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Article

Voltammetric Determination of Zn^{2+} in Antiseptic Dusting Powder and Multivitamins Using a Carbon Paste Electrode Modified with Bi Anchored on Amberlite® IR120

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This work presents a voltammetric method for Zn^{2+} determination in antiseptic dusting powder and multivitamin commercial samples, combining an alkaline extraction using NaOH aqueous solution with a carbon paste electrode chemically modified with Bi anchored on Amberlite® IR120 ion exchange resin (CPEAmb/Bi). The best conditions for electrode preparation were: 10% (m/m) of Amberlite® IR 120; 30 s Bi^{3+} accumulation time (open circuit) in 0.5 mmol L^{-1} Bi^{3+} solution prepared in 0.1 mol L^{-1} acetate buffer (pH = 5.5). The analytical curve for Zn^{2+} using the CPEAmb/Bi presented linear range from 0.05 to 8.2 µmol L^{-1} and the limit of detection was 10 nmol L^{-1}. The voltammetric method was simple, fast, efficient and low-cost for the Zn^{2+} determination in antiseptic dusting powder and multivitamin samples.

Keywords: anodic stripping voltammetry, chemically modified electrode, electrodeposition, Zn^{2+}

Introduction

Zinc is an essential metal for various physiological, biochemical,[1] catalytic, structural and regulatory functions.[2] The human diet based on foods containing low amounts of Zn^{2+} may result in the onset of various syndromes.[3] Ingestion of food containing phytic acid can also lead to metal deficiency, due to the precipitation of Zn^{2+} in the presence of this acid.[4] Zn^{2+} is widely added in food, medicament and food supplements. Therefore, it is necessary to enforce quality control of products containing this metal, developing analytical methods to perform the quality control.

Zn^{2+} quantification has been performed using energy dispersive X-ray fluorescence,[5] spectrophotometry,[6] flame atomic absorption spectrometry (FAAS),[7] inductively coupled plasma atomic emission spectrometry (ICP-AES)[8] and inductively coupled plasma mass spectrometry (ICP-MS).[9] In spite of the low detection limits achieved with these techniques, they have some limitations to be applied in routine analysis, such as: high instrumental cost, low analytical frequency and the production of a large amount of residues.[10-12]

Anodic stripping voltammetry (ASV) is an alternative and promising analytical technique for metal determination. Attractive features of ASV include low reagent and sample consumption, increased sensitivity, low detection limits and low cost.[13] The use of carbon paste electrodes[14] (CPEs) as working electrodes in ASV is a particularly interesting approach for metal ions determination,[15] since these electrodes can be prepared in a very simple and inexpensive way, and they are easily chemically modified.[15-17] Literature has demonstrated that CPEs modified with mercury,[18] tin[19] and bismuth[20] can be successfully used for metal ions determination. Among these modifiers, Bi is specially advantageous due to its low toxicity, insensitivity to dissolved oxygen and high ability to form alloys with various metal species.[21]

Several procedures can be used to prepare Bi-modified CPEs being the most common methods the *in situ*[22] or *ex situ*[23] Bi film electrodeposition or the introduction of

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bismuth compounds, such as Bi_2O_3[24] in the CPE. The modification of CPEs with Bi nanostructures (NBi) is very attractive because it allows to explore the properties of the nanomaterials such as the high conductivity, high surface area, mechanical stability, mass transport efficiency and high electronic transfer capacity.[20,25,26]

Two interesting methods for the preparation of NBi were described in the literature: in the first one, NBi were synthesized from metallic Bi;[27] in the second method, NBi were prepared by reducing Bi^{3+} with $NaBH_4$.[28] In spite of the good performance of NBi obtained by these procedures, these methods are time-consuming, requiring complex instrumentation, and produce a large amount of chemical residues. An alternative procedure to prepare NBi is the use of functionalized materials able to efficiently accumulate Bi^{3+} on the electrode surface. The subsequent electrochemical reduction of the accumulated Bi^{3+} leads to NBi formation.[20] This NBi preparation method is very attractive, since NBi are synthesized directly onto electrode surface in a very fast, simple and inexpensive way.

Among the functionalized materials able to accumulate metal ions at electrode surface, ion exchange resins are very promising.[29] Usually, these resins consist of styrene-divinylbenzene copolymers and they can be classified as basic or acidic exchange resins, according to the active group. The basic resins (or anionic) have quaternary ammonium salts ($–CH_2–NR_3^+$) as active group, while strongly acid resins (or cationic) are functionalized with sulfonic groups ($–SO_3^-$).[30] There are several commercial ion exchange resins available on the market with high chemical stability and high exchange capacity over a wide pH range. Among the acid resins, the Amberlite® IR120 cation exchange resin was successfully used as a CPE modifier for the preconcentration and determination of Pb^{2+} in ethanol fuel samples.[31] Oliveira *et al.*[32] have demonstrated that Amberlite® IR120 combined with carbon nanotubes was a very efficient chemical modifier for a CPE used for the simultaneous determination of Pb^{2+} and Cd^{2+} in ethanol fuel, gasoline for aviation and spiked water samples. Moreover, the literature[33] has reported that Amberlite® IR120 presents both high metal accumulation capacity and high kinetic of adsorption for Cu^{2+}, Zn^{2+} and Cd^{2+}. Therefore, the Amberlite® IR120 has a great potential as a chemical modifier able to promote the formation of NBi on the CPE surface after an electrochemical reduction step.

In this context, this work describes, for the first time, the use of a CPE chemically modified with Bi anchored on the Amberlite® IR120 cationic resin for Zn^{2+} quantification in antiseptic dusting powder and multivitamins samples using square wave anodic stripping voltammetry (SW-ASV).

Experimental

Reagents and solutions

All reagents used in this work were analytical grade and all solutions were prepared with ultrapure water (ASTM type I), with resistivity ≥ 18 MΩ cm, produced by using a Megapurity® ultrapurification system (Billerica, USA). KNO_3 and glacial acetic acid, both from Vetec (Rio de Janeiro, Brazil) and sodium acetate from Merck (Darmstadt, Germany) were used to prepare the supporting electrolyte solutions. The extractive solution used was prepared with NaOH, obtained from Vetec (Rio de Janeiro, Brazil). Phosphate buffer solutions were prepared with KH_2PO_4 and K_2HPO_4, both from Vetec (Rio de Janeiro, Brazil). To adjust the pH of the solutions a 6 mol L^{-1} NaOH aqueous solution was used.

Zn^{2+} stock solutions were prepared daily from dilution of a 1000 mg L^{-1} Zn^{2+} atomic absorption standard solution (Fluka, St. Louis, MO, USA) in the supporting electrolyte. A stock solution of 0.01 mol L^{-1} Bi^{3+} was prepared by dissolving $Bi(NO_3)_3.5H_2O$ (Vetec, Rio de Janeiro, Brazil) in a 10% (v/v) HNO_3 (Vetec, Rio de Janeiro, Brazil) aqueous solution. This stock solution was properly diluted in acetate buffer (pH = 5.5) to produce Bi^{3+} solutions at the desired concentration.

Glassy carbon powder with 2-12 µm spherical particles was obtained from Sigma-Aldrich (St. Louis, MO, USA). A solid paraffin from Synth (São Paulo, Brazil) was used as the binder agent for the preparation of CPE. Amberlite® IR120 strongly acidic ion exchange resin was obtained from Fluka (St. Louis, MO, USA).

Apparatus

All the electrochemical experiments were performed using a potentiostat/galvanostat µAutolab (Eco Chemie, Utrecht, Netherlands), model µAutolab type III interfaced with a microcomputer and controlled by GPES software version 4.9. A conventional single compartment electrochemical cell filled with 10 mL of supporting electrolyte solution was used in all electrochemical measurements. The reference and auxiliary electrodes were: Ag/AgCl immersed in KCl saturated solution ($Ag/AgCl_{sat}$) and spiral platinum wire, respectively. The working electrodes used were CPEs chemically modified with Bi anchored on Amberlite® IR120 (CPEAmb/Bi). All the electrochemical experiments were performed at room temperature. FAAS experiments performed for comparative purposes were conducted with a Shimadzu-FAAS spectrophotometer model AA-680 (Kyoto, Japan).

Atomization was achieved with an acetylene-air flame and a Zn hollow cathode lamp was used as radiation source. The measurements were performed at 213.9 nm and calibration was performed by standard addition method.

The pH of the solutions was measured with a pH meter (Hanna Instruments, Woonsocket, USA) model HI 3221 with a combined glass electrode. Scanning electron microscopy (SEM) images of the surface of the electrodes were obtained using a scanning electron microscope model VEGA3-Tescan (Brnokohoutovice, Czech Republic) operated at 20 kV. All the samples were sputter-coated with gold prior to the SEM analysis.

Electrode preparation

The unmodified CPEs, used for comparison purposes, were prepared with 70% glassy carbon powder and 30% solid paraffin. The paraffin was initially heated in a heated bath (65-70 °C) and after melting, it was mixed to the carbon powder for about 10 min, time required to provide a uniform consistency to the paste. Subsequently, the carbon paste was introduced and compacted into a cylindrical poly(tetrafluoroethylene) (PTFE) holder, containing a copper plunger as an electrical contact.

Amberlite® IR120 (Amb) was used as the CPEs modifier. The modified electrodes were prepared with a 65% by weight ratio of glassy carbon powder, 25% paraffin and 10% Amb (CPEAmb). In this procedure, the modifier was added to the glassy carbon powder and both were mixed with mortar and pestle for approximately 20 min. Thereafter, the modified glassy carbon powder was employed to prepare the CPEs in a method analogous to the unmodified CPEs using the paraffin as a binder. All the CPEs were polished on sulfite paper duly affixed to a glass plate until the electrode had a smooth, uniform and bright surface. Posteriorly, the CPEs were transferred to the electrochemical cell containing the supporting electrolyte for the recording of 25 successive cycles with potential scan from –1.3 to +0.5 V *vs.* $Ag/AgCl_{sat}$ at 100 mV s^{-1} by cyclic voltammetry technique. This procedure was performed prior to each set of experiments.

Modified carbon paste electrode with Bi anchored on Amberlite® IR120

The modification procedure of the CPEAmb with Bi basically consists of three steps: (*i*) Bi^{3+} immobilization: immersion of the CPEAmb in a solution of Bi^{3+} prepared in the supporting electrolyte maintained under agitation (open circuit) for a predefined time; (*ii*) washing: immersion of CPEAmb/Bi^{3+} in a 10 mL beaker containing ultrapure water; (*iii*) reduction: transfer of CPEAmb/Bi^{3+} to the voltammetric cell to the electrochemical reduction of Bi^{3+} ions to Bi^0 at controlled potential conditions.

Figure 1 presents a schematic representation of the steps involved on the Bi immobilization at CPEAmb.

The procedure to modify the CPEAmb with Bi was performed before each voltammetric study. In this procedure, it is possible to immobilize the Bi^{3+} ions on the surface of the CPEAmb by means of the electrostatic attractions between the metallic cation and the sulfonic groups of the Amberlite® resin. Subsequently, the immobilized Bi^{3+} is reduced to metallic bismuth at controlled potential conditions. Therefore, after this procedure, Bi particles are immobilized at CPEAmb surface by electrodeposition. To avoid Bi^{3+} lixiviation by ion exchange with the cation of the supporting electrolyte, the Bi^{3+} reduction step was always performed immediately after the immersion of CPEAmb/Bi^{3+} in the supporting electrolyte solution.

Initially, the choice of the best concentration of the Bi^{3+} solution for the immobilization of Bi^{3+} ion under open circuit conditions in the CPEAmb was performed. In this study, the concentration of Bi^{3+} was varied from 0.1 to 1.0 mmol L^{-1}. Posteriorly, different Bi^{3+} contact times (open circuit) were studied. The evaluated times were 0.5; 1.0; 3.0 and 5.0 min. The choice of the best pH for the formation of Bi on CPEAmb was performed. In this study, the pH of the Bi^{3+} solution was varied from 4.5 to 6.2. Then,

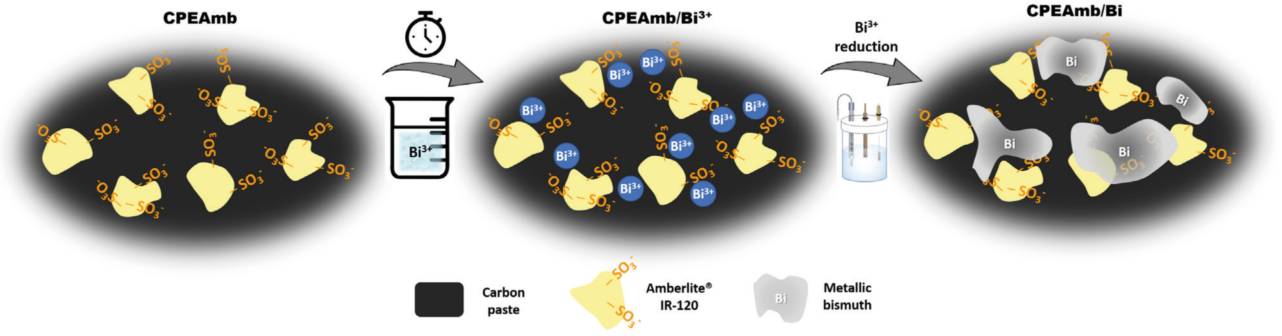

Figure 1. Schematic representation of the steps involved on the preparation of CPEAmb/Bi.

the parameters of the SW-ASV for Zn^{2+} detection were optimized. The optimized parameters were: deposition potential (E_{dep}), deposition time (t_{dep}), frequency (f), pulse amplitude (ΔE) and step potential (ΔE_s). Analytical curves were constructed using the optimized conditions, varying the concentration of Zn^{2+} in the electrochemical cell from 0.05 to 8.2 μmol L^{-1}.

Analytical procedure

All analytical studies were accomplished by SW-ASV using an aqueous solution of 0.1 mol L^{-1} acetate buffer (pH = 5.5). The analytical procedure involves three steps (without electrode preparation): (*i*) Zn^{2+} electrodeposition under controlled potential conditions; (*ii*) SW-ASV registration; (*iii*) electrochemical surface cleaning by application of –0.25 V (*vs*. Ag/AgCl) for 60 s in 0.1 mol L^{-1} acetate buffer (pH = 5.5).

The applicablity of the CPEAmb/Bi was evaluated by determining Zn^{2+} in antiseptic dusting powder and multivitamins real samples. All the analyzed samples were partially soluble in water and the alkaline extraction procedure described by Fonseca *et al.*[34] was used for sample pretreatment.

Results and Discussion

CPEAmb/Bi preparation

In this work, it was used CPEs chemically modified with 10% (m/m) of the cation exchange resin Amberlite® IR120. It was observed that lower resin percentages led to low intensity voltammetric peaks for Zn^{2+}. On the other hand, CPEs containing more than 10% of Amberlite® IR120 suffered strong swelling effect when in contact with aqueous solutions, which caused electrode desagregation. Therefore, CPEs containing 10% of Amberlite® IR120 have presented the best breakdown between Zn^{2+} peak intensity and mechanical resistance and, therefore, this electrode composition was adopted in all subsequent experiments.

The first step in this study was to evaluate the effect of the Bi^{3+} concentration on the amount of bismuth immobilized onto CPEAmb surface and on the Zn^{2+} voltammetric response. This study was performed in a mixture of acetate buffer solution (pH = 4.5) and KNO_3 solution, both 0.1 mol L^{-1} containing 2 μmol L^{-1} Zn^{2+}. The contact time (open circuit) of CPEAmb with Bi^{3+} solution was kept constant at 5 min and Bi^{3+} concentrations studied were 0.1, 0.5 and 1.0 mmol L^{-1}. The SW voltammograms obtained in this study are presented in Figure 2.

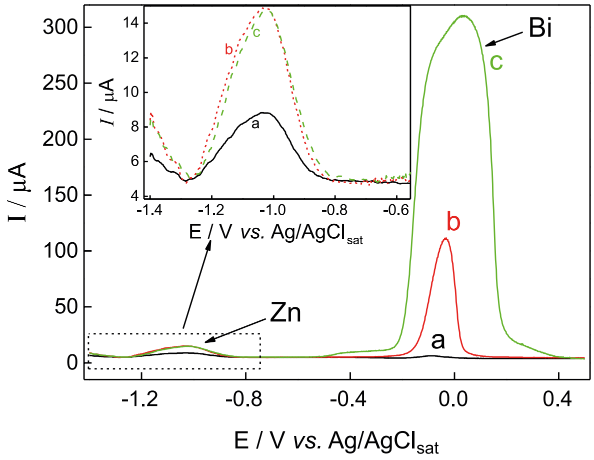

Figure 2. SW-ASVs recorded in 0.1 mol L^{-1} acetate buffer (pH = 4.5) + 0.1 mol L^{-1} KNO_3 in presence of 2 μmol L^{-1} Zn^{2+} using CPEAmb with 5 min (open circuit) in Bi^{3+} solutions: (a) 0.1; (b) 0.5 and (c) 1.0 mmol L^{-1}. E_{dep} = –1.4 V; t_{dep} = 180 s; f = 100 Hz; ΔE = 25 mV; ΔE_s = 2 mV.

Figure 2 shows that by increasing the Bi^{3+} concentration, an increase on the anodic stripping peak of Bi^{3+} is observed, indicating that a larger amount of bismuth was immobilized on the surface of the CPEAmb. This result confirms that spontaneous immobilization of Bi^{3+} at CPEAmb due to electrostatic interactions is effectively occurring. Moreover, Figure 2 shows that the intensity of the Zn^{2+} anodic stripping peak increases with Bi^{3+} concentration up to 0.5 mmol L^{-1}. Higher Bi^{3+} concentrations did not improve the voltammetric response for Zn^{2+}. Therefore, 0.5 mmol L^{-1} Bi^{3+} was used in all the subsequent experiments.

The effect of the contact time between CPEAmb and Bi^{3+} solution was evaluated, and the results are presented in Figure S1 (presented in Supplementary Information (SI) section). It can be observed that the amount of Bi^{3+} immobilized at CPEAmb increases by increasing the contact time. It was also observed that the contact time of the CPEAmb with the solution of 0.5 mmol L^{-1} Bi^{3+} has a strong influence on the voltammetric response for Zn^{2+} (Figures 3a and 3b).

Figure 3a shows that contact times longer than 1.0 min cause a decrease in the voltammetric response of Zn^{2+}. A similar behavior was described by Agustini *et al.*[20] for a CPE chemically modified with biochar and Bi^{3+} immobilized at open circuit conditions. These authors have observed that long contact times between the CPE and Bi^{3+} solution lead to less intense anodic stripping peaks for Pb^{2+}. According to them, contact times higher than 30 s could promote an increase in the size of the bismuth clusters.[20] Probably, the same effect occurs at the CPEAmb/Bi, explaining the behavior observed at Figure 3a. The highest response for Zn^{2+} was obtained for the CPEAmb/Bi prepared with the contact time of 1.0 min, however, this electrode presented

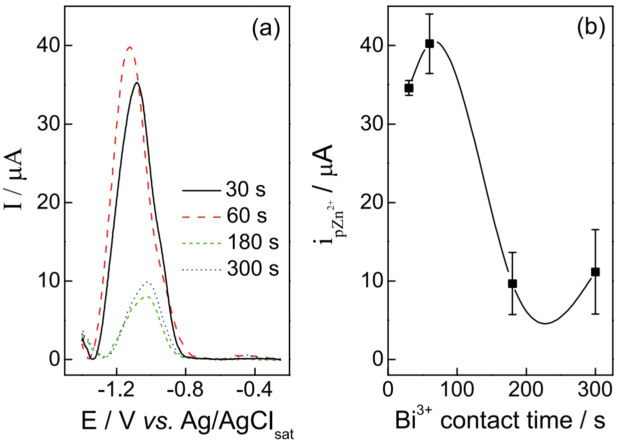

Figure 3. (a) SW-ASVs recorded in 0.1 mol L^{-1} acetate buffer (pH = 4.5) + 0.1 mol L^{-1} KNO_3 in the presence of 2.0 µmol L^{-1} of Zn^{2+} employing CPEAmb/Bi prepared with different contact times. E_{dep} = –1.40 V; t_{dep} = 180 s; f = 100 Hz; ΔE = 25 mV; ΔE_s = 2 mV; (b) Zn^{2+} peak current as a function of the contact time.

a poor repeatability (Figure 3b). The best combination between peak intensity and repeatability was achieved with CPEAmb/Bi prepared with 30 s of contact time in 0.5 mmol L^{-1} Bi^{3+}. Therefore, this contact time was chosen for the modification of the CPEAmb in further studies.

Subsequently, the influence of the pH of the Bi^{3+} solution on the amount of bismuth immobilized on the CPE was studied. The values of pH studied were 4.4; 5.5 and 6.2, this last value was obtained with phosphate buffer solution (0.1 mol L^{-1}) and the other two values were obtained with acetate buffer solution (0.1 mol L^{-1}). Figure S2 (SI section) shows a decrease in the anodic stripping peak of Bi^{3+} with the increase of the pH of the Bi^{3+} solution. This effect can be explained by the hydrolysis of Bi^{3+} to form a $Bi(OH)_3$ precipitate, which is favored by increasing the pH (reaction 1).[35]

$$Bi^{3+} + 3H_2O \rightleftarrows Bi(OH)_3 + 3H^+ \qquad (1)$$

The precipitation of Bi^{3+} in the form of $Bi(OH)_3$ impairs the immobilization of the Bi^{3+} on the surface of the CPEAmb, compromising the ion exchange process between Bi^{3+} ions and H^+ in the strongly acidic matrix Amberlite®. This fact results in a lower amount of Bi^{3+} immobilized at the electrode and less intense voltammetric peaks for bismuth at higher pH values. Subsequently, SW-ASVs were recorded for the electrodes modified with Bi^{3+} at pH = 4.4 and 5.5 in the presence of 1.0 µmol L^{-1} of Zn^{2+} in the electrochemical cell (Figure S3, SI section). Figure S3 shows that a more intense anodic stripping peak for Zn^{2+} is obtained at pH = 5.5. At pH = 4.4 it was observed not only a less intense anodic stripping peak for Zn^{2+}, but also a non-identified anodic peak at –0.5 V. In addition, at pH = 4.4, it was noted the hydrogen evolution reaction concomitating with Zn^{2+} electrodeposition. The non-identified voltammetric peak at –0.5 V could be attributed to impurities present in the electrode modifier that are released to the supporting electrolyte solution due the generation of $H_{2(g)}$ on the surface of the CPEAmb/Bi. In addition, the hydrogen evolution reaction could also damage the electrode surface. At pH = 5.5, the H_2 formation was not observed, which improves the efficiency of Zn electrodeposition leading to the better voltammetric response for Zn^{2+}. Therefore, in view of the presented results, the best pH for the immobilization of Bi^{3+} and anodic stripping of Zn^{2+} was 5.5. This pH value was chosen for the accomplishment of the later studies for the anodic stripping of Zn^{2+}.

Afterwards, Zn^{2+} anodic stripping was evaluated using three electrodes: CPE (unmodified), CPEAmb (modified with 10% Amberlite®) and CPEAmb/Bi (modified with 10% Amberlite® and Bi). Figure 4 shows the SW-ASVs obtained in acetate buffer solution 0.1 mol L^{-1} (pH = 5.5) in the presence of 1.0 µmol L^{-1} of Zn^{2+} employing each prepared CPE.

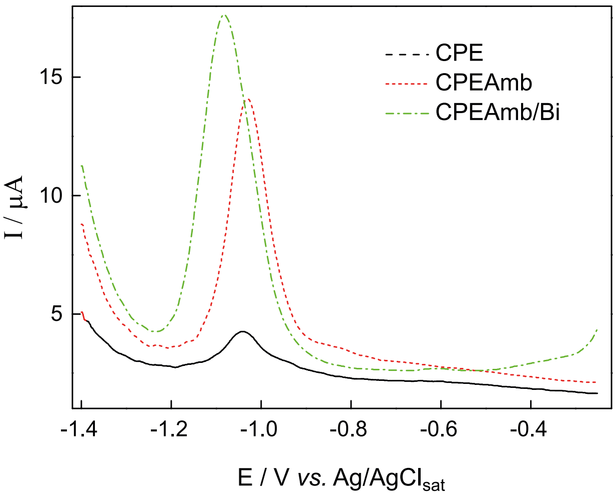

Figure 4. SW-ASVs recorded in 0.1 mol L^{-1} acetate buffer (pH = 5.5) in the presence of 1.0 µmol L^{-1} of Zn^{2+} using different electrodes. E_{dep} = –1.40 V; t_{dep} = 180 s; f = 100 Hz; ΔE = 25 mV; ΔE_s = 2 mV.

Figure 4 shows that the introduction of Amberlite® IR120 on the CPE improves the voltammetric response for Zn^{2+}. However, the best voltammetric signal for Zn^{2+} is obtained when the CPE is chemically modified with both Amberlite® IR120 and metallic Bi particles reduced onto Amberlite® IR120 active sites. The electrochemical properties of bismuth significantly improve the performance of the electrodes for the anodic stripping of various metals,[21,36-38] which could explain the better performance of CPEAmb/Bi for Zn^{2+} detection compared with CPE and

CPEAmb. Moreover, some authors[20] have demonstrated that the accumulation (at open circuit conditions) of Bi^{3+} on functionalized materials produces Bi nanostructures leading to CPEs with superior voltammetric performance. Therefore, these Bi nanostructures could be also formed at CPEAmb/Bi, which would be an additional factor that could be responsible for the better voltammetric performance of CPEAmb/Bi for Zn^{2+} detection. Aiming to evaluate this hypothesis, the SEM technique was employed. The characterization of CPEAmb/Bi was performed after exposure of the CPEAmb for 30 s to a solution of 0.5 mmol L^{-1} Bi^{3+} under open circuit conditions followed by a step of electrochemical reduction of Bi^{3+} to Bi^0 by applying –1.40 V for 180 s. As shown in Figures S4b and S4b$_1$ (SI section), spheres of Amberlite® can be observed at CPEAmb/Bi and they are absent in non-modified CPEs (Figures S4a and S4a$_1$, SI section), which have a smooth and relatively uniform appearance. However, it was impossible to visualize Bi nanostructures, even using a 30,000 times magnification or backscattering mode (Figure S4c). Energy dispersive X-ray (EDX) analysis has not detected Bi as well. However, the Bi anodic stripping peak observed for CPEAmb/Bi confirms that this electrode contains Bi. Probably, the size and/or the number of Bi nanostructures formed are too small to be detected with SEM and EDX. Despite of that, the introduction of Bi clearly improves the voltammetric response for Zn^{2+} (Figure 4), suggesting that Bi nanostructures are formed on CPEAmb/Bi. Moreover, literature[20] has shown that Bi nanostructures are formed on functionalized CPE prepared in similar conditions to the one described in the present work. Therefore, the Zn^{2+} signal enhancement observed for the CPEAmb/Bi is probably ascribed to the formation of Bi nanostructures at CPEAmb/Bi surface. In addition, residual active sulfonic groups from Amberlite® could also contribute for the Zn^{2+} signal enhancement observed at Figure 4.

Electrode repeatability and analytical studies

The SW-ASV parameters were optimized using the CPEAmb/Bi. The optimized parameters were, E_{dep} = –1.35 V, t_{dep} = 240 s, f = 100 Hz, ΔE = 25 mV and, ΔE_s = 3 mV. Subsequently, all the optimized voltammetric conditions were maintained for the repeatability study. In this study, five SW-ASVs were recorded for 2.0 µmol L^{-1} Zn^{2+} in 0.1 mol L^{-1} acetate buffer solution (pH = 5.5) using the same surface of a CPEAmb/Bi prepared under optimized conditions (Figure S5, SI section). The relative standard deviation (RSD) value obtained in this study was 2.9% for the same electrode surface using CPEAmb/Bi. These results demonstrate that satisfactory repeatability is obtained when employing the same electrode surface using CPEAmb/Bi.

Posteriorly, the same procedure was repeated using five different electrode surfaces and the results are presented in Figure S6 (SI section). The value of RSD obtained in this study was 9.97%. Interday precision was evaluated by using five different electrode surfaces in five different workdays (Figure S7, SI section). At this condition, an RSD of 9.55% was obtained. This RSD value is very close to the obtained for different electrode surfaces, indicating that the electrode surface renewing is the main factor affecting the precision. These results indicate that the CPEAmb/Bi provides satisfactory precision for the quantification of Zn^{2+} by SW-ASV even using different electrode surfaces at different workdays.

The optimized voltammetric conditions of SW-ASV were employed to construct an analytical curve for Zn^{2+} by varying the concentration of this metal from 0.05 to 8.20 µmol L^{-1} in a solution of 0.1 mol L^{-1} acetate buffer (pH = 5.5) employing the CPEAmb/Bi. The analytical curves were constructed using the area under the Zn^{2+} voltammetric peak (A_{Zn}) as the analytical signal. Figure 5 presents the results obtained in this study.

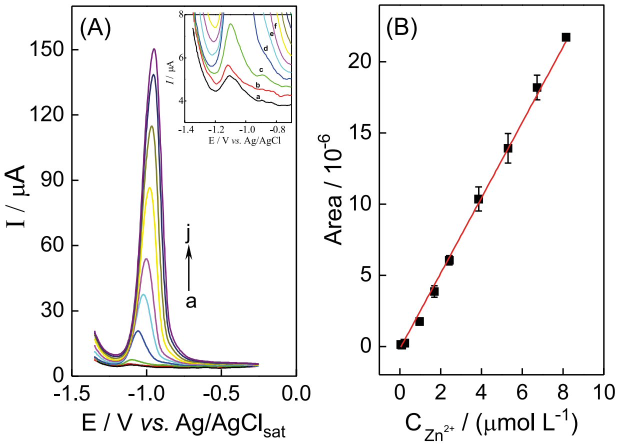

Figure 5. (A) SW-ASVs recorded in 0.1 mol L^{-1} acetate buffer (pH = 5.5) employing the CPEAmb/Bi at different concentrations of Zn^{2+}: (a) 0.05; (b) 0.10; (c) 0.24; (d) 1.00; (e) 1.70; (f) 2.40; (g) 3.90, (h) 5.30, (i) 6.70 and (j) 8.20 µmol L^{-1}. t_{dep} = 240 s; E_{dep} = –1.35 V; f = 100 Hz; ΔE = 25 mV; ΔE_s = 3 mV; (B) analytical curve obtained for Zn^{2+}.

The linear equation obtained for the analytical curve presented in Figure 5B was A_{Zn} = –0.17 + 2.65 $C_{Zn^{2+}}$ (µmol L^{-1}) with linear correlation coefficient (R) equal to 0.991. The limits of detection (LOD) and quantification (LOQ) calculated from the analytical curve obtained in the Figure 5B were, respectively, 10 (0.65 ppb) and 32 nmol L^{-1} (2.09 ppb). LOD and LOQ were calculated from the equations: LOD = 3 sd/b and LOQ = 10 sd/b, where b is the slope of the analytical curve and sd is the standard deviation

Table 1. Methods described in the literature for the determination of Zn^{2+} by ASV

Electrode type	t_{dep} / s	Electrochemical technique	LOD / ppb	Reference
Bimetallic Hg–Bi/SWCNCE	300	SW-ASV	2.00	11
HMDE	300	DP-ASV	1.37	13
CPE-biocharNanoHg	60	DP-ASV	11.18	18
NBi-SPE	120	SW-ASV	4.90	27
In situ plated BiFE onto GCE	180	SW-ASV	2.70	34
Iron oxide/graphene composite	300	DP-ASV	0.11	39
CPEAmb/Bi	240	SW-ASV	0.65	this work

SWCNCE: single-walled carbon nanotubes composite electrode; HMDE: hanging mercury drop electrode; CPE: carbon paste electrode; NBi-SPE: screen-printed electrodes with Bi nanoparticles; BiFE: bismuth film electrodes; GCE: glassy carbon electrode; SW-ASV: square wave anodic stripping voltammetry; DP-ASV: differential pulse anodic stripping voltammetry.

for the signal of blank, which was estimated from the error of the intercept of the analytical curve.[34] The value of LOQ found is close to the first point of the analytical curve, 50 nmol L^{-1}, which can be used as a more realistic LOQ value. The analytical parameters obtained with CPEAmb/Bi are very promising and a comparison between LOD for Zn^{2+} obtained with CPEAmb/Bi and other electrodes previously described in literature is presented in Table 1.

The methods described in Table 1 present t_{dep} and LOD close to those found by the proposed method using CPEAmb/Bi, which shows that the results obtained agree with those reported in the literature. The method proposed by Rico *et al.*[27] employing the NBi-SPE uses a t_{dep} of 120 s. However, this method involves a synthesis procedure of Bi nanostructures that requires several hours and high temperatures. It is important to emphasize that the LOD for Zn^{2+} presented by the CPEAmb/Bi was lower than the LOD obtained with a bismuth film deposited *in situ* onto a glassy carbon electrode (2.7 ppb).[34] Therefore, the proposed method using the CPEAmb/Bi not only presents a great analytical performance with low detection limit value (0.65 ppb), but also has a simple and low-cost procedure to prepare a Bi-based CPE.

The influence of other metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+} and Fe^{3+}) on the voltammetric response of 2.0 µmol L^{-1} Zn^{2+} was evaluated. These metal ions were studied as potential interferents since some of them are usually quantified by ASV methods (Pb^{2+} and Cd^{2+}) and some of them are present in multivitamin samples (Cu^{2+}, Cr^{3+} and Fe^{3+}). In this study, the concentration of the interfering ion was kept at 2.0 µmol L^{-1}, leading to a concentration ratio interfering ion/Zn^{2+} equal to 1. Higher concentration ratios were not studied since they are not expected to be found in multivitamin or antiseptic dusting powder samples. At these conditions, all metal ions studied have produced variations on the voltammetric signal of Zn^{2+} higher than 10% (Figure S8, SI section) and, therefore, they can be considered as interfering species. However, this interference could be overcome by using the standard addition method. As will be discussed in the next section, multivitamin samples have other metal ions in their composition which have not interfered on Zn^{2+} determination (Table 2).

Table 2. Determination of Zn^{2+} in antiseptic dusting powder and multivitamin samples employing CPEAmb/Bi and the FAAS technique

Sample	Labeled value	FAAS[c]	SW-ASV[c]	*F*-value[d]	*t*-value[e]
I	11.7[a]	12.7 ± 1.1	11.0 ± 0.5[a]	4.8	2.44
II	23.9[b]	24.7 ± 1.2[b]	23.2 ± 0.4[b]	9.0	2.05
III	23.9[b]	26.3 ± 1.8[b]	24.8 ± 1.2[b]	2.0	1.74
IV	11[b]	10.2 ± 1.0[b]	10.6 ± 0.3[b]	11	0.66

[a] gZnO *per* 100 g of antiseptic dusting powder; [b] mgZn^{2+} *per* tablet; [c] values expressed as mean value ± standard deviation; [d] $F_{2/2}$ = 39;[40] [e] t = 2.78 (p = 0.05 and 4 degrees of freedom).[40] FAAS: flame atomic absorption spectrometry; SW-ASV: square wave anodic stripping voltammetry.

Sample analyses

Aiming to evaluate the ability of the CPEAmb/Bi to quantify Zn^{2+} in real samples, these electrodes were used for the quantification of Zn^{2+} in commercial antiseptic dusting powder (sample I) and multivitamins formulations (samples II, III and IV). All the analyzed samples were pretreated by the alkaline extraction procedure described by Fonseca *et al.*[34] All experiments were performed in triplicate and quantifications were carried out using the standard addition method. For all analyzed samples, the concentration of Zn^{2+} in the electrochemical cell was kept close to 2.0 µmol L^{-1}. Figure 6 presents the results obtained for the quantification of Zn^{2+} in the sample I, whose behavior is representative of the other analyzed samples.

The standard addition curve obtained for sample I was linear according to the equation: $A_{Zn} = 2.38 + 1.56\ C_{Zn^{2+}}$ (µmol L^{-1}); R = 0.996. The angular coefficient of the standard addition curve is significantly lower than the

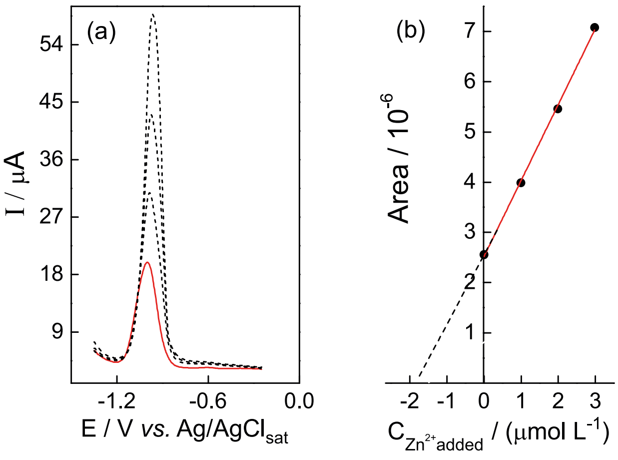

Figure 6. (a) SW-ASVs recorded in 0.1 mol L^{-1} acetate buffer (pH = 5.5) using CPEAmb/Bi, (solid line) 25 μL sample I aliquot after alkaline extraction and (dashed line) successive standard additions of 1.0 μmol L^{-1}. t_{dep} = 240 s; E_{dep} = –1.35 V; f = 100 Hz; ΔE = 25 mV; ΔE_s = 3 mV; (b) standard addition curve obtained for Zn^{2+}.

obtained from the analytical curve, which shows that matrix effects are present in the antiseptic dusting powder sample. This same behavior was also observed for the other analyzed samples, demonstrating that these samples also present matrix effects. Despite of that, the Zn^{2+} contents found in these samples were in close agreement with both the labeled values and the results obtained by FAAS (Table 2), indicating that the standard addition method is efficient to overcome these matrix effects.

As shown in Table 2, the *F* and *t* values have not exceeded the critical values, indicating that the precision and the results from FAAS and SW-ASV are statistically equivalent. This is a good evidence of the accuracy of the SW-ASV method. It is important to emphasize that multivitamin samples have other metal ions as components such as Fe (27 mg), Mn (1 mg), Cu (0.5 mg), Cr (15 mg), besides Se (15 mg), vitamins and organic acids. The numbers in parentheses refer to average content *per* tablet. Table 2 shows that these species are not interfering in the Zn^{2+} determination by the SW-ASV method. This can be explained by the low content of some of these metal ions in the multivitamin samples (Cu^{2+}) combined with the alkaline extraction, which prevents interference from metal ions unable to form soluble hydroxy-complexes (Fe^{3+}, Cr^{3+} and Mn^{2+}). Therefore, these results indicate that the CPEAmb/Bi coupled to SW-ASV can be successfully used to determine Zn^{2+} in antiseptic dusting powder and multivitamin samples if alkaline extraction and calibration by standard addition method are used.

Conclusions

This work demonstrated that Amberlite® IR 120 acts as an effective functionalized material for Bi^{3+} accumulation onto CPEs surface. After an electrochemical reduction step, accumulated Bi^{3+} is converted to very active Bi particles, leading to high sensitivity for Zn^{2+} with a detection limit of 10 nmol L^{-1} (0.65 ppb). The CPEAmb/Bi were successfully used for Zn^{2+} determination in antiseptic dusting powder and multivitamin commercial samples after a relatively simple and fast alkaline extraction procedure as sample pretreatment. Therefore, this work describes a simple and inexpensive way to prepare Bi-modified CPEs with great potential for the determination of metal ions by ASV.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.org.br as PDF file.

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