Simultaneous Determination of Cadmium, Lead, Copper and Mercury Ions Using Organofunctionalized SBA-15 Nanostructured Silica Modified Graphite – Polyurethane Composite Electrode

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Abstract

A new sensor has been developed for the simultaneous detection of cadmium, lead, copper and mercury, using differential pulse and square wave anodic stripping voltammetry (DPASV and SWASV) at a graphite–polyurethane composite electrode with SBA-15 silica organofunctionalized with 2-benzothiazolethiol as bulk modifier. The heavy metal ions were preconcentrated on the surface of the modified electrode at -1.1 V vs. SCE where they complex with 2-benzothiazolethiol and are reduced to the metals, and are then reoxidized. Optimum SWASV conditions lead to nanomolar detection limits and simultaneous determination of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} in natural waters was achieved.

Keywords: Graphite – polyurethane composite electrode, SBA-15 nanostructured silica, 2-Benzothiazolethiol, Heavy metals, Natural waters, Cadmium, Lead, Copper, Mercury

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1. Introduction

In recent decades, there has been a strong demand for designing integrated chemical systems that make use of the intrinsic properties of selected materials to particular redox processes occurring at electrode/solution interfaces. This has led to the emergence of a wide range of chemically-modified electrodes (CMEs) [1], which have found numerous applications in various fields and especially in electroanalysis [2–6]. Silica-modified electrodes, a subclass of CMEs [6], have been widely used because of their attractive properties, particularly as well-ordered nanoreactors containing a high number of accessible active centers. Mesoporous silica can be modified and functionalized by incorporation of organic groups in the silica structure that can bond to the silanol groups on the surface of the silica. A wide range of functional groups, such as thiols, amines, epoxides, imadizoles, chromophores, phenyls and alkyorganosilanes has been incorporated [7–11].

Electrochemical sensors based on stripping voltammetry have been demonstrated to be useful for determining trace heavy metals in aqueous solutions. These sensors are usually sensitive, compact, low-cost and easily integrated into field-deployable units [12, 13]. Cadmium, lead, copper and mercury are cumulative toxic metals whose presence in the environment has been of increasing concern. Contamination by cadmium, lead and mercury is one of the most serious environmental problems because of their stability in contaminated sites and complex mechanism of biological toxicity. Once absorbed, these metals can be accumulated in the body and greatly threaten human health [14–16]. Copper is an essential element at the trace level (i.e. catalytic action in heme synthesis) [17], but the intake of large quantities can be toxic. According to Portuguese regulations, natural waters may contain up to 0.010 mg L^{-1} (90.0 nmol L^{-1}) of cadmium, 0.050 mg L^{-1} (0.2 μmol L^{-1}) of lead, 0.100 mg L^{-1} (1.6 μmol L^{-1}) of copper and 0.001 mg L^{-1} (5.0 nmol L^{-1}) of mercury [18].

Although atomic spectrometric techniques are accurate for determining heavy metal ions, they involve high-cost instrumentation, maintenance and operation. Electrochemical methods possess multielement detection and speciation capability and need instrumentation of relatively low acquisition, maintenance and operation costs. Using differential pulse or square wave anodic stripping voltammetry techniques, limits of detection lower than the regulatory levels of concentrations of heavy metals can usually be reached [19, 20].

Solid carbon composite electrodes, prepared with polymers, have the advantages of surface regeneration by polishing, rigidity and ease of fabrication [21]. In this context, we have proposed a rigid graphite-polyurethane composite electrode for use in electroanalysis [22].

This work describes graphite – polyurethane rigid composite electrodes modified with 2-benzothiazolethiol functionalized SBA-15 nanostructured silica (BTSBA), achieved by incorporating BTSBA in the composite. They are successfully employed in the simultaneous determination of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} in natural water samples by differential pulse and square wave anodic stripping voltammetry (DPASV and SWASV). The main advantage of such a sensor is its robustness in relation to carbon paste electrodes previously described for this purpose [4].

2. Experimental

2.1. Apparatus

All voltammetric measurements were carried out in a 20.0 mL total capacity thermostatted glass cell at 24.0 °C, using a graphite–polyurethane electrode modified with BTSBA as a working, saturated calomel as reference (SCE) and platinum wire (1.0 cm log., 0.5 cm diameter) as reference and auxiliary electrodes respectively. DPASV and SWASV were performed in a µAutolab Type III PGSTAT (Ecochemie, Netherlands) potentiostat/galvanostat coupled to a personal computer and controlled with GPES 4.9 software.

2.2. Reagents and Solutions

All solutions were prepared with water purified in a Millipore Milli-Q system (resistivity ≥ 18 MΩ cm). All chemicals were of analytical grade and were used without further purification. A 0.10 mol L^{-1} potassium chloride (Fluka, Switzerland) electrolyte solution was used for most experiments.

3-(chloropropyl)-trimethoxysilane (Aldrich, Germany) and 2-benzothiazolethiol (Sigma. Germany) were used in the organofunctionalization of the SBA-15 silica, which was synthesized and characterized according to a previously-described procedure [23], as follows. A mass of 3.0 g of SBA-15 silica was refluxed with 2 mL of 3-(chloropropyl)-trimethoxysilane in 40 ml dry xylene for 24 h to introduce 3-chloropropyl on the surface. Following this, a sample of 3-chloropropyl SBA-15 silica was suspended in a *N,N′*-dimethylformamide solution containing 2-benzothiazolethiol with constant stirring and refluxing during 24 h. The functionalized particles were then treated with hot ethanol in a Soxhlet extractor during 8 h to eliminate excess organoalkoxysilane. Finally, the product was dried in air at 80 °C for 12 h.

A 1–2 µm particle size graphite powder (Aldrich, Germany) and polyurethane resin (Poliquil, Araraquara, SP, Brazil) were used for the preparation of the composite, see below.

A standard 1000 mg L^{-1} Cd^{2+} solution (Tec-Lab, Brazil, traceable to SRM 3108 NIST, USA); 1000 mg L^{-1} Pb^{2+} solution (Tec-Lab, Brazil, traceable to SRM 3128 NIST, USA); 1000 mg L^{-1} Cu^{2+} solution (Tec-Lab, Brazil, traceable to SRM 3114 NIST, USA) and 1000 mg L^{-1} Hg^{2+} solution (Tec-Lab, Brazil, traceable to SRM 3133 NIST, USA) were used for the preparation of the working cadmium, lead, copper and mercury solutions.

2.3. Preparation of the Modified Composite Electrodes

The polyurethane (PU) resin was prepared by mixing 0.8 parts of the prepolymer (A-249) with 1.0 part of the polyol (491-ID), according to the manufacturer's instructions. Previous results [22] showed that the best composition of the material was 60% (w/w) graphite and 40% (w/w) PU. Modified composites were prepared by substituting corresponding amounts of the graphite powder and PU by BTSBA to obtain the desired composition. First, the proportion of PU was fixed at 40% (w/w) and corresponding amounts of the graphite powder were replaced by the modifier in order to prepare electrode materials containing 5, 10, 15, 20% of BTSBA (w/w). Then, the proportion of graphite powder was fixed at 60% (w/w) and the respective PU amounts were replaced by BTSBA. However, it was only possible to prepare this type of electrode with 5 and 10% (w/w) of BTSBA, since when larger amounts of PU are removed homogenization becomes difficult.

The electrode was prepared from rods of the composite (4 mm diameter) extruded in a press [22]. For this purpose, 50 mm long rods were cut and attached to a copper wire using silver epoxy (Electron Microscopy Sciences, Hatfield, PA, USA) and left to cure for 24 h. The electrode was sealed in a glass tube using epoxy resin (Silaex, São Paulo, SP, Brazil) and used only after at least 24 h. After curing, the excess of polymer was removed using a 600-grit abrasive paper. Finally the electrode surface was polished with γ-Al_2O_3 suspension on a polishing wheel and sonicated for 5 minutes in water.

2.4. Sample Preparation and Analysis of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} in Natural Water

Exactly known amounts of the standard cadmium, lead, copper and mercury solutions were added to a 10.0 mL aliquot of a natural river water sample collected near Coimbra, Portugal in order to reach a final concentration of 6.0 µmol L^{-1} Cd^{2+}, 3.0×10^{-7} mol L^{-1} Pb^{2+}, 3.0 µmol L^{-1} Cu^{2+} and 6.0×10^{-7} mol L^{-1} Hg^{2+}. This sample was mixed with 10.0 ml of 0.10 mol L^{-1} potassium chloride pH 3.0, was stored in the refrigerator and used after 3 days. No further sample treatment was done.

The Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} contents were determined by three successive additions of aliquots of standard cadmium(II), lead(II), copper(II) and mercury(II) solutions.

3. Results and Discussion

3.1. Characterization and Optimization of the Differential Pulse and Square Wave Anodic Stripping Voltammetry Process

The potentiality of the SBA-15 silica organofunctionalized with 2-benzothiazolethiol composite electrodes was evaluated for DPASV and SWASV as described below.

Table 1. Optimum parameters for the simultaneous determination of cadmium, lead, copper and mercury ions using the graphite–polyurethane electrode modified with organofunctionalized SBA-15 silica/2-benzothiazolethiol by differential pulse and square wave anodic stripping voltammetry.

Parameter	Evaluated range	Optimized values	
		DPASV	SWASV
Scan rate	5–40 mV s^{-1}	10 mV s^{-1}	–
Pulse amplitude	15–100 mV	100 mV	50 mV
Accumulation potential	−1.3 to −0.9 V	−1.1 V vs. SCE	−1.1 V vs. SCE
Frequency	10–100 Hz	–	50 Hz
Step potential	2–10 mV	–	5 mV

DPASV and SWASV of 1.0×10^{-5} mol L^{-1} Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} each solutions in 0.1 mol L^{-1} phosphate buffer solution pH 3.0, showed four anodic peaks at −0.76 (Cd^{2+}), −0.53 (Pb^{2+}), −0.04 (Cu^{2+}) and +0.23 V (Hg^{2+}) vs. SCE. Parameters such as accumulation potential, pulse amplitude, scan rate, frequency that affects the voltammetric peak current were optimized, as presented in Table 1, before the simultaneous determination of these cations.

Preliminary studies were performed in phosphate buffer solution in order to have a better pH control. However, the optimized determinations were performed in pH 3 acidified KCl since this electrolyte proves to be better than phosphate buffer as will be discussed later.

3.1.1. *Influence of the Electrode Composition*

The influence of the composition of the electrode material on the voltammetric response of the electrode bulk-modified with BTSBA was evaluated by DPASV and SWASV of 1.0×10^{-5} mol L^{-1} Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} in 0.1 mol L^{-1} phosphate buffer solution pH 3.0 in the optimized conditions described in Table 1 and using a preconcentration time of 120 s.

The anodic peak current increased significantly when the amount of graphite powder was fixed at 60% (w/w) and substituting some of the PU by BTSBA, probably due to the higher content of the conducting phase at the electrode surface. The material of composition 5% (w/w) BTSBA, 60% (w/w) graphite and 35% (w/w) PU was chosen for further studies because it presented higher anodic peak currents than the composition 10% (w/w) BTSBA, 60% (w/w) graphite and 30% (w/w) PU.

3.1.2. *Effect of pH and Supporting Electrolyte*

The effect of pH on the voltammetric response of the graphite–polyurethane-BTSBA electrode was investigated in the pH range 2.0 and 5.0 in a solution containing 1.00×10^{-5} mol L^{-1} Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} added to 0.1 mol L^{-1} phosphate buffer solution.

The anodic peak current for Cd^{2+} and Cu^{2+} increased as the pH was changed from 2.0 to 3.0, reaching a maximum at pH 3.0 and then remaining almost constant up to pH 5.0. For Pb^{2+}, the anodic peak current increased significantly when the pH was changed from 2.0 to 3.0, remained constant from 3.0 to 4.0 and then decreased at pH 5.0. For Hg^{2+}, the anodic peak current was nearly constant as the pH was changed from 2.0 to 3.0 and then decreased significantly up to pH 5.0. Therefore, pH 3.0 continued to be used in further studies.

We believe that the increase in the response when the pH is increased from 2 to 3 is due to a complexation mechanism with BT, as described before for Cd^{2+} [24]. At higher pH the decrease of the stripping signal may be related with cation hydrolysis. Based on these findings, a possible mechanism for the metal accumulation was formulated, as presented in Scheme 1.

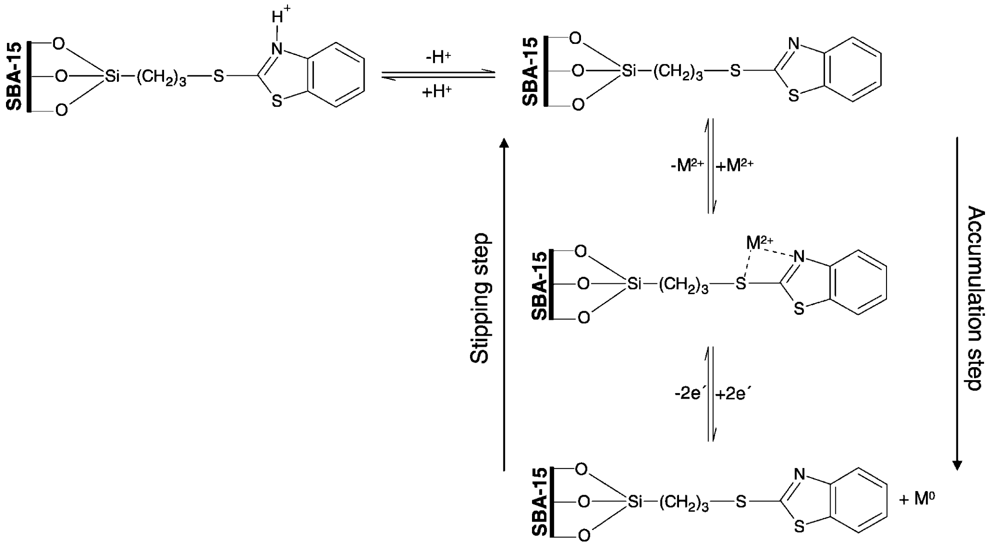
The voltammetric behavior was then examined at pH 3.0 in five different supporting electrolytes: 0.10 mol L^{-1} phosphate buffer, 0.10 mol L^{-1} acetate buffer, 0.10 mol L^{-1} potassium chloride, 0.10 mol L^{-1} potassium nitrate and 0.10 mol L^{-1} sodium perchlorate solution with pH adjusted to 3.0 by addition of a small microliter volume of 0.10 mol L^{-1} HNO_3. Voltammetric peaks were observed in all electrolytes (Fig. 1); however, in KCl solution (Fig. 1b) the anodic peak currents were higher and better-defined peak shapes were observed for all cations. Thus acidified 0.10 mol L^{-1} potassium chloride solution, adjusted to pH 3.0, was employed in further experiments.

This rather surprising result can be attributed to complexation. Although it is well known that these metal ions form stable complexes with chloride, it is possible that the stability of the modified silica complexes is higher than that of the metal-chloride complexes and aids in increasing accumulation efficiency at the negative potential employed during preconcentration.

3.1.3 *Comparison of Voltammetric Behavior of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} at Modified and Unmodified Composite Electrodes*

Figure 2 presents differential pulse anodic stripping voltammograms obtained with unmodified, SBA-15 silica modified and BTSBA-modified composite electrodes in 0.10 mol L^{-1} potassium chloride solution, pH 3.0. No peaks were observed in the potential range −1.1 to +0.4 V vs. SCE at the BTSBA bulk-modified composite electrode (curve a) in the absence of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}.

When the accumulation process was carried out for 120 s at −1.1 V in a solution containing 0.5 μmol L^{-1} Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}, at the unmodified composite electrode



Scheme 1. Schematic representation of the accumulation mechanism and stripping of the metals on the modified electrode surface.

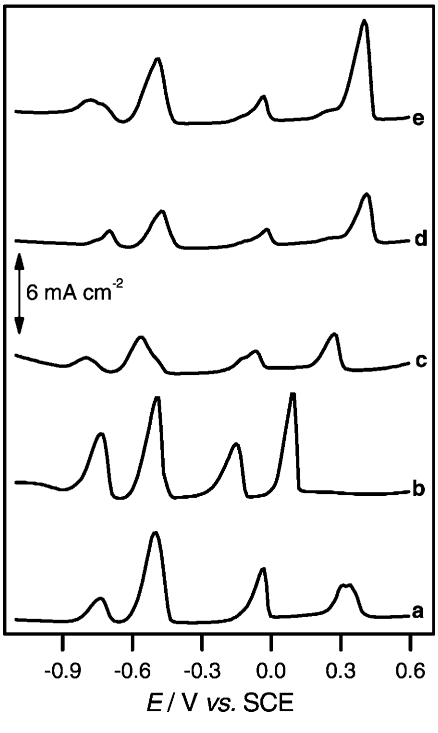


Fig. 1. Effect of supporting electrolytes: a) KH_2PO_4, b) KCl, c) CH_3COONa, d) $NaClO_4$, e) KNO_3 on the voltammetric response of the electrode modified with BTSBA evaluated by DPASV of 8 μmol L^{-1} Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} under the optimized conditions described in Table 1 and accumulation time of 120 s.

(curve b), peaks appeared in the stripping voltammograms at −0.76 V (Cd^{2+}), −0.50 V (Pb^{2+}), −0.15 V (Cu^{2+}) and +0.09 V (Hg^{2+}) vs. SCE.

Peaks are exhibited at almost identical potentials of −0.74 V (Cd^{2+}), −0.49 V (Pb^{2+}), −0.15 V (Cu^{2+}) and +0.10 V (Hg^{2+}) vs. SCE when the SBA-15 silica modified composite electrode (curve c) is used. At the BTSBA modified composite electrode (curve d) the oxidation peaks appear at −0.74 V (Cd^{2+}), −0.50 V (Pb^{2+}), −0.14 V (Cu^{2+}) and +0.10 V (Hg^{2+}) vs. SCE, with higher anodic stripping currents in comparison to those observed at the other electrodes. The increase in stripping currents at the modified composite electrode demonstrates that the organofunctionalization of SBA-15 nanostructured silica with 2-benzothiazolethiol plays an important role in the accumulation process of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} on the electrode surface, with advantages of increased sensitivity.

3.1.4. Effect of Preconcentration Time

The dependence of anodic peak currents on the preconcentration time for 0.5 μmol L^{-1} Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} was also investigated and is presented in Figure 3. The anodic peak currents increased linearly with increasing preconcentration time between 3 and 15 min, above which it became practically constant. This behavior indicates that after 15 min preconcentration time, a steady-state equilibrium between adsorption/complex formation and desorption/complex dissociation is reached, typical of stripping methods based on adsorptive or complex formation accumulation [25].

3.2. Analytical Parameters and Recovery

Analytical curves for Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} in the presence of the other metal ions were obtained by fixing the concentration of three of the species at 0.5 μmol L^{-1}, the concentration of the other species being changed. Analytical curves were constructed with preconcentration times of 5 and 15 min (the latter to examine if there is a need for longer accumulation times), using DPASV and SWASV with optimized parameters, summarized in Table 1.

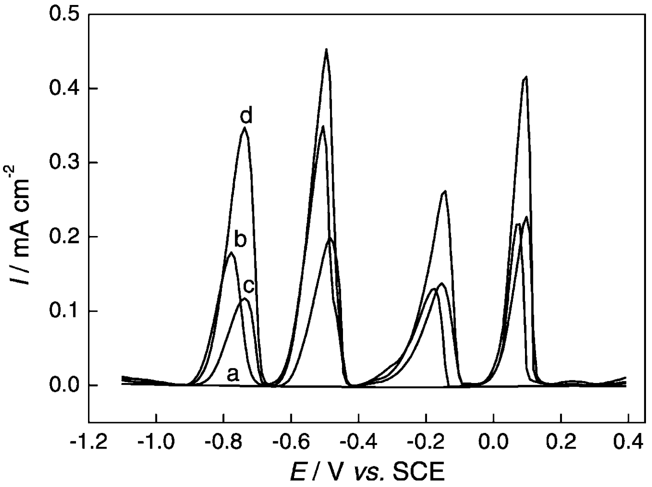


Fig. 2. Differential pulse anodic stripping voltammograms obtained in 0.10 mol L^{-1} KCl solution pH 3.0 for: (a) BTSBA modified composite electrode, (b) unmodified composite electrode in the presence of 0.5 μmol L^{-1} Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}, (c) SBA-15 silica modified composite electrode in the presence of 0.5 μmol L^{-1} Cd^{2+}, Pb^{2+}, Cu^{2+}, $Hg^{2+}$and (d) BTSBA modified composite electrode in the presence of 0.5 μmol L^{-1} Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}. Accumulation time 120 s; stripping parameters: potential interval -1.1 to $+0.4$ V vs. SCE scan rate 10 mV s^{-1}, pulse amplitude 100 mV.

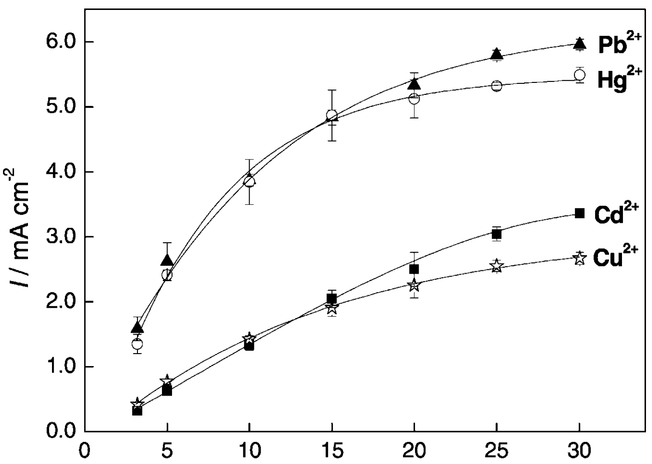


Fig. 3. Effect of the accumulation time on the DPASV response at the electrode modified with BTSBA of 0.5 μmol L^{-1} Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} using the optimized conditions described in Table 1.

Table 2 shows the analytical parameters for each metal ion using preconcentration times of 5 min and Table 3 with 15 min. It can be seen that there are some differences in the linear ranges and detection limit achieved with accumulation times of 5 and 15 min: the limits of detection obtained with an accumulation time of 5 min are sufficiently low to determine Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} below the maximum allowed by the Portuguese Law in natural water samples [20]. Differences in the sensitivity between DPASV and SWASV can be attributed principally to the kinetics of the redissolution process having a greater or lesser effect on peak shape (the timescale of the determination step in SWASV is shorter). Kinetic limitations will lead to broader peaks and lower peak currents. Accumulation times longer than 15 min could improve limits of detection but this will also cause an increase in the time of analysis. Conversely, in order to extend the linear range to higher values, shorter preconcentration times can be employed, but this was not the objective of the present study.

It can be seen that square wave voltammetry is slightly more sensitive than differential pulse voltammetry and the sensitivity to lead, mercury, copper and cadmium decreases in this order. Calibration curves for Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} obtained with a preconcentration time of 5 min using SWASV are presented in Figure 4.

One of the advantages of the composite electrode modified with BTSBA described here is that it can be used repeatedly without regenerating or reactivating the surface between successive determinations and with a low total experimental time, compared with other methods, such as atomic spectrometric techniques that usually require pretreatment of the sample before the determinations [26, 27].

Comparing the graphite-PU electrode with a carbon paste electrode, also used by us [4], the detection limits are lower and the repeatability in voltammetric measurements is better. The higher sensitivity of this electrode assembly could be related with the presence of functional groups present in the polyurethane as well as to the modifier. In addition, this sensor is much more robust then the carbon paste previously used and exhibits long term stability, one single electrode of each type was used during the all experimental work described here with no change in response characteristics.

Lower detection limits in relation to many previously reported potentiometric and voltammetric stripping methods are obtained: around 40 nM for Cd^{2+}, 50 nM for Pb^{2+}, 80 nM for Cu^{2+} and 87 nM for Hg^{2+} were found in [28–33]. Similar values were reported by other authors using stripping voltammetry around 6 nM for Cd^{2+}, 6 nM for Pb^{2+} and 20 nM for Cu^{2+} [34–36]. Procedures proposed for the determination of cadmium, lead, copper and mercury with lower detection limits (0.2 nM for Pb^{2+} and 0.1 nM for Hg^{2+}) used longer deposition times [37, 38].

3.3. Evaluation of Mutual Interferences

The influence of the presence in solution of one metal ion on the anodic peak currents of the others was evaluated through calibration curves, in which the concentration of metal ions of all except one are kept constant. The results of this study are shown in Table 4, and Figure 5 gives an example of the square wave anodic stripping voltammograms obtained for the calibration curve of Pb^{2+} with an accumulation time of 15 min under these circumstances, the concentration of other metal ions being fixed at 0.5 μmol L^{-1}. It can be observed that lead caused a decrease in the

Table 2. Parameters of analytical curves for Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} obtained with preconcentration time of 5 min and using DPASV and SWASV.

Metal ion		Linear regression equations for peak current I_{pa} (μA) (*C* in μM)	Upper limit of linear range (M)	Detection limit (nM) [a]	*R*	*n*
Cd^{2+}	DPASV	$I_{pa} = 0.8 + 35.3\ C_{Cd2+}$	1.0×10^{-6}	43.0	0.999	5
	SWASV	$I_{pa} = 0.5 + 57.5\ C_{Cd2+}$	1.0×10^{-6}	29.0	0.999	6
Pb^{2+}	DPASV	$I_{pa} = 2.33 + 277.8\ C_{Pb2+}$	1.0×10^{-7}	5.3	0.998	6
	SWASV	$I_{pa} = 0.01 + 378.6\ C_{Pb2+}$	9.0×10^{-8}	0.8	0.999	5
Cu^{2+}	DPASV	$I_{pa} = 0.7 + 45.5\ C_{Cu2+}$	9.0×10^{-7}	13.0	0.998	6
	SWASV	$I_{pa} = 0.6 + 139.8\ C_{Cu2+}$	9.0×10^{-7}	8.0	0.995	6
Hg^{2+}	DPASV	$I_{pa} = 0.4 + 117.5\ C_{Hg2+}$	4.0×10^{-7}	3.0	0.999	6
	SWASV	$I_{pa} = 0.4 + 408.4\ C_{Hg2+}$	1.0×10^{-7}	0.9	0.999	6

[a] Signal to noise ratio (*SNR*) of 3 [43]

Table 3. Parameters of analytical curves for Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} obtained with preconcentration time of 15 min and using DPASV and SWASV.

Metal ion		Linear regression equations for peak current I_{pa} (μA) (*C* in μM)	Upper limit of linear range (M)	Detection limit (nM) [a]	*R*	*n*
Cd^{2+}	DPASV	$I_{pa} = 1.11 + 67.8\ C_{Cd2+}$	8.0×10^{-7}	10.0	1.000	6
	SWASV	$I_{pa} = 0.08 + 166.4\ C_{Cd2+}$	6.0×10^{-7}	6.0	0.999	5
Pb^{2+}	DPASV	$I_{pa} = 0.1 + 698.1\ C_{Pb2+}$	1.0×10^{-8}	0.3	0.999	5
	SWASV	$I_{pa} = 0.3 + 852.5\ C_{Pb2+}$	1.0×10^{-8}	0.09	0.999	5
Cu^{2+}	DPASV	$I_{pa} = 1.87 + 323.4\ C_{Cu2+}$	1.0×10^{-7}	5.0	0.999	5
	SWASV	$I_{pa} = 0.9 + 460.2\ C_{Cu2+}$	1.0×10^{-7}	1.0	1.000	5
Hg^{2+}	DPASV	$I_{pa} = 0.5 + 547.2\ C_{Hg2+}$	8.0×10^{-8}	1.8	0.999	5
	SWASV	$I_{pa} = 0.3 + 785.4\ C_{Hg2+}$	4.0×10^{-8}	0.6	0.999	5

[a] Signal to noise ratio (*SNR*) of 3 [43]

cadmium signal, an increase in the copper signal and the mercury signal was almost unaffected.

Varying the concentration of cadmium ions, it was found that they increased the mercury signal, while the signal of lead and copper remained the same. Copper ions increased the mercury and lead signals slightly and significantly reduced the cadmium signal. Mercury caused an increase in the cadmium signal, and a decrease in copper and lead signals.

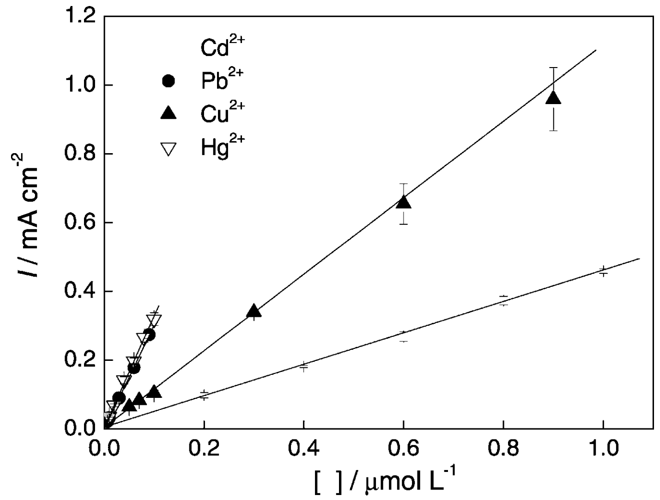


Fig. 4. SWASV for Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} obtained with a preconcentration time of 5 min and under the optimized conditions described in the text.

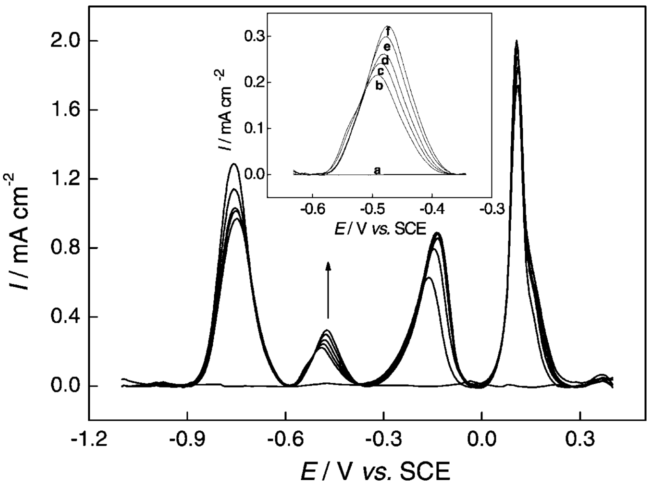


Fig. 5. Square wave anodic stripping voltammograms obtained with a preconcentration time of 15 min for: a) 0.0; b) 2.0; c) 4.0; d) 6.0; e) 8.0, f) 10.0 nmol L^{-1} Pb^{2+}, showing the interference of higher concentrations of lead ions on the anodic peak currents of 0.5 μmol L^{-1} Cd^{2+}, Cu^{2+} and Hg^{2+}.

Table 4. Effect of the metal ion interferents on the recovery of 0.5 μmol L^{-1} of each cation under the optimized SWASV conditions and accumulation time of 15 min, considering the first point of each analytical curve as 100%.

Metal ion studied	[ ] (nmol L^{-1})	Recovery of Cd^{2+} (%)	Recovery of Pb^{2+} (%)	Recovery of Cu^{2+} (%)	Recovery of Hg^{2+} (%)
Pb^{2+}	2.0	100.0	–	100.0	100.0
	4.0	95.0	–	108.2	102.5
	6.0	85.2	–	113.5	105.5
	8.0	84.1	–	114.9	106.3
	10.0	80.0	–	115.3	106.5
Cd^{2+}	100.0	–	100.0	100.0	100.0
	200.0	–	97.9	98.4	104.3
	400.0	–	98.2	101.2	110.5
	600.0	–	98.4	101.8	115.0
	800.0	–	99.4	102.3	115.8
Cu^{2+}	20.0	100.0	100.0	–	100.0
	40.0	98.6	101.0	–	100.4
	60.0	95.2	102.4	–	103.6
	80.0	91.2	103.6	–	104.5
	100.0	85.6	105.6	–	106.9
Hg^{2+}	5.0	100.0	100.0	100.0	–
	7.0	104.0	99.8	98.7	–
	9.0	108.4	98.9	97.8	–
	20.0	110.2	95.6	95.6	–
	40.0	118.2	94.3	94.4	–

These effects can be related to the different interactions of the metal ions with the bulk modifier. The stability constants of metal complexes with sulfur and nitrogen reported in the literature [39—42], show that cadmium is the least stable ($\lg K = 4.6$), the stability of copper ($\lg K = 12.5$) and lead ($\lg K = 12.1$) are almost equal and mercury ($\lg K = 18.8$) is more stable. The results in Table 4 showed that cadmium suffered more interference when the concentration of the other species changed, that can be ascribed to the fact that cadmium has a lower stability constant than the other metals. This means a particular cation can interfere positively or negatively in the response of the others. However, if the standard addition procedure is used as in the natural water matrix analyzed, the analytes can be successfully determined simultaneously as described below.

3.4. Analysis of Cadmium, Lead, Copper and Mercury in Natural Water

The organosilica-bulk modified electrode was applied to the SWASV determination of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} in a spiked natural water sample. The amounts added were: 6.0×10^{-7} mol L^{-1} for Cd^{2+}, 3.0×10^{-8} mol L^{-1} for Pb^{2+}, 3.0×10^{-7} mol L^{-1} for Cu^{2+} and 6.0×10^{-8} mol L^{-1} for Hg^{2+}. The results obtained (mean ± *SD*) using the standard addition method, for three determinations, were: $6.1 \pm 0.2 \times 10^{-7}$ mol L^{-1} for Cd^{2+}, $3.1 \pm 0.1 \times 10^{-8}$ mol L^{-1} for Pb^{2+}, $3.1 \pm 0.1 \times 10^{-7}$ mol L^{-1} for Cu^{2+} and $6.0 \pm 0.3 \times 10^{-8}$ mol L^{-1} for Hg^{2+}. Recoveries between 98.3 and 102.7% of Cd^{2+} from natural water samples ($n = 3$) were obtained, for 0.4, 0.6, 0.8 μmol L^{-1} of Cd^{2+} spiked in each sample. For Cu^{2+}, recoveries between 97.0 and 101.6% from natural water samples ($n = 3$) were obtained, for 0.2, 0.4, 0.6 μmol L^{-1} of Cu^{2+} spiked in each sample. Recoveries between 98.6 and 102.4% of Pb^{2+} and 95.6 and 102.5% of Hg^{2+} from natural water samples ($n = 3$) were obtained, for 4.0, 6.0, 8.0×10^{-8} mol L^{-1} of Pb^{2+} and Hg^{2+} spiked to each sample.

There were no significant differences between the found and the added concentrations, indicating that the graphite–polyurethane composite electrode modified with BTSBA can be successfully used for the simultaneous determination of cadmium, lead, copper and mercury ions in natural water samples, under the optimized conditions and using the standard addition approach.

4. Conclusions

A new chemically modified composite electrode was developed using 2-benzothiazolethiol organofunctionalized SBA-15 nanostructured silica for the simultaneous determination of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} in natural water samples. Despite some mutual interference effects, these ions can be reliably determined simultaneously when the standard addition procedure is used, with nanomolar detection limits. BTSBA, SBA-15 silica organofunctionalized with 2-benzothiazolethiol, is shown to be a good modifier, improves the sensitivity of the composite electrode, and shows long-term stability, which augurs well for future applications in this area.

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