward species present in ocean environments. Stripping techniques are frequently used, due to their sensitivity and selectivity. In this investigation we were able to determine, efficiently, the concentration of lead(II), zinc(II) and copper(II), in coastal waters, using Differential Pulse Anodic Stripping Voltammetry (DPASV) and Differential Pulse Adsorptive Cathodic Stripping Voltammetry (DPACSV) techniques. For the determination of metal ion detection limits, synthetic samples were used, pH 2 for lead and zinc and pH 9 for copper. In order to check the accuracy of the procedure a certified coastal marine sample (CASS-4) was used and a concentration of 10.3 nmol L⁻¹ for Cu(II) was obtained. The enrichment and recovery method was used for the metals analyzed, the following percent recoveries being obtained: 95±10 (Pb²⁺), 110±11 (Zn²⁺) and 95±8 (Cu²⁺). The total metal concentrations obtained were considered low, when compared with the indices established by CONAMA, particularly for lead and zinc. For the copper ion the higher concentration may be attributed to its use in the anti-fouling paint, and industrial processes.

Keywords: stripping analysis, trace metals, coastal waters

Introduction

Environmental contamination caused by human activities has been extensively discussed. Despite the efforts of the scientific community in developing research to show that marine organisms are contaminated by chemical products, particularly metals, the levels of waste

disposed to water bodies in urban areas continues to rise.¹ The toxicity of dissolved metals to aquatic organisms is related to the extent to which they alter the functioning of the biological membrane.² Some metals such as copper, iron, manganese, nickel and zinc are essential to life, because they participate in enzymatic structures related to biochemical processes. Cadmium and lead do not play a biological role and are very toxic even in low concentrations. High levels of metal ions in the aquatic

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environment are toxic and tend to concentrate in all matrices (suspended matter, sediment and biota) being taken up by marine species which form part of the human food chain.³

Since the toxicity of a metal is attributable mainly to its labile fraction in aquatic environments, many studies have sought to identify the ligands which dominate the speciation of metals in natural waters and to develop methods to measure the concentration of the trace metal fraction, which may be toxic to aquatic biota. For example, dissolved copper and its species, free Cu^{2+} (hydrated), $\text{Cu}(\text{OH})\text{Cl}$ and $\text{Cu}(\text{OH})_2$, are strongly controlled by the pH of the medium,⁴ and in seawater they can form several labile and inert complexes with organic and inorganic ligands. When organic matter is composed mainly of humic substances present in natural waters it can interact with different metals, such as copper, affecting its solubility and bioavailability. The chemical speciation is, therefore, important for an evaluation of the bioavailability and toxicity of a substrate, since measurements of total concentration of a nutrient or trace element provide little information regarding its distribution and occurrence.⁵⁻⁷

In Figure 1, a scheme of metal speciation in seawater is given, distinguishing between the dissolved form and the particulate form retained in a $0.45 \mu\text{m}$ membrane filter.

The importance of water resources for the maintenance of life on the planet has driven ever more researchers to

study the dynamics of natural aquatic environments, with special attention being given to the dangers of contamination resulting from the accumulation of metals in these environments. Techniques such as spectrometry and voltammetry are suitable for the analysis of metals ions due to their high sensitivity, selectivity, simultaneous determination, simplicity and relatively low cost. This last factor makes these techniques especially attractive in the field of environmental chemistry.^{3,5,8,9}

The utilization of differential pulse voltammetric techniques as Adsorptive Cathodic Stripping Voltammetry (ACSV) for the analysis of natural waters allows the determination of the concentrations of labile trace metals and inorganic complexes, along with the fraction of relatively labile organic complexes. In this technique, the added ligand competes for the metals bound to natural complexing agents. Also, the Anodic Stripping Voltammetry (ASV) is one of the most used techniques in the determination of trace metal speciation in natural waters.^{10,11}

In Brazil, many studies have been carried out to evaluate the contamination levels of fishes and other marine species commonly found and consumed in coastal regions where there is considerable industrial development and high population densities, such as Baía de Santos, Estuário de Santos and São Vicente, Baía de Guanabara, Baía de Todos os Santos and, recently, the metal levels of mussels and oysters along the coastal region of the Ilha de Santa Catarina was evaluated.^{1,4,12,13}

In the State of Santa Catarina, metal pollution is concentrated in a river named Rio Tubarão and a lagoon system called Sistema Lagunar (in the South), due to contamination of effluents by mining waste and the use of coal, as well as from waste from thermoelectric power stations, the extraction of fluorite, activities associated with ceramics and domestic sewage. The Rio Itajaí estuary and the bay known as Baía de São Francisco (in the North) are affected by port activities and by the industrial complex of Joinville, while in the bays around the Ilha de Santa Catarina known as Baía Norte and Baía Sul the pollution arises from the disordered growth of both tourism and the resident population and from industries located on the adjacent continent.¹⁴ As a consequence, on the Ilha de Santa Catarina, most waste, whether domestic or industrial, has been disposed of directly to the urban drainage system which, in turn, discharges to the bays which wash around the shores of the city itself.^{1,14,15}

The objective of this study is to determine the metal ion concentrations in seawater samples collected from different points around Baía Norte and Baía Sul of the Ilha de Santa Catarina, with a view to developing a systematic

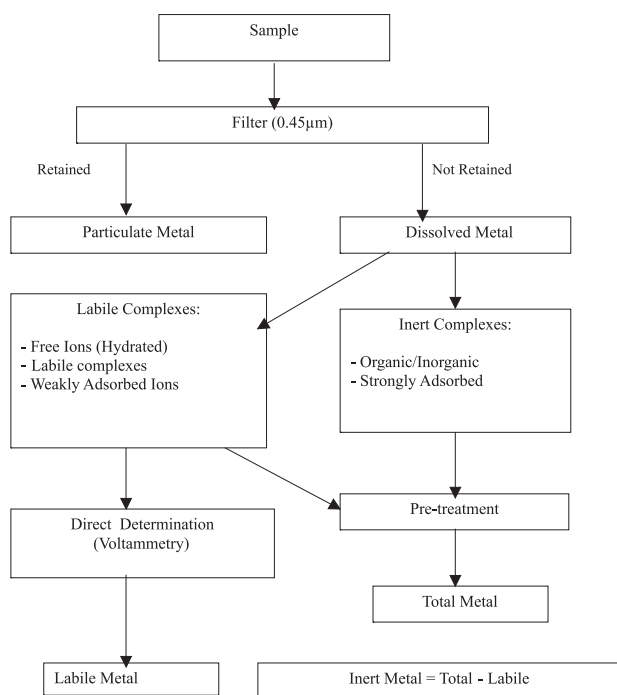


Figure 1. Scheme of trace metal speciation in the marine environment.

evaluation practice for their concentration levels using Differential Pulse Adsorptive Cathodic Stripping Voltammetry (DPACSV) and Differential Pulse Anodic Stripping Voltammetry (DPASV). Several tests were carried out using the above techniques in order to obtain a set of electrochemical parameters suitable for a quantification of the concentration of total metal ions for lead, copper and zinc.

Experimental

Apparatus

Voltammetric measurements were carried out with a PAR 263A potentiostat, equipped with a 15 mL glass cell and a working electrode, an Ag/AgCl reference electrode (KCl saturated) and a platinum counter electrode. The working electrodes used were: a hanging mercury drop electrode (HMDE), part of a mercury electrode system EG&G PARC model 303A and a mercury film electrode (MFE). The mercury film was deposited *ex situ*, on a vitreous carbon rotatory electrode (RDE), EG&G PARC model 616, approximate diameter 3 mm, for 20 minutes, from a solution of 10^{-3} mol L⁻¹ HgCl₂ and HNO₃, at pH 2.0.

Chemicals and procedures

The lead, copper and zinc standards of 10^{-4} , 10^{-5} , 10^{-6} mol L⁻¹ were prepared from stocks solutions of 1000 ppm (Spectrosol, Merck). To determine copper(II) a stock solution of the 8-hydroxyquinoline ligand (Analar R-BDH), 4.3×10^{-3} mol L⁻¹ was prepared. All the reagents used were of analytical grade.

The determination of salinity was carried out with a JENCO conductivimeter (model 1671), calibrated with a 7.4191 g/L solution of KCl. The scale of practical salinity was adopted, which expresses the relation between salinity and conductivity in parts per thousand (‰), considering the conductivity ratio and the temperature of the samples, in °C, in relation to the standard value for seawater ($S = 35$).^{16,17}

The pH measurements were taken with an ORION 720A pHmeter with a combination electrode.

Ultraviolet radiation was used in order to avoid interference due to the adsorption of organic matter (OM) on the surface of the working electrode. The samples were irradiated for 4h in a UV digester with a 125W high pressure Hg vapor lamp, with the external cover removed in order to achieve total exposure of the samples to the radiation.¹⁸ 30 mL samples were placed in quartz tubes equipped with glass caps.

For each metal, three determinations were carried out in order to calculate the standard deviation.

Purification of the reagents

Considering that metal ions are present in seawater in trace levels, purification of reagents to minimize contamination risks during the analytical procedures is essential. Purified solutions of 7.4 mol L⁻¹ HCl and 6.9 mol L⁻¹ NH₄OH,¹⁹ were obtained by means of isothermal distillation from analytical grade reagents (Quimex).

Accuracy of techniques

The accuracy of the techniques was checked using a Nearshore Seawater Reference Material for trace metals (CASS-4), acquired from the National Research Council of Canada, collected at a depth of 12 meters, with a salinity of 30.7, filtered using 0.45 μm membrane filters, and acidified to pH 1.6.

Sampling

The seawater samples for metal ion determination were collected in high density polyethylene sample bottles, which had been soaked in 1.0 mol L⁻¹ HNO₃ for two weeks and then rinsed and filled with deionised water and left again for two weeks. After sampling the seawater was filtered using cellulose filters (0.45 μm), acidified (HCl pH 2.0) and subsequently stored in a freezer.

During the sample collection carried out around the Ilha de Santa Catarina seawater samples were taken from fourteen points in Baía Sul (January 2002) and eight points in Baía Norte (April 2002), near the sewage outfalls and at locations considered critical in relation to pollution (see Figure 2). The samples were collected at a depth of approximately 30 cm.

Results and Discussion

Method optimization

The parameters optimized for lead and zinc were the pre-concentration potential and time (analyzing the level of the current in the relative potential of the metal under study), utilizing the Differential Pulse Anodic Stripping Voltammetry (DPASV) technique. To determine the Pb²⁺ and Zn²⁺, synthetic samples were prepared in a solution of HNO₃ at pH 2.0. Figure 3 illustrates the results for the Pb²⁺ determination (A and B) and Figure 4 the results for the Zn²⁺ determination (A and B), both carried out with a

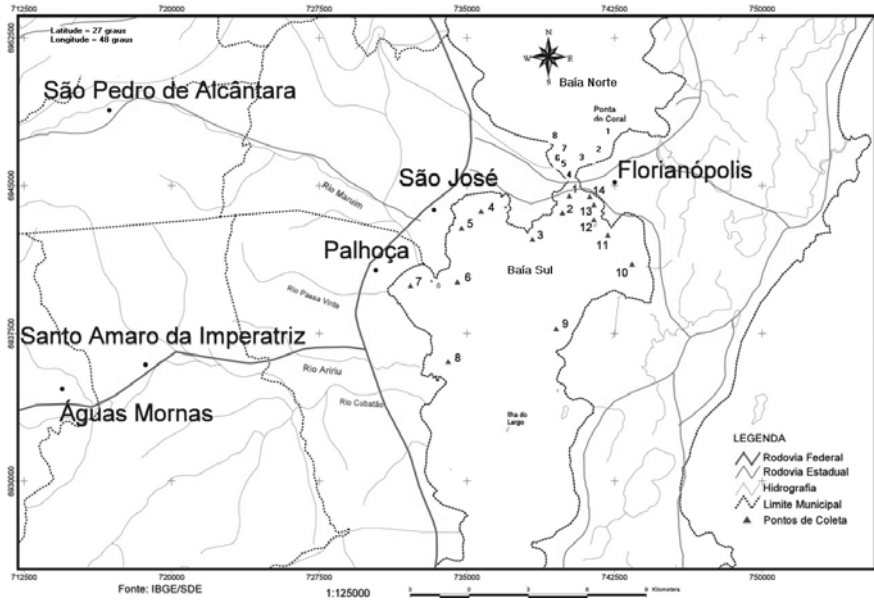


Figure 2. Location of sampling points in Baía Sul and Baía Norte, Ilha de Santa Catarina, Florianópolis-SC.

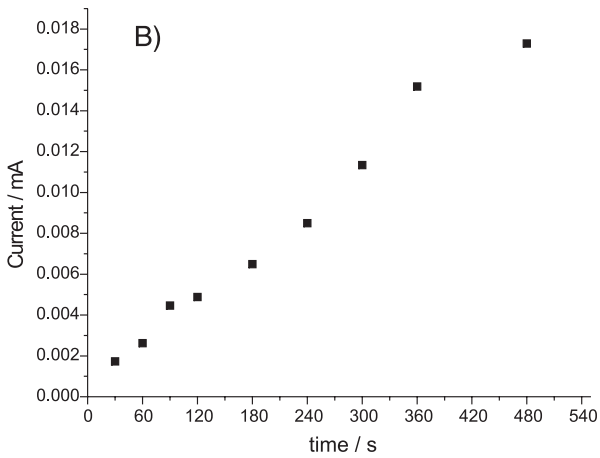
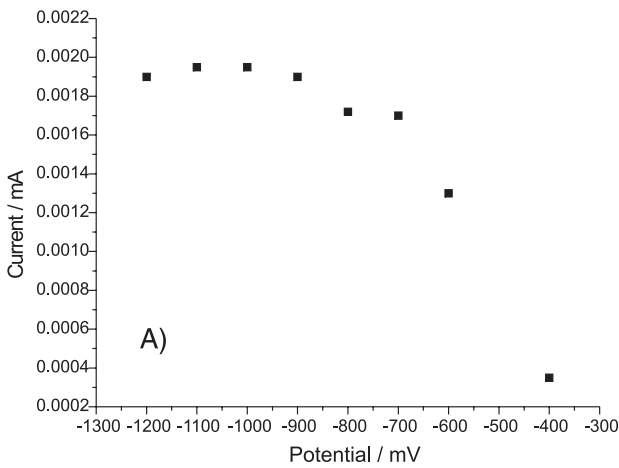


Figure 3. (A): Peak current as a function of pre-concentration potential; (B): Peak current as a function of pre-concentration time. Sample in HNO₃ at pH 2.0 enriched with 5 nmol L⁻¹ of Pb²⁺ and analyzed by DPASV.

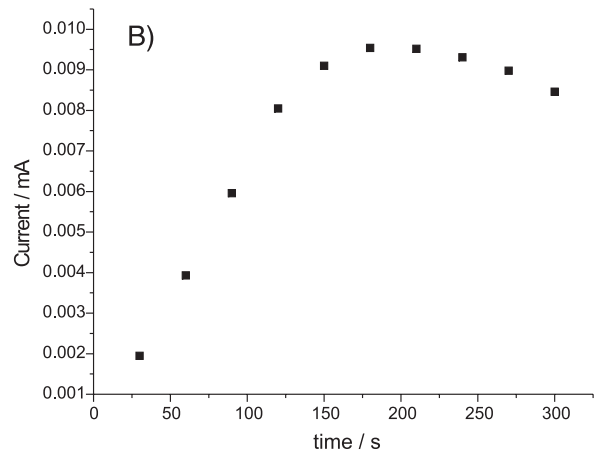
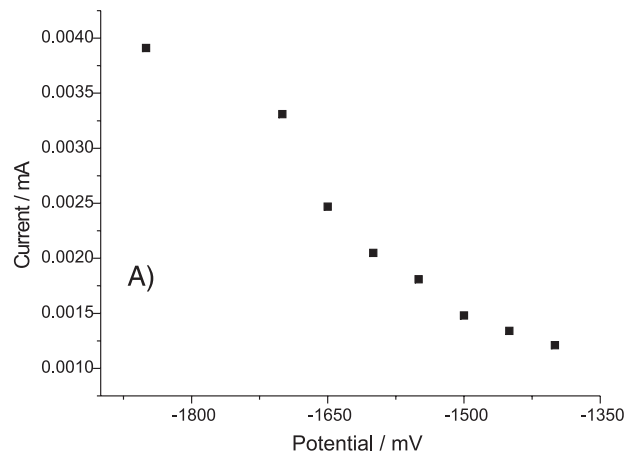


Figure 4. (A): Peak current as a function of pre-concentration potential; (B): Peak current as a function of pre-concentration time. Sample in HNO₃ at pH 2.0 enriched with 5 nmol L⁻¹ of Zn²⁺ and analyzed by DPASV.

mercury film electrode, at a scan speed of 50 mV s^{-1} , a differential pulse height of 50 mV and width of 0.050 s and an equilibrium time of 5 s .

From the profile obtained, shown in Figure 3A a potential region ranging between -1100 a -900 mV was found, which had almost constant, but significant, current peak values. The profile shown in Figure 3B shows a good correlation of points and the region between 30 and 120 s had the highest sensitivity. However, a value of -1100 mV was selected for the pre-concentration potential and a time of 120 s for subsequent determinations.

The profile shown in Figure 4A indicates a region with higher current values, between -1550 and -1750 mV and lower, almost constant, values in the range -1300 to -1500 mV . Thus, a potential of -1400 mV was adopted for the analysis, ensuring that the metal pre-concentration did not suffer interferences due to the reduction of the H^+ ion. The curve shown in Figure 4B shows a linear region with great stability which extends from 30 to approximately 120 s .

From then on there is a tendency toward stabilization. Considering the results obtained and the necessity to carry out analysis which favors a good peak resolution, without the risk of wearing out the mercury film, a time of 120 s was chosen for the Zn^{2+} determination for this methodology.

In the copper determination the Differential Pulse Adsorptive Cathodic Stripping Voltammetry (DPACSV) technique was used, with an evaluation of the time and potential of adsorption, pH and ligand concentration. Small amounts of 8-hydroxyquinoline and ammonia solution were added, so as to obtain a $20 \mu\text{mol L}^{-1}$ concentration of the ligand and pH 9.0 , respectively. The 8-hydroxyquinoline ligand ($\text{C}_9\text{H}_7\text{OH}$) has a conditional stability constant with copper (K_{CuL_2}) of $5.75 \times 10^{16} (\text{mol L}^{-1})^{-2}$.²⁰

The electrochemical parameters obtained in the optimization stage are shown in Table 1, along with the working electrodes used.

Determination of detection limits (DL) and accuracy of techniques

The detection limits for the Pb^{2+} and Zn^{2+} were obtained using ultra-pure water, adjusted to pH 2 with HNO_3 , by

DPASV. For the Cu^{2+} a detection limit was obtained using ultra-pure water in an ammoniacal medium at pH 9 , at 8-hydroxyquinoline ligand concentration of $20 \mu\text{mol L}^{-1}$, by DPACSV.

The limit of detection is considered a practical limit of measurement, generally defined as 3 times the standard deviation of the blank.²¹ In Figure 5 (A and B) the voltammograms and the analytical curve obtained for Pb^{2+}

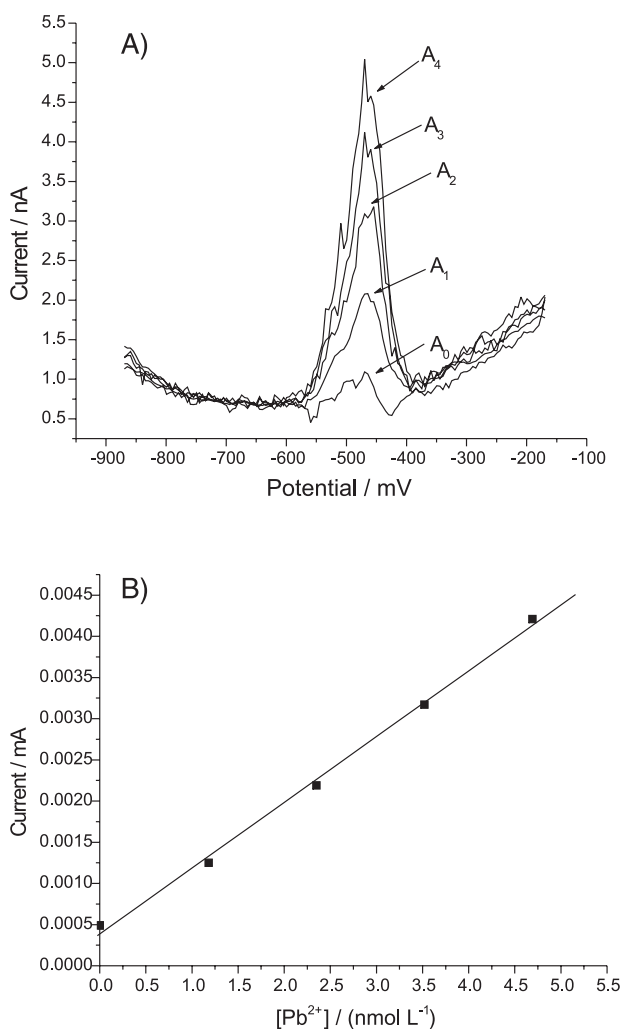


Figure 5. (A): Voltammograms resulting from successive additions of $10^{-6} \text{ mol L}^{-1}$ solutions of Pb^{2+} to the blank; A_0 = blank, $A_1 = 1.2$, $A_2 = 2.3$, $A_3 = 3.5$ and $A_4 = 4.7 \text{ nmol L}^{-1}$; (B): Profile of the calibration curve giving the straight line equation generated by linear regression $Y = 0.40 + 0.80 X$ and correlation coefficient $R = 0.9986$.

Table 1. Pre-concentration parameters: time, potential and potential range (E_{range}) for the trace metal determinations, lead and zinc by DPASV and copper by DPACSV

Metal	Electrode	time (s)	E(mV)	E_{range} (mV)
Lead	MFE ^a ; HMDE ^b	120; 180	-1100; -1100	-850 to -150; -1100 to -200
Zinc	MFE ^a ; HMDE ^b	120; 180	-1400; -1450	-1250 to -850; -1450 to -200
Copper	HMDE ^b	110	-500	-200 to -800

^aMercury film electrode (deposited *ex situ*); ^bHanging mercury drop electrode.

is shown. In Table 2, the limits of detection obtained in the analysis using the parameters mentioned above are presented, the values being in agreement with the range of concentration expected for metal analysis.

Table 2. Detection limits for Pb(II), Zn(II) and Cu(II) metal ions

Metal	Pb(II)	Zn(II)	Cu(II)
Detection limit	0.254±0.004 ^a 0.100±0.004 ^b	0.30±0.04 ^a 0.20±0.02 ^b	0.22±0.06 ^b

^a Mercury film electrode (deposited *ex situ*) (MFE); ^b Hanging mercury drop electrode (HMDE).

In order to ensure good accuracy of the analytical procedure the concentration of copper was measured using a certified sample CASS-4 (9.3 nmol L⁻¹), being obtained a close value of 10.3 nmol L⁻¹. For the coastal water sample previously analyzed and enriched, the following recovery percentages were obtained: 95±10 (Pb²⁺), 110±11 (Zn²⁺) and 95±8 (Cu²⁺).

Figure 6 shows the application of the enrichment and recovery procedure to the coastal water sample for Cu²⁺, previously analyzed according to the parameters described in Table 1.

The methods used show the viability of the voltammetric techniques in the evaluation of metal ions carried out, the relative errors found through the standard deviation being compatible with the concentration range in which the ions under analysis are present.

Results for the seawater sample analyses

In the seawater analyses the methods developed were used. The results for the samples collected from Baía Norte and Baía Sul of the Ilha de Santa Catarina, at distinct times, are given in Tables 3 and 4.

Table 3. Values for total metal concentration obtained for water samples from Baía Sul, collected in January 2002, determined by Anodic Stripping Voltammetry and Adsorptive Cathodic Voltammetry techniques, using an electrode with a mercury film deposited *ex situ* and a hanging mercury drop electrode

Sampling Point	pH	Practical Salinity	[Pb ²⁺] _T / nmol L ⁻¹	[Zn ²⁺] _T / nmol L ⁻¹	[Cu ²⁺] _T / nmol L ⁻¹
1 – Ponte P. Ivo Campos outfall	8.2	30	3.3±1.1	2.1±0.1	53±5
2 – Praia da Saudade	8.2	30	5.0±1.6	1.5±0.3	67.0±0.3
3 – Praia de Itaguaçu	8.2	29	4.0±0.9	2.3±0.5	58±2
4 – Praia da Praça	8.3	30	5.4±0.4	2.4±0.2	51±3
5 – Ponta de Baixo	8.3	29	6.5±0.7	1.9±0.3	65±7
6 – Rio Alto Aririú outfall	8.3	29	4.0±0.9	2.0±0.7	22±1
7 – Beach next to MaruimRiver outfall	8.3	29	2.8±0.8	1.0±0.2	18±4
8 – Rio Aririú outfall	8.3	30	4.2±1.0	1.1±0.4	57±5
9 – Aeroporto Hercílio LuzCanal	8.3	29	13.0±0.2	2.6±0.8	48±4
10 – Costeira do Pirajubáé	8.3	29	15.0±1.4	5.4±1.2	54±2
11 – Praia do Curtume	8.3	30	5.3±0.2	6.8±0.2	78±1
12 – Praia do José Mendes	8.4	29	5.7±0.1	2.0±0.3	11.0±0.3
13 – Clube Veleiros da Ilha(Sailing club)	8.3	26	3.8±0.1	1.6±0.1	7.8±0.4
14 – Sewage Treatment Works	8.3	30	4.2±0.6	4.9±0.4	59±6

The values for the physico-chemical parameters analyzed, pH and practical salinity, showed little

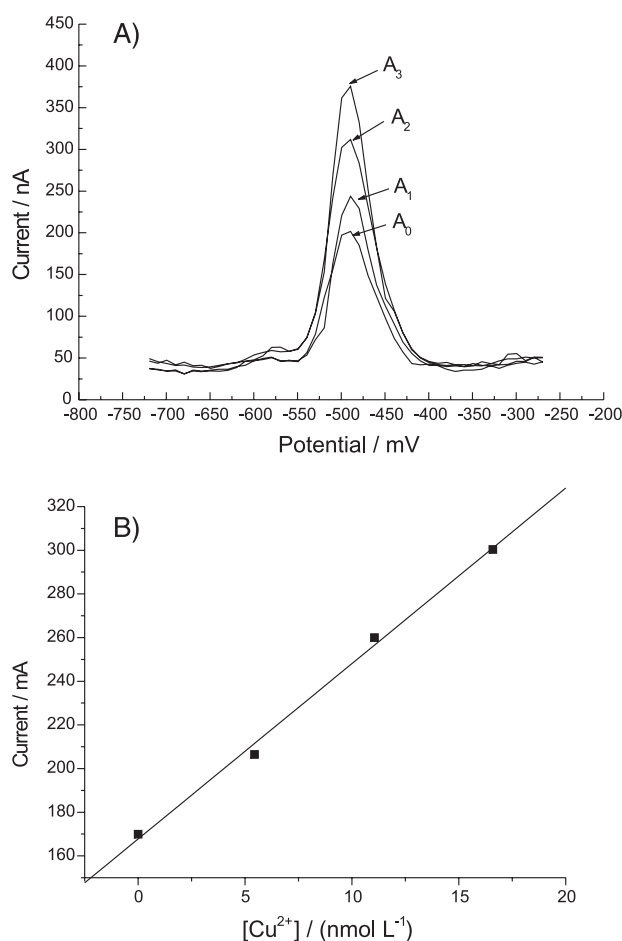


Figure 6. Enrichment and recovery of copper(II) in the natural sample. (A): Voltammograms relating to the addition of 10⁻⁶ mol L⁻¹ solutions of the Cu²⁺ standard. (A₀ = blank, A₁ = 5.5, A₂ = 11.0, A₃ = 16.3 nmol L⁻¹); (B): Straight line equation obtained by linear regression Y = 167.25 + 8.16X and correlation coefficient R = 0.9950.

Table 4. Values for total metal concentration obtained for water samples from Baía Norte, collected in April 2002, determined by Anodic Stripping Voltammetry and Adsorptive Cathodic techniques, using hanging mercury drop electrode

Sampling Point	pH	Practical Salinity	[Pb ²⁺] / nmol L ⁻¹	[Zn ²⁺] / nmol L ⁻¹	[Cu ²⁺] / nmol L ⁻¹
1 - Mangrove	8.2	29	2.1±0.2	5.0±0.8	24±3
2 - Sewage outfall I	8.3	29	1.8±0.1	3.2±0.2	23.5±0.2
3 - Fire Station	8.3	29	4.4±0.3	18±1	37±4
4 - Boat yard	8.3	30	3.8±0.6	1.8±0.2	54±5
5 - Sewage outfall II	8.2	30	2.0±0.2	5.4±0.7	46±1
6 - Sewage outfall III	8.2	26	2.4±0.3	4.2±0.2	42±4
7 - River I	8.1	29	0.33±0.05	4.8±0.2	53±4
8 - River II	7.8	25	8±1	12±2	213±22

difference in relation to expected values for coastal seawater samples, with salinity values being less than or equal to 30.²²

As shown in Tables 3 and 4, the results obtained were within the ranges of 0.33 to 15 nmol L⁻¹ for Pb²⁺, 1.0 to 18 nmol L⁻¹ for zinc and 7.8 to 213 nmol L⁻¹ for copper concentration.

It was found that the concentrations of total metal for the Pb²⁺ and Zn²⁺ ions were relatively low. For Cu²⁺, however, the values obtained were higher than those for the other metals, indicating the presence of possible pollution sources, with greater inputs of this metal to the coastal waters analyzed.²³

The total metal contents detected in the samples analyzed may be compared with those obtained in similar studies²⁴ where the concentrations of several metals were determined for some points along the coast of the Ilha de Santa Catarina, such as Praia da Joaquina, Ilha de Ratoes Grande and Ponta do Lessa, the latter being located near the Mangue do Itacorubi. The technique used was Inductively coupled Plasma - Mass Spectroscopy (ICP-MS). In relation to copper and lead, the concentrations determined were close to those found in this study. For lead, the highest value determined by ICP-MS was approximately 45 µg L⁻¹, or 216 nmol L⁻¹.

This study highlights that the concentrations obtained for the coastal water samples are below the limits established by CONAMA,²² for the management of Class 5 waters with salinities suitable for aquaculture: 48 (Pb²⁺), 2576 (Zn²⁺) and 769 (Cu²⁺) nmol L⁻¹.

Conclusions

The optimization of electrochemical parameters shown in Table 1 and the determination of the accuracy of the methods indicated a good method accuracy. Utilizing certified coastal water CASS-4 (Cu²⁺ 9.3 nmol L⁻¹), a value of 10.3 nmol L⁻¹ was obtained, which is close to the certified value. The enrichment procedure applied to a

previously analyzed natural sample gave percent recoveries of 95±10 (Pb²⁺), 110±11 (Zn²⁺) and 95±8 (Cu²⁺).

The analysis of the blank showed that the sample collection, filtration, preservation and irradiation procedures maintained a low level of contamination. It is worth noting that these procedures are indispensable for the obtention of more precise and reliable results in environmental contamination studies.

From Tables 3 and 4 it can be seen that the values for concentrations of Cu²⁺ were higher than those for lead and zinc, probably due to anthropogenic pollution, related to anti-fouling paints used to protect boats and also to industrial process close to the collection points.

Although the values obtained here are considered low according to the CONAMA indices, in particular for lead and zinc, the monitoring of the degree of pollution at these locations allows an estimation of the level of contamination occurring in this environment and aids in the quality control of mariculture products farmed in these waters.

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