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Differential Pulse Anodic Stripping Voltammetric Determination Of Mercury (II) In Natural Water At A Carbon Paste Electrode Modified With Organofunctionalized Amorphous Silica

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ABSTRACT

The determination of mercury using a carbon paste electrode modified with organofunctionalized amorphous silica with 2-benzothiazolethiol was investigated. The Hg (II) oxidation peak was observed around 0.080 V (vs. SCE) in potassium chloride solution 0.1 mol L^{-1} (pH 2.0) in differential pulse anodic stripping voltammetry. The best results were obtained under the following optimized conditions: 2 minute accumulation time, 50 mV pulse amplitude, 5 mV s^{-1} scan rate in potassium chloride solution 0.1 mol L^{-1} pH 2.0. Using such parameters four linear dynamic regions could be observed for the anodic peak current at the Bzt-CPE in relation to the concentration of the Hg(II) in a range from $8.24 \cdot x\ 10^{-7}$ to $9.88 \cdot x\ 10^{-5}$ mol L^{-1}. Hg (II) spiked in a natural water sample was determined with 99.1% mean recovery (n=3) at 10^{-6} mol L^{-1} level. Interference from cationic species was also evaluated.

KEYWORDS

Mercury;
Carbon paste electrode;
Amorphous silica;
2-Benzothiazolethiol;
Differential pulse anodic stripping voltammetry.

INTRODUCTION

Chemically modified electrodes (CMEs) have received much attention in analytical techniques, however, they are still only laboratory made and there are many difficulties with their routine and reproducible preparation. In addition to mixed carbon paste electrodes[1-3], modified carbon composite electrodes[4,5], are very attractive from this point of view, the concept of bulk modified electrodes.

The advantage of these non-traditional modified electrodes is their simple and rapid preparation, versatility, mechanical and chemical stability and renewability[6].

Anodic stripping voltammetric methods for the determination of trace mercury have been introduced successfully some years ago being the gold considerate the best electrodic material since the gold-mercury amalgam allows to lower detection limits while graphite electrodes require long Faradaic reductive pre-concentration steps[7].

The use of modified silica has widely been described in several areas of chemistry[1,8,9]. In analytical chemistry it can be an interesting support for different groups, which can be used for preparation of stationary phases in chromatographic methods, extraction of several species from solutions and improvement of selectivity and sensitivity in the preparation of electrodes for electroanalysis. Walcarius[2,3] presented extensive reviews about the preparation and application of silica modified electrodes showing their importance as electroanalytical sensors.

Mercury is a cumulative toxic metal whose presence in the environment has increasing concerning. Mercury toxicity may be manifested by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects[6]. The mercury is one of the most toxic metals, and its determination is very important in environmental and biological studies in general terms, and it should be considered that the organic forms of this metal could cross the biological membranes more easily than the corresponding inorganic forms improving toxicity[10,11].

In the present work the use of a amorphous silica organofunctionalized with 2-benzothiazolethiol in the preparation of carbon paste electrodes is described in the determination of mercury spiked in natural water samples. The amorphous silica presented the advantage of no need of surface pre-treatment before modification and the lower cost when compared with silica gel usually employed in such methods[12,13]. The best conditions for a differential pulse anodic stripping voltammetric procedure were optimized and the electrode was applied in the determination of Hg(II) with good results.

EXPERIMENTAL

Apparatus

All the voltammetric measurements were carried out in a 30 ml thermostated glass cell at 25.0 °C, using a carbon-paste as a working electrode, saturated calomel as reference electrode (SCE) and platinum wire as auxiliary electrode. High purity nitrogen was used for deaeration of the electrolyte solution. Differential pulse anodic stripping voltammetry were performed in a BAS CV50-W (Bioanalytical Systems, USA) controlled by the BAS 50W Windows Control Software, version 2.3.

Reagents and solutions

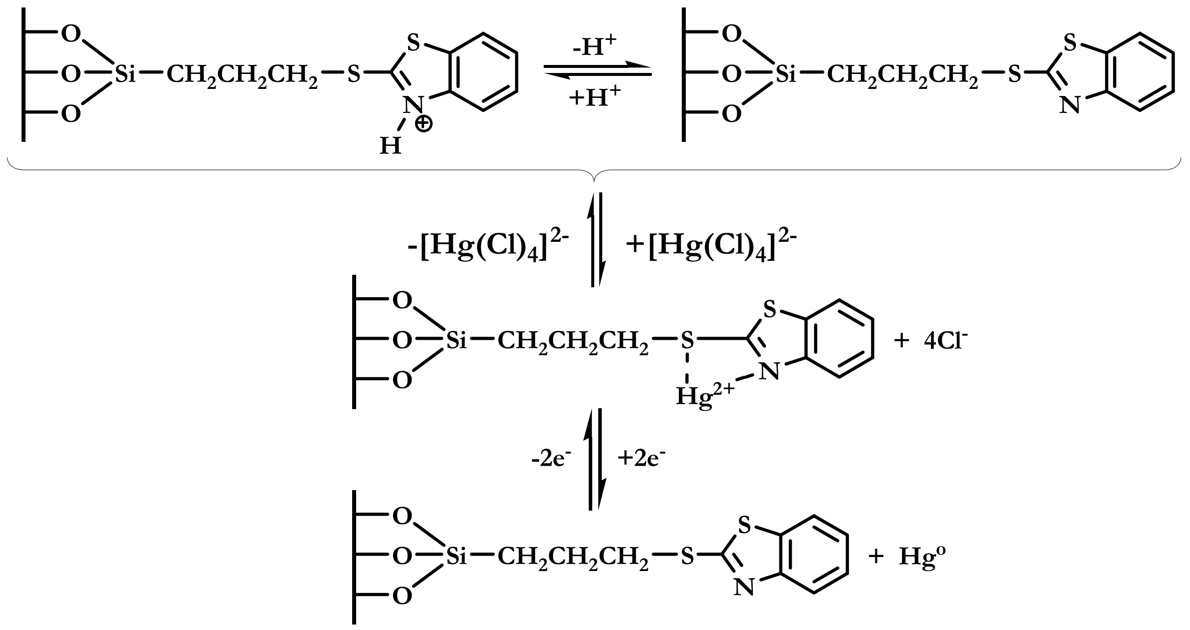
All the solutions were prepared with water purified in a Millipore Milli-Q system. All the chemicals were of analytical grade and used without further purification. The supporting electrolyte used for most experiments was a 0.10 mol L^{-1} potassium chloride pH 2.0. Stock standard solutions containing 4.985 x 10^{-3} mol L^{-1} Hg(II) were prepared daily by dissolving an appropriate amount of a 1000 ppm mercury(II) chloride standard solution (Merck) in 100 ml of the 0.10 mol L^{-1} potassium chloride pH 2.0.

The 3-chloropropyl-trimethoxysilane (Aldrich) and 2-benzothiazolethiol (Sigma) were used in the modification of the amorphous silica, Gasil 200 tp (Crosfield).

Graphite powder (1-2 μm particle size, Aldrich) and mineral oil (Aldrich) of high purity were used for the preparation of the carbon pastes. Graphite powder was previously treated by reflux in HNO_3: HCl 3:1 (v/v) for 12 hours, filtered, washed with deionized water until neutrality, reflux for 4 hours in water purified in a Millipore Milli-Q system, filtered again and dried in a oven at 120°C for 8 hours. This treatment eliminated some peaks observed in the voltammograms even in blank solutions.

Preparation of the organofunctionalized amorphous silica

Amorphous silica with a specific surface area of 498.6 m^2 g^{-1} and an average pore volume of 306.87.10^{-3} cm^3 g^{-1} was used without further treatment, in a procedure described by Marino et al.[14]. Thus 12.5 g of amorphous silica was refluxed with 4 ml of the 3-chloropropyl-trimethoxysilane in 40 ml dry xylene for 24 hours. The solid was filtered and washed with xylene, ethanol, acetone and ethyl ether, respectively.



SCHEME 1: Tentative representation of the pre-concentration mechanism and stripping of Hg(II) on the modified electrode surface.

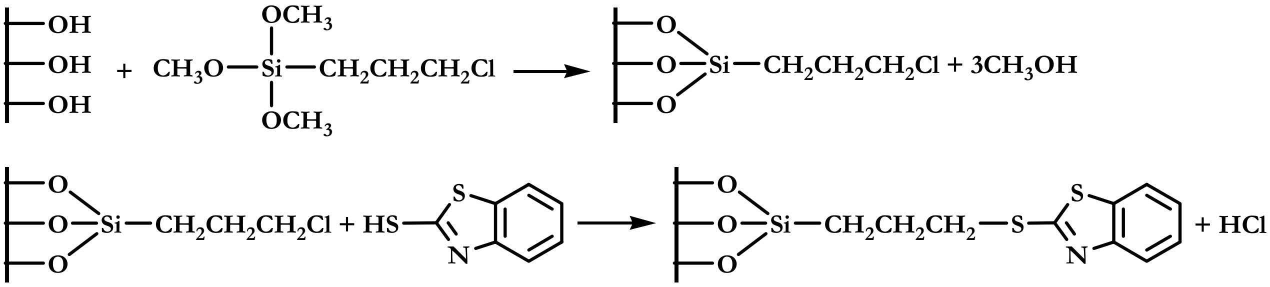


Figure 1: Covalent modification of amorphous silica surface by silanization reaction with 3-chloropropyltrimethoxysilane and conversion to organofunctionalized amorphous silica with 2-benzothiazolethiol.

For conversion to organofunctionalized amorphous silica with 2-benzothiazolethiol, a sample of 3-chloropropyl amorphous silica was treated in a N, N′-dimethylformamide solution containing 2-benzo thiazolethiol kept under constant stirring and reflux during 24 hours. The suspension was filtered and washed successively with N,N′-dimethylformamide, ethanol, acetone and ethyl ether. The solid was treated with hot ethanol in a Soxlet extractor during 8 hours for elimination of the excess of organoalcoxi silane. Finally, the product was dried in air at 80°C for 8 hour and kept in a dessicator. Figure 1 summarizes the silica modification procedure.

The organofunctionalized amorphous silica was characterized by elemental analysis, IR spectroscopy, thermal analysis (TG and DSC) and NMR in solid phase (^{1}H, ^{13}C and ^{29}Si)[14].

Preparation of the modified carbon paste electrodes

Modified carbon paste electrodes were prepared by carefully mixing 0.550g of the pretreated graphite powder with 0.200 g of the organofunctionalized amorphous silica. Thus the resulting 0.750 g of this mixture was subsequently added to 0.250 g of mineral oil and mixed in a mortar for at least 20 min to produce the final paste. The carbon paste electrode was finally obtained by packing the paste into a plastic tube 4.5 mm i.d. (geometrical area 0.16 cm^2) and arranged with a copper wire serving as an external electric contact. Appropriate packing was achieved by pressing the electrode surface against a bond paper until a smooth surface was obtained.

Sample preparation and analysis of mercury (II) in well water

A well-known amount of mercury was spiked to an aliquot of well water in order to reach a final concentration of 8.00 x 10^{-6} mol L^{-1} in Hg^{2+}. The pH of the well water was previously adjusted to 2.0 with HNO$_3$ purified by sub-boiling distillation. Aliquots of these samples were diluted in equal volumes of 0.20 mol L^{-1} KCl pH 2.0 before analysis.

The Hg^{2+} content in these samples was determined by three successive additions of a standard mercury (II) solution. The optimized parameters of differential pulse anodic stripping voltammetry for mercury(II) determination in the sample were: potential window -0.9 to 0.2 V (vs. SCE); 50 mV pulse amplitude; scan rate of 5 mV s^{-1} and accumulation time 120 s at -0.9 V. All measurements were performed in solutions deaerated by bubbling N$_2$ for 10 minutes.

RESULTS AND DISCUSSION

Characterization of the chemically modified amorphous silica

The specific surface area of the amorphous silica after chemical modification with 2-benzothiazole thiol decreases from 498.6 to 148.2 m^2 g^{-1}, as determined by the BET N$_2$ adsorption method[15]. This decrease was attributed to the blocking of some of the smaller pores during the modification process of the silica.

Voltammetric behavior of Hg(II) on modified carbon paste electrode

The differential pulse voltammograms after 120 s of accumulation at an unmodified carbon paste electrode (CPE), a carbon paste electrode modified with an unfunctionalized amorphous silica (Si-CPE) and a carbon paste electrode modified with amorphous silica organofunctionalized with 2-benzothiazolethiol (Bzt-CPE) are presented in figure 2. A single mercury oxidation peak was observed between 58 – 80 mV (vs. SCE), depending on the electrode used. As depicted in this figure the organofunctionalized silica improved the peak current as well as showed a better peak resolution. The displacement of the peak potential from 58 mV at the CPE to 80 mV (vs. SCE) in the Bzt-CPE suggests an interaction of the metal ion with the modifier.

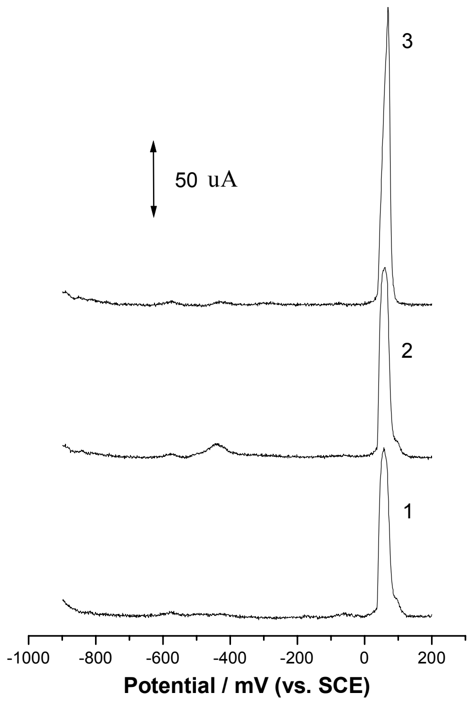


Figure 2: Differential pulse anodic stripping voltammograms obtained at 25.0°C and scan rate of 5 mV s^{-1} for: (1) unmodified carbon paste electrode (CPE) in the presence of 1.0 x10^{-5} mol L^{-1} Hg(II), (2) carbon paste electrode modified with an unfunctionalized amorphous silica (Si-CPE) in the presence of 1.0 x10^{-5} mol L^{-1} Hg(II), (3) carbon paste electrode modified with amorphous silica organofunctionalized with 2-benzothiazolethiol (Bzt-CPE) in the presence of 1.0 x10^{-5} mol L^{-1} Hg(II). Potential interval -0.9 to 0.2 V (vs. SCE) and accumulation time 120 s.

The pretreatment of the graphite as described in the experimental section minimized the peaks of unknown origin observed in the -600 to -300 mV range and presented lower capacitive current.

Electrode composition effect

The effect of the carbon paste composition in the voltammetric response of the electrode modified with Bzt-CPE was evaluated by DPASV using 1.0.10^{-5} mol L^{-1} Hg(II) in 0.10 mol L^{-1} KCl pH 2.0. The anodic peak current increased with the amount of orgnofunctionalized amorphous silica in the paste up to 20% (w/w). The anodic peak current decreased significantly when more than 20% (modified silica, w/w) is used in the electrode preparation. This probably occurs due to a decrease in the conductive area at the electrode surface. According to these results a carbon-paste composition of 20% (w/w) modified amorphous silica, 55% (w/w) graphite and 25% (w/w) mineral oil was used in further studies.

Effect of supporting electrolyte and pH

The voltammetric behavior of the Bzt-CPE was examined in different supporting electrolytes with pH adjusted to 4.0. The supporting electrolytes evaluated were 0.10 mol L^{-1} sodium hydrogenphos phate, 0.10 mol L^{-1} sodium acetate and 0.10 mol L^{-1} potassium chloride containing 1.0 x 10^{-5} mol L^{-1} Hg(II). Voltammetric peaks were observed in all these electrolytes, however in KCl the anodic peak currents was higher and better-defined peak shapes were observed. According to these results this supporting electrolyte was chosen for next experiments.

The effect of pH on the voltammetric response of the Bzt-CPE was studied over a pH range between 2.0 and 6.0 in a solution containing 1.0 x 10^{-5} mol L^{-1} Hg(II) in 0.1 mol L^{-1} KCl. The maximum anodic peak current was observed at pH 2.0. Although higher currents were observed in pH 3.0 the peak resolution was worst. At pH range 4.0 - 6.0 the current presented a slight decrease associated to the broader peaks. In this sense pH 2.0 was chosen for further studies.

Otimization of the differential pulse anodic stripping voltammetry parameters

Parameters such as accumulation potential, pre-concentration time and scan rate that affects the voltammetric peak current in DPASV analysis were optimized as described bellow. The differential pulse anodic stripping voltammograms were recorded at the Bzt-CPE electrode using a 1.0 x10^{-5} mol L^{-1} Hg(II) solution in 0.10 mol L^{-1} KCl pH 2.0. The parameters were optimized on the basis of the anodic peak current around 80 mV (vs. SCE).

1. Effect of accumulation potential

Accumulation potentials between -1200 and 200 mV were investigated. For this purpose pre-concentrations were performed for 60 s. Then Hg(0) was oxidized by differential pulse voltammetry at 20 mV s^{-1} and pulse amplitude of 50 mV. It was observed that in the interval between -1200 and -900 mV there was no influence of accumulation potential on the anodic peak current. At more positive potentials a decrease in the anodic peak current caused by an inefficient reduction of Hg(II) to Hg(0) at the electrode surface. Thus -900 mV was chosen as the accumulation potential in further studies.

2. Effect of pre-concentration time

The dependence of anodic peak current with the pre-concentration time was also investigated. The anodic peak current increases with the increasing in the pre-concentration time between 0 and 180 s. In this entire time interval the peak current increased, however the increase is lower above 120 s of accumulation. Considering the low gain in current compared to the analytical frequency 120 s was chosen as the best accumulation time.

3. Effect of scan rate and pulse amplitude

The anodic peak currents for cadmium in DPASV were also evaluated as a function of scan rate of the anodic scan between 5 and 50 mV s^{-1} and pulse amplitudes from 5 to 100 mV, under the same conditions as above. The peak current increased and the potential peaks shifts toward more anodic values in faster scan rates. The scan rate of 5 mV s^{-1} (with pulse amplitude of 50 mV) was chosen because it presented higher currents and better peak definition. Higher scan rates and pulse amplitudes caused loss in peak definition.

Analytical curve, precision, detection limit and recovery in KCl solutions

Differential anodic stripping pulse voltammo grams for different Hg(II) concentrations are pre-

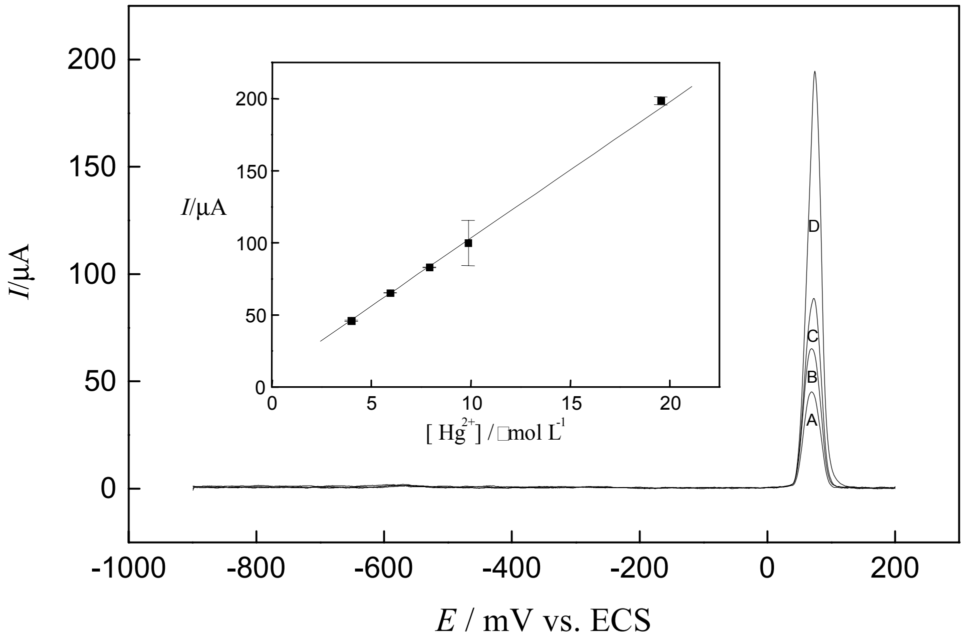


Figure 3: Differential pulse anodic voltammograms obtained under the conditions described in the TABLE 1: A) 4.00; B) 6.00; C) 8.00; D) 20.00 µmol L^{-1} Hg(II). The analytical curve is shown in the detail.

TABLE 1: Optimized parameters for mercury determination using the carbon paste electrode modified with organofunctionalized amorphous silica with 2-benzothiazolethiol in differential pulse anodic stripping voltammetry

Parameter	Optimized value
Electrode composition	20% (m/m) modified amorphous silica, 55% (m/m) graphite and 25% (m/m) mineral oil.
Supporting electrolyte and pH	0.10 mol L^{-1} potassium chloride - pH 2.0
Accumulation potential	-900 mV (vs. SCE)
Pre-concentration time	120 s
Scan rate	5 mV s^{-1}
Pulse amplitude	50 mV

sented in figure 3 obtained under the set of optimum conditions resumed in TABLE 1.

Four linear dynamic regions could observed for the anodic peak current at the Bzt-CPE in relation to the concentration of the Hg(II) in a range from 8.24 x 10^{-7} to 9.88·x 10^{-5} mol L^{-1}. The details of these linear relationships are presented in TABLE 2.

Despite the higher sensitivities observed in the LOD 1, 2 and 4 (TABLE 2), the linear region 3 presented the larger range of concentration as well as a

TABLE 2: Analytical parameters relative to the linear regions

Linear dynamic range	Concentration range µmol L^{-1}	Sensitivity* µA µmol L^{-1}	Intercept (a)* µA	R (n)
1	0.824 - 3.91	4.72	-0.15	0.9673 (5)
2	3.91 - 9.85	6.14	-23.84	0.9772 (5)
3	9.85 - 68.4	2.06	11.63	0.9995 (5)
4	68.4 - 98.8	3.57	-92.11	1.0000 (3)

* y = a + bx

TABLE 3: Effect of some divalent cations in the Hg(II) recovery under the optimized DPASV conditions. Mercury(II) concentration fixed at 4 x 10^{-6} mol L^{-1} in 0.10 mol L^{-1} KCl pH 2.0, other conditions as in TABLE 1

Interferant	Concentration / 10^{-6} mol L^{-1}	Recovery of Hg(II) /%
Zn(II)	2.00	113
	4.00	113
	10.00	113
Pb(II)	2.00	105
	4.00	135
	10.00	188
Mn(II)	2.00	103
	4.00	109
	10.00	113
Cu(II)	2.00	186
	4.00	262
	10.00	259
Cd(II)	2.00	132
	4.00	173
	10.00	181

acceptable linear correlation coefficient. This region gave a detection limit of 1.0·x 10^{-7} mol L^{-1} (three times the signal blank/slope) and obeyed the following linear equation (see detail in figure 3) is:

$$\mathbf{I_{pa}\ (\mu A) = 11.63\ \mu A + 2.06\ \mu A\ \mu mol^{-1}\ L\ [Hg^{2+}]\ (r = 0.9995;\ n = 5)} \qquad (1)$$

The successive changes in the sensitivities were attributed to the mercury deposition in the active sites of the electrode. EDX data showed the deposition of Hg at Bzt-CPE electrode.

Interferences

TABLE 4: Determination of Hg(II) in a well water sample by differential pulse anodic stripping voltammetric proposed method

Repetiton	Hg(II) / μmol L^{-1} Added	Found	E_r %
1	8.00	7.94	0.75
2	8.00	7.96	0.50
		Mean = 7.95 ± 0.01	

E_r = relative error = added versus found using the voltammetric proposed method.

The influence of Cd(II), Zn(II), Pb(II), Cu(II), and Mn(II) in the Hg (II) peak current has been evaluated and the results are presented in TABLE 3. Severe increase in the Hg(II) recovery was observed in the presence of Cd(II) and Cu(II) in all the concentrations investigated. Zn(II) presented a constant level of interference in all the concentrations used, but the effect is much less marked then observed for the Cd(II) and Cu(II) ions. Pb(II) presented a positive interference in the Hg(II) signal, that increases with the increase in the interferant concentration, being tolerable up to 2.00 μmol L^{-1}, when Hg(II) is 4.00 μmol L^{-1}.

The lowest interfering effect was observed for Mn(II). Up to the same level of concentration of Hg(II) the interference is almost negligible, increasing for concentrations of Mn(II) 10.0 μmol $L^{-1,}$ when the Hg(II) is 4.00 μmol L^{-1}.

The positive effect of the interferants on the Hg(II) signal should be attributed to a possible formation amalgams with the cations after the Hg deposition.

Analysis of mercury in well water

Finally, the proposed electrode was applied for the differential pulse anodic stripping voltammetric determination of Hg(II) spiked in a well water sample. The results obtained using the standard addition method are presented in TABLE 4. The Hg(II) concentration spiked was 8.00 μmol L^{-1} and that determined in the present work was 7.95 μmol L^{-1}, mean

TABLE 5: Concentration of some metals in the original well water sample, determined by flame atomic absorption

Metallic cation	Concentration / mol L^{-1}
Fe^{3+}	3.52 x 10^{-7}
Zn^{2+}	3.01· x 10^{-7}
Al^{3+}	-*
Cu^{2+}	-*
Na^{+}	1.40· x 10^{-4}
K^{+}	2.60 x 10^{-5}
Mg^{2+}	4.90 x 10^{-5}
Ca^{2+}	3.33· x 10^{-4}

*** Not detected**

of two determinations.

TABLE 5 presents the concentration of some metallic cations in the original well water determined by flame atomic absorption spectrophotometry for evaluation of the potentially interfering species. In the presence of the cations naturally present in the original water no interference in the voltammetric response of the modified electrode has been observed, at the concentration level determined showing that the electrode is useful in such kind of samples in case of Hg(II) contamination.

Recoveries of 97.1 and 101 % of Hg(II) from well water samples (n = 3) was obtained using the electrode (TABLE 6) for 4.00, 4.50, 5.00 and 5.99 μmol L^{-1} of Hg(II) added to each sample. This is an evidence of the accuracy of the proposed procedure.

TABLE 6: Results of the addition-recovery experiment in well water in four standard additions of Hg (II)

Added/ μmol L^{-1}	Found / μmol L^{-1}	% Rec. = $\frac{\text{Rec.}}{\text{Add.}}$ x 100
4.00	3.98	99.5
4.50	4.37	97.1
5.00	4.94	98.8
5.99	6.07	101

The statistical calculations for the assay results showed suitable precision of the proposed voltammetric method. According to the F test, there were no significant differences between the calculated and added concentrations at the 95% confidence level and within an acceptable range of error, indicating that carbon paste electrode modified with organofunctionalized amorphous silica with 2-benzothiazolethiol can be used for voltammetric determinations of Hg(II) in water samples.

CONCLUSION

The use of the organofunctionalized amorphous silica with 2-benzothiazolethiol in the preparation of modified carbon paste electrodes showed to be an interesting alternative in the electroanalytical determination of Hg(II) in well water samples. Reproducible, accurate and sensitive determination can be achieved using the DPASV procedure.

In spite of severe interference of same cations the naturally occurring metallic species seem to have no influence suggesting this electrodes as an alternative to mercury electrode usually employed in such determinations.

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