

Preparation of a Silica Gel Modified with 2-Amino-1,3,4-thiadiazole for Adsorption of Metal Ions and Electroanalytical Application

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Uma sílica gel, com área específica de 382 m² g⁻¹ e diâmetro médio de poro de 60 Å, foi modificada quimicamente com 2-amino-1,3,4-tiadiazol, com o propósito de adsorção seletiva de íons de metais pesados e possível utilização como um eletrodo de pasta de carbono quimicamente modificado (CMCPE). São discutidas as seguintes propriedades desta sílica gel funcionalizada: adsorção seletiva de íons de metais pesados, medida pelas técnicas "batch" e coluna cromatográfica, e utilização como agente de preconcentração em um eletrodo de pasta de carbono quimicamente modificado (CMCPE), para determinação de mercúrio(II). A seletividade química deste grupo funcional e a seletividade da voltametria foram combinadas para preconcentração e determinação.

Silica gel with a specific area of 382 m² g⁻¹ and an average pore diameter of 60 Å was chemically modified with 2-amino-1,3,4-thiadiazole, for the purpose of selective adsorption of heavy metals ions and possible use as a chemically modified carbon paste electrode (CMCPE). The following properties of this functionalized silica gel are discussed: selective adsorption of heavy metal ions measured by batch and chromatographic column techniques, and utilization as preconcentration agent in a chemically modified carbon paste electrode (CMCPE) for determination of mercury(II). The chemical selectivity of this functional group and the selectivity of voltammetry were combined for preconcentration and determination.

Keywords: silica gel functionalized, preconcentration, carbon paste electrode, mercury

Introduction

The preparation and of organofunctionalized silica gels has been of great interest due to their multiple uses in high efficiency liquid chromatography,¹ preconcentration and separation processes,²⁻⁴ ion exchange⁵ and chemical sensors.⁶⁻¹⁰ Most organofunctional groups attached on silica gel surfaces with the aim of adsorbing metal ions from aqueous and nonaqueous solutions invariably have nitrogen as the donor atom. Organofunctional groups with sulfur as the donor atom in order to adsorb mainly heavier metal ions from solution have also been immobilized on the silica gel surface.¹¹⁻¹⁵ These materials have been prepared in order to obtain adsorbents having the following characteristics: good sorption capacity, chemical stability under conditions of use, and especially, high selectivity.

The graphite modified electrodes (GMEs) have potential uses in electrocatalysis and are very promising as sensors in electroanalytical chemistry. GMEs offer advantages over the conventional electrode due to: *i*) mercury electrodes presents high toxicity and rapid deterioration of electrode response and *ii*) the possibility of oxide formation on the platinum and gold electrodes surface, causing complications with analytical applications.¹⁶

In this context, the graphite modified electrodes (GMEs) offer a possibility of lowering the overpotential and increasing sensitivity and selectivity of some electroactive species.

The organo or inorganically functionalized silica gel is an important material support used for modification of graphite, in view of the well known chemical stability and preconcentration of electroactive species.¹⁷

Determination of mercury at trace levels in environmental samples is of great importance nowadays because

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mercury is one of the most poisonous and accumulatable metals in biological systems. It also has a persistent character in the environment and living organisms.¹⁸

Modern analytical methods often fail to determine elements in the analysis of environmental samples and biological materials, because of limitations such as inadequate detection limits and interference from various species, which makes direct determinations impossible.

Recently, we have reported on the preparation and uses of silica gel with organic functional groups covalently bonded on its surface.¹⁹⁻²⁴

In this work, a silica gel surface chemically modified with 2-amino-1,3,4-thiadiazole was employed as an effective solid-phase selective sorbent for Hg(II) and as a preconcentration agent in a CMCPE. 2-amino-1,3,4-thiadiazole was incorporated in the silica gel surface by reaction with (3-chloropropyl) silica gel, resulting in the product 3-(2-amino-1,3,4-thiadiazolyl) propyl silica gel (SiATD).²⁴

This work focuses on the preparation and utilization of the SiATD looking at the following properties: *i*) selective adsorption towards mercury(II) ions measured by batch and chromatographic column techniques and *ii*) utilization as preconcentration agent in a chemically modified graphite paste electrode (CMGPE) for determination of mercury(II), as this element belongs to the most toxic metals.

Experimental

Apparatus

All measurements were recorded with an EG & G Princeton Applied Research Model 273A polarographic analyzer connected to a microcomputer for data collecting. The electrochemical behaviour of SiATD was monitored by cyclic voltammetry and differential pulse anodic stripping voltammetry (DPASV). A three-electrode cell involving a SiATD-GPE as the working electrode, a KCl saturated Ag/AgCl, as the reference electrode, and a Pt-wire as the auxiliary electrode were used for all investigations. The optimized potential scan rate and pulse magnitude, used in differential pulse voltammetric (DPV) technique were of 10 mV s⁻¹ and 50 mV, respectively.

Chemicals and reagents

All chemicals were of analytical reagent grade unless stated otherwise. Solutions were prepared from doubly-demineralized water obtained by passing distilled water through a Millipore Milli-Q water purification system. Dilute solutions ($\leq 1 \times 10^{-3}$ mol L⁻¹) of Hg(II) and other ions were

prepared fresh daily. The modified silica gel functionalized with 3-(2-amino-1,3,4-thiadiazolyl) propyl groups (SiATD) was prepared according to the reported by Dias Filho.¹⁹

Preparation of the SiATD-CPE

The chemically modified carbon paste electrodes were prepared by thorough mixing of graphite powder (Aldrich), 35% (m/m) Nujol oil (Aldrich) and silica gel functionalized with 3-(2-amino-1,3,4-thiadiazolyl) propyl groups (SiATD) in proportions of 4, 8, 12, 16, 20, 24 and 28% (m/m), respectively. The electrode body was fabricated from a glass tube of i.d. 3 mm and a height of 14 cm. After the mixture has been homogenized, the paste was packed carefully into the tube tip to avoid possible air gaps, which often enhance electrode resistance. A copper wire was inserted through the opposite end to establish electrical contact. The external surface of the electrode was smoothed on soft paper. A new surface can be produced by scraping out the old surface and replacing the carbon paste.

Adsorption isotherms and preconcentration experiments

The adsorption isotherms of metal ions by 3-(2-amino-1,3,4-thiadiazolyl) propyl groups (SiATD) were determined for Hg(II), Cd(II), Pb(II), Cu(II), Zn(II), Co(II), Ni(II) and Mn(II) metal ions in aqueous solutions at different pH values by batch method. About 0.5 g of the sorbent were immersed in 50 mL solutions of metal ions of 2.5×10^{-3} mol L⁻¹ and shaken using magnetic stirrer for 30 min at 298 ± 0.2 K. The quantity of the metal in each flask was determined by AAS.

The quantity of the adsorbed metal, N_f in each flask was determined by the equation:

$$N_f = (N_a - N_s)/m \quad (1)$$

where N_a is the initial mole number of the metal in the solution phase, N_s is the metal mole number under equilibrium condition and m is the mass of the adsorbent.

For the preconcentration of individual metal ions by column method, each metal was quantitatively adsorbed adjusting the pH solutions according to the values found in the previous batch method. For these experiments, a glass column with 20×0.8 cm i.d. was packed with about 5 g of the sorbent. Initially the column was washed with pure water and then 1000 mL of solution of metal ion of 0.5×10^{-6} mol L⁻¹ was percolated through the column with a flow rate of 5.0 ml min⁻¹. In every run, the effluent was collected and a quantity of metal ion analysed. Elution of

the metals from the column were made by passing 25 mL of hydrochloric or nitric acid of different concentrations. Quantitative elution of Hg(II) was possible passing 25 mL of 0.05 mol L⁻¹ cysteine solution acidified with 3.0 mol L⁻¹ HCl solution.

Adsorption and elution studies of a mixture of the metal ions Hg(II), Cd(II), Pb(II), Cu(II), and Zn(II) as well interference of other metal ions, such as Co(II), Ni(II), Mn(II), Bi(III), Fe(II) and Fe(III) were also carried out. The interference of some anions, such as chloride, nitrate, sulphate, fluoride, thiocyanate, bromide, phosphate, acetate, oxalate, and tartrate have also been investigated in this work. In these studies, a series of aqueous solutions were prepared in which the metal ion concentrations were fixed at 0.25×10^{-6} mol L⁻¹ except for one of them fixed at 2.5×10^{-6} or 25.0×10^{-6} mol L⁻¹. For adsorption, 1000 mL of aqueous elution was percolated through the column. The adsorbed metal ions were eluted using solutions previously known from study of preconcentration of individual metal ions.

Procedure

Electrode conditioning. Fresh SiATD-CPE surfaces were conditioned by exposure to a 1.0 mg L⁻¹ mercury solution at pH 2.00, adjusted with HNO₃, for 10 min with open circuit. The speed of stirring was 500 rpm. The electrode was then rinsed with deionized water for 30 s. The DPASV was recorded over the range -0.2 to +0.8 V in 0.02 mol L⁻¹ KNO₃ solution. The electrode was then rinsed for 2 min in 0.05 mol L⁻¹ cysteine solution acidified with 3.0 mol L⁻¹ HCl solution with open circuit. This conditioning cycle was repeated five times for each new SiATD-GPE surface.

Determination of mercury. The SiATD-CPE electrode was placed in 25 mL of stirred 10^{-6} - 10^{-8} mol L⁻¹ mercury solution under open circuit conditions for a pre-determined time. The electrode is then removed from the pre-concentration solution, washed with water, dried with absorbent paper and placed in the measurement cell containing 0.02 mol L⁻¹ KNO₃ solution. Voltammograms were then recorded over the range -0.2 and +0.8 V. Several "cleaning" solutions were evaluated and The supporting electrolyte was changed after each measurement and the electrode was cleaned with 0.05 mol L⁻¹ cysteine solution acidified with 3.0 mol L⁻¹ HCl solution as in the conditioning step. Cysteine was used for "cleaning", due its the best cleaning efficiency and reproducibility. The electrode SiATD-CPE displayed high stability under the various adsorption-elution cycles of mercury ions, even when it was eluted using a medium of highly concentrated mineral acids.

Determination of mercury(II) in natural waters

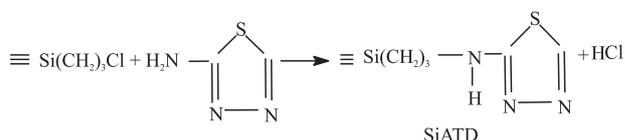
The water samples were collected from the Tiete and Pinheiros River and Ubatuba and Santos beach in São Paulo state (Brazil). Successive additions of known concentrations of mercury(II) were introduced into the reference solution of 25 mL sample of river or sea water. The mercury was determined by the DPASV method already described to obtain the dependence between peak heights and the concentration of mercury(II) (calibration plot). Finally, the mercury peaks heights of the spiked water samples were compared with a calibration plot obtained for the reference solution.

Results and Discussion

Properties of the SiATD-CPE

The preparation and the properties of the material, 3-(2-amino-1,3,4-thiadiazolyl) propyl silica gel (SiATD), used in the adsorption of heavy metals ions and in the fabrication of the graphite paste electrode, were studied by Dias Filho *et al.*²⁴

The reaction, which describes the preparation of this material can be represented by the following, where $\equiv\text{Si}(\text{CH}_2)_3\text{Cl}$ is the chloropropyl silica gel.



The complexation of mercury at the SiATD surface is achieved by direct coordination with the ligand acting possibly as a unidentate towards one metal ion,²⁴ involving sulphur and/or nitrogen atoms of the product of above reaction, 3-(2-amino-1,3,4-thiadiazolyl) propyl silica gel (SiATD).

The quantity of functional groups attached on the surface, N_0 , was 0.51×10^{-3} mol of ATD *per* gram of silica. Assuming that the molecules uniformly cover the surface, and knowing that the specific surface area was $S_{\text{BET}} = 382$ m² g⁻¹, the average density, d , of the attached molecules and the average intermolecular distance, l , can be calculated by applying the equations:

$$d = N_0 / S_{\text{BET}} \quad (2)$$

and

$$l = (1/d)^{1/2} \quad (3)$$

where N is the Avogadro's number. The calculated values are $d = 0.7 \text{ molec.nm}^{-2}$ and $l = 1.2 \text{ nm}$.

The thermogravimetric (TG) curves showed that SiATD is very stable (Figure 1), with no detectable loss of mass up to 250 °C. This experiment is important because the temperature used in the present case to degas the material under vacuum was about 100 °C. No loss of the adsorption capacity of the material was detected upon heating the sample at this temperature. The small loss of mass observed between room temperature and 100 °C is due to physically adsorbed water. To ascertain this, the TGA curve was also obtained for SiO₂ (solid line in Figure 1).

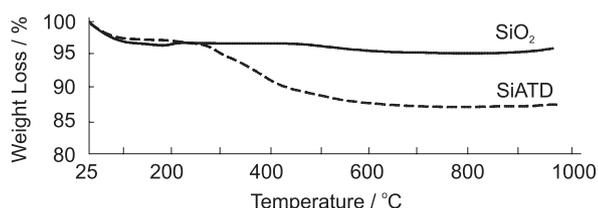


Figure 1. Thermogravimetric analyses of SiATD and SiO₂. Heating rate of 10 °C min⁻¹ under a synthetic air atmosphere.

Isotherms of adsorption. Preconcentration and recovery of metal ions

The isotherms of adsorption of metal ions by SiATD from aqueous solutions at different pH were determined for Hg(II), Cd(II), Pb(II), Cu(II), Zn(II), Co(II), Ni(II) and Mn(II) metal ions using the batch method. Fixing the initial concentration of metal ion and changing the pH solutions

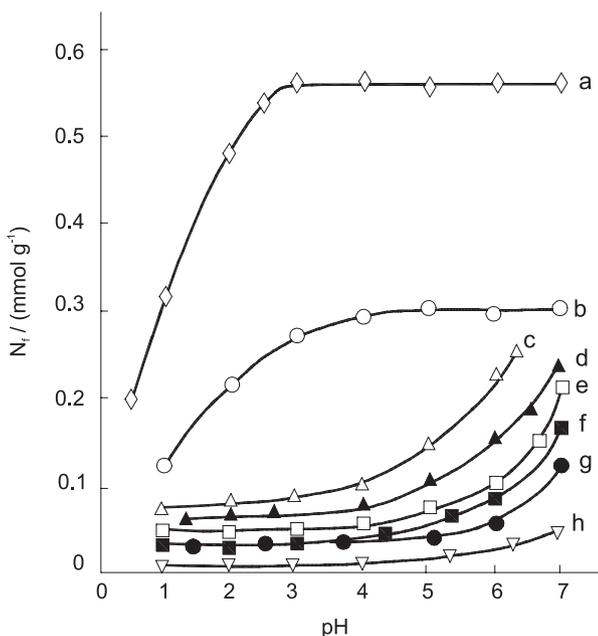


Figure 2. Isotherms of adsorption of metal ions from solutions by SiATD, as a function of pH. (a) Hg(II), (b) Cd(II), (c) Cu(II), (d) Zn(II), (e) Pb(II), (f) Co(II), (g) Ni(II) and (h) Mn(II).

and plotting N_f vs. pH, the set of curves shown in Figure 2 was obtained. For Hg(II) the adsorption achieved a constant value (saturation condition) at pH 3 with an adsorption capacity of 0.55 mmol g⁻¹. For Cd(II) the saturation condition was achieved at pH 5 with an adsorption capacity of 0.30 mmol g⁻¹. For the remaining ions, Pb(II), Cu(II), Zn(II), Co(II), Ni(II) and Mn(II), the adsorption curves did not show a plateau such as was observed for Hg(II) and Cd(II). The curves profiles observed for these ions are probably due to hydrolysis of the metal ions in the solutions phase, which may occur above pH 5,²⁵ or by the adsorption of the metal ions by the unreacted free silanol groups which are ionized, *i.e.*, $\equiv\text{SiO}^-$.²⁶

The fraction of surface-attached ligand bonded to Hg(II) ion is given by equation 4

$$\varnothing^{\max} = N_f^{\max} / N_0 \quad (4)$$

where N_0 is the amount of ATD organofunctional groups (mol) per mass of SiATD (g), and N_f^{\max} is the quantity of the adsorbed metal, N_f , under saturation conditions. The value of \varnothing^{\max} for Hg(II) in all the pH solutions range is 1.07. As $\varnothing^{\max} \approx 1$ for Hg(II), it is clear that this result provide good argument that the complexes formed, presumably, are of the type metal/ligand=1:1. The ligand ATD can act as a unidentate towards one Hg(II) ion. The coordination can occur simultaneously through nitrogen and sulfur atoms.

Preconcentration of each metal ion by SiATD from an aqueous solution was examined by column method. In the experiments, each metal was quantitatively adsorbed and was eluted according to shown in Figure 3. It can be observed that, in the experimental conditions used, only Cd(II), Pb(II), Cu(II), Zn(II), Co(II), Ni(II) and Mn(II) could be quantitatively eluted with until 0.1 mol L⁻¹ HCl or HNO₃. Mercury forms a strong complex on the surface

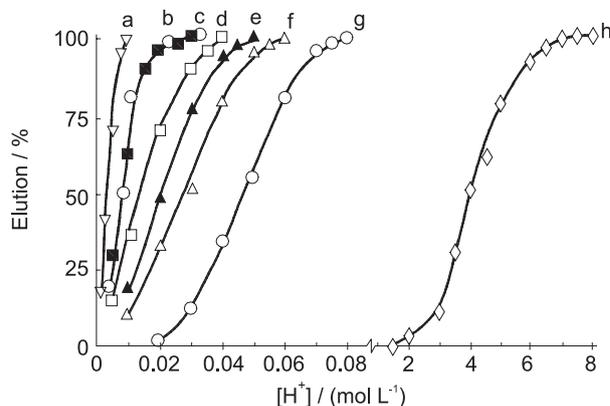


Figure 3. Elution of metal ions adsorbed on SiATD by acid solutions. (a) Mn(II), (b) Co(II), (c) Cd(II), (d) Zn(II), (e) Pb(II), (f) Cu(II), (g) Cd(II), (h) Hg(II).

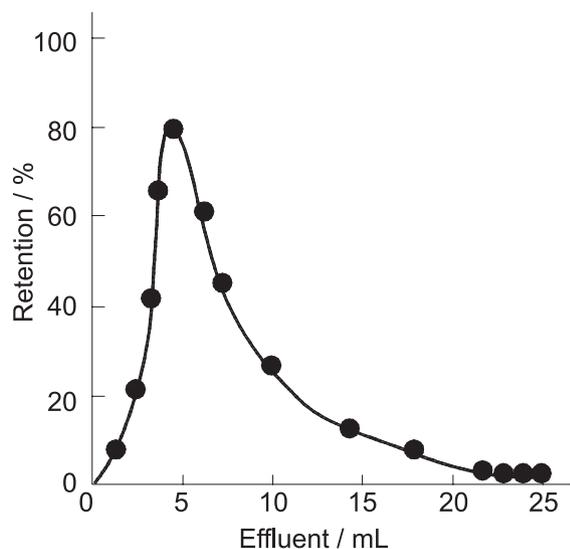


Figure 4. Elution of Hg(II) adsorbed on SiATD by 0.05 mol L⁻¹ cysteine solution in 3.0 mol L⁻¹ HCl.

of the sorbent SiATD, and therefore a quantitative desorption is possible by using hydrochloric or nitric acid at a high concentration (~8 mol L⁻¹). Quantitative elution of Hg(II) was also possible using 25 mL of 0.05 mol L⁻¹ solution of cysteine in 3 mol L⁻¹ HCl (Figure 4).

The high affinity of SiATD by Hg(II) is explained well by the Pearson rule because ATD and Hg(II) are soft base and acid, respectively.²⁷

In the studies of adsorption and recovery of a mixture of ions, could be observed that recovery of Hg(II) in the presence of other metal ions, such as Cd(II), Pb(II), Cu(II), Zn(II), Co(II), Ni(II), Mn(II), Ag(I), Bi(III), Fe(II) and Fe(III), in ten or a hundred times higher concentrations, was not significantly affected. These metals are sorbed at higher pH values, so that a selective preconcentration of Hg(II) can be carried out in their presence. A 1000-fold excess of chloride, nitrate, sulphate, fluoride, thiocyanate, bromide, phosphate, acetate, oxalate, and tartrate ions also does not interfere with the determination.

Optimization of experimental conditions

In order to establish the most suitable conditions for retention of mercury on the SiATD-CPE, several characteristics were examined. Figure 5 shows a repetitive cyclic voltammogram of mercury(II) solution in the potential range -0.2 to +0.8 V vs. Ag/AgCl, and two peaks were observed. However, the cathodic wave peak, around 0.0 V, is irregular and changes its form in each cycle. This peak at about 0.0 V is the reduction current for mercury(II) accumulated in the SiATD-CPE. The anodic wave peak at 0.30 V is well defined and does not change during the cycles. This peak is due to oxidation of the

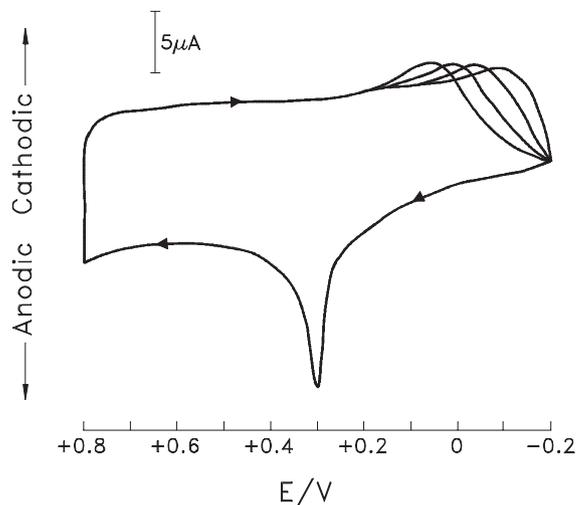


Figure 5. Repetitive cyclic voltammogram of mercury obtained at a carbon paste electrode modified with 20% of SiATD. The reference electrode was KCl saturated Ag/AgCl, and the auxiliary electrode was a platinum wire. Supporting electrolyte, 0.02 mol L⁻¹ KNO₃ solution. Concentration of Hg(II), 0.5 mg L⁻¹. Potential range, -0.2 to +0.8 V; scan rate 20 mV s⁻¹. Arrows indicate scan direction.

mercury metal. The electrode process is then irreversible and the anodic peak was therefore further investigated for analytical purposes. Since the anodic peak at 0.30 V is sharp enough to be used for the determination of mercury, the procedure including reduction of the accumulated mercury(II) is recommended. After the accumulation step made with open circuit, the electrode was placed in the voltammetric cell with the supporting electrolyte and a potential of -0.2 V was applied at the beginning of the scan. When the potential scan reaches the value of 0.30 V, an anodic peak is produced owing the oxidation of mercury as indicate the equation 5.



The scan rate of 10 mV s⁻¹ used in the differential-pulse mode showed no necessity for a fixed time at -0.2 V for the reduction of mercury and the scan started immediately after the connection of the electrodes.

For anodic stripping several media were tested (KNO₃, KCl, KSCN, KI, KNO₂, KBr and KCN). The best developed peaks were recorded in 0.02 mol L⁻¹ KNO₃. This medium allows the reduction and the anodic stripping to be done in a single electrolyte without decreasing the sensitivity and, moreover, the determination may be carried out in the presence of dissolved oxygen. This was confirmed by comparison of results obtained in aerobic and anaerobic media.

The influence of the pH solution on the accumulation of mercury(II) was examined in the concentration range 0.1-0.6 mg L⁻¹ and pH range 1.0-7.0. The signal showed

an increasing from pH 1.0 to 7.0 (Figure 6). Then, larger signals were obtained for lower acid concentration, though the dependence was not linear.

The effect of the amount of functionalized silica gel on the accumulation of mercury(II) was investigated by altering the weight ratio of modified silica gel to graphite powder in carbon paste (Table 1). For a 0.5 mg L⁻¹ mercury(II) solution the peak current increased with increasing amount of functionalized silica gel up to 20% and then remained constant and decreased above 24%. This might be related to the destruction of the mechanical integrity of the paste. It is thought that conductivity at the CMCPE is adversely affected by increasing the amount of functionalized silica gel. The ratio of functionalized silica gel to graphite in the paste was fixed at 20% so that the peak current was constant. A CMCPE with 20% functionalized silica gel was used for most of this work.

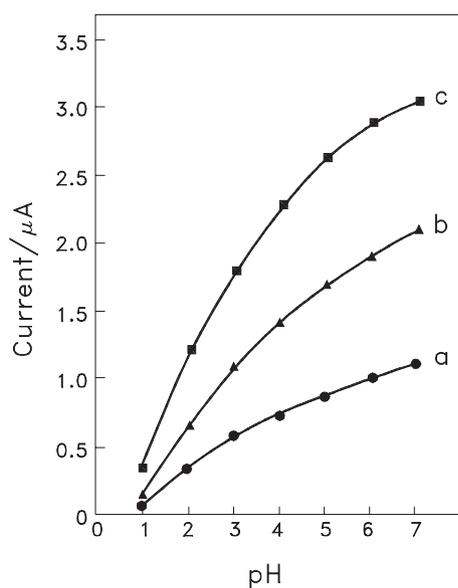


Figure 6. Dependence of the anodic peak current of Hg(II) on the pH of the preconcentration solution of Hg(II). Differential pulse anodic stripping voltammetry with 10 mV s⁻¹ scan rate, 50 mV amplitude and 5 min preconcentration time. Hg(II) concentration: (a) 0.2, (b) 0.4, (c) 0.6 mg L⁻¹.

A final parameter expected to be of primary importance to the mercury(II) preconcentration was the length of time allowed for the deposition process to take place. The results obtained as a function of accumulation time for three different mercury(II) concentrations are shown in Figure 7. For each of the three concentrations, the steady-state quantity of mercury(II) deposited was different. For each of the three concentrations the signal increased sharply until 5 min and, then, remained constant time. In all three cases, the greatest increase in current occurred in the first 3 min and this time was chosen for the preconcentration step. Compared to previously reported rates

Table 1. Effect of carbon paste composition on the peak current^a of mercury(II)

Concentration of DDTIPSG in carbon paste (%)	Current (μA)	R.S.D. (%) (n = 6)
4.0	0.97	4.5
8.0	1.32	4.1
12.0	1.60	3.7
16.0	1.85	3.8
20.0	1.97	3.5
24.0	1.87	3.0
28.0	1.50	3.9

^aCurrent intensity for accumulation at a blank silica gel paste electrode was of 0.08 μA.

of uptake of metal ions at various CMCPE surfaces, the present process was fast.²⁸⁻³¹

Calibration graph, precision, and detection limit

The calibration graph of current vs. mercury concentration in the range 0.01 - 2 mg L⁻¹ in 0.02 mol L⁻¹ KNO₃ solution for a preconcentration time of 5 min is shown in Figure 8. Figure 9 shows some voltammograms of points on this graph. The calibration graph was linear over the range 0.01 - 0.8 mg L⁻¹ mercury(II) and obey the straight-line equation 6,

$$I(\mu\text{A}) = 4.385[\text{Hg}^{2+}] - 0.030 \quad (6)$$

with a correlation coefficient of 0.998. For points between 0.8 and 2.0 mg L⁻¹, the plot shows non-linear behaviour,

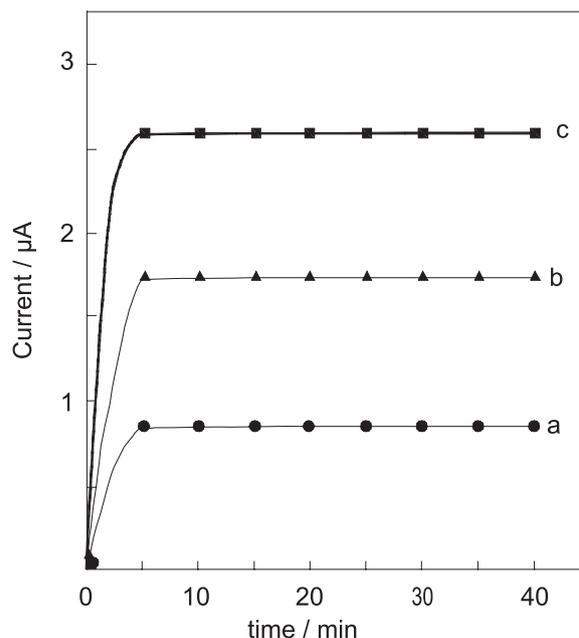


Figure 7. Dependence of the anodic peak current on preconcentration time at different mercury concentrations: (a) 0.2, (b) 0.4, (c) 0.6 mg L⁻¹.

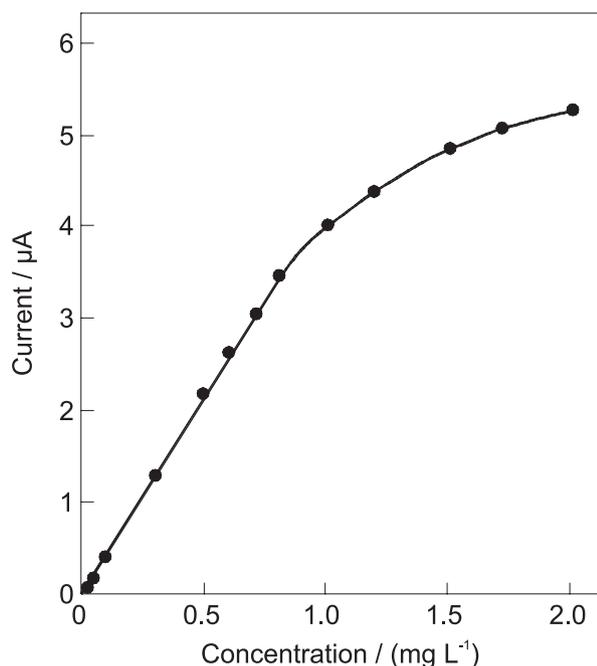


Figure 8. Calibration Graph of current *versus* mercury concentration.

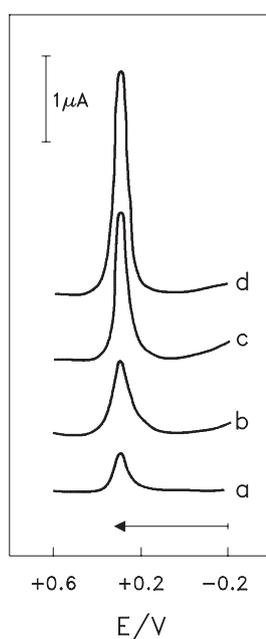


Figure 9. Differential pulse anodic stripping voltammograms for different mercury(II) concentrations, obtained after 5 min accumulation: (a) 0.1, (b) 0.2, (c) 0.4, (d) 0.6 mg L⁻¹.

which requires the use of a calibration graph in this concentration range.

The reproducible accumulation and effective cleaning was illustrated by the precision obtained for a series of six repetitions ($n=6$), with 0.03 and 0.10 mg L⁻¹ mercury(II) during a continuous 48-min period. Such series yielded a relative standard deviation of 3.6 and 2.5%, respectively. The initial preconditioning scheme (described in the

Experimental section) is essential for achieving such good precision. Reproducible results were obtained with different batches of the same modified carbon paste and functionalized silica gel.

The detection limit was estimated as 5.0 mg L⁻¹ mercury(II) by means of 3:1 current-to-noise ratio in connection with the optimization of the various parameters involved and using the highest-possible analyser sensitivity.

This detection limit is similar or lower and the concentration range with a linear response is wider than those obtained with other CMCPEs. For instance, the detection limits for the determination of Hg(II) on the carbon paste electrode modified with clay,²⁸ diphenylcarbazone,³² diphenylcarbazide,³¹ humic acid,³³ amberlite LA2,³⁴ and amberlite IRC,³⁵ are 10 µg L⁻¹, 10 µg L⁻¹, 10 µg L⁻¹, 1.0 µg L⁻¹, 1.0 µg L⁻¹, and 25 µg L⁻¹, respectively, and for a glassy carbon electrode modified with polypyrrole derivative³⁶ is 2 µg L⁻¹.

As other electrode materials like Au and Pt and other techniques, such as ICP-AES or AAS often in connection with a preconcentration step, are not the subject of this work, they are not considered here.

Influence of foreign ions and speciation

The selectivity of the chemically modified carbon-paste electrode containing silica gel functionalized with 2-amino-1,3,4-thiadiazole was evaluated by intentionally introducing concentrations of other metal ions into Hg(II) solutions during preconcentration. The ions chosen for study were Ag(I), Zn(II), Co(II), Pb(II), Cu(II), Ni(II), Mn(II), Cd(II), Bi(III), Fe(II) and Fe(III). These ions were chosen either because they have been reported to show some complexation tendencies with the 3-(2-amino-1,3,4-thiadiazolyl) propyl silica gel modifier or because they might reasonably be expected to exhibit redox activity in roughly the same potential range as Hg(II)-3-(2-amino-1,3,4-thiadiazolyl) propyl silica gel.²⁴ The interference of some anions and organic compounds have also been investigated in this work.

When Hg(II) preconcentration was performed from solutions containing known concentrations of the test ions, an appreciable effect on the analyte signal was observed only for Ag(I) and this only when the interferent was present in distinct excess. A 100-fold excess of Zn(II), Co(II), Pb(II), Cu(II), Ni(II), Mn(II), Cd(II), Bi(III), Fe(II) and Fe(III), a 1000-fold excess of SO₄²⁻, NO₂⁻, F⁻, Cl⁻ and Br⁻ had no influence on the determination of 0.05 mg L⁻¹ Hg(II). Intentional spiking of the sample solution with Ag(I) produced more serious effects. Overlapping peaks of mercury and silver occur at a concentration ratio of 60:1 ([Ag]/[Hg]),

as usually occurs in the voltammetric determination of mercury in presence of silver. A 100-fold excess of Ag(I) produced a > 40% increase in Hg response under the same preconcentration conditions that had been employed above for the other interferents. No significant effects were found in the case of molar ratio Ag(I):Hg(II), (1:50). Although the mechanism of the interference is not definitely known, the most likely explanation is that, when present in sufficient excess, other ions possessing a limited capacity for complexation with 3-(2-amino-1,3,4-thiadiazolyl) propyl silica gel can compete effectively with Hg(II) for the available modifier sites on the SiATD-CPE surface. In the presence of EDTA, cysteine, thiourea, SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, SCN^- and CN^- a gradual suppression of the Hg signal became evident. Strong chelates probably do not release Hg(II) ions even in acidic solution and the bound fraction of mercury is not accessible to determination.

The results obtained are of great importance, for instance for the analysis of natural waters. The electrode is capable of measuring mercury(II) bound in labile (halide, sulphate and hydroxide) complexes.

Determination of mercury(II) in natural waters

The determination of mercury(II) was carried out in both river and sea water. However, as expected, this method is not sensitive enough to determine the concentration of mercury(II) at its base level in these matrices, which has been quoted to be extremely low (e.g. in sea water about 2 ng L⁻¹).³⁷ Hence, the determinations were carried out in "spiked" water samples. No pretreatment of samples to remove any matrix component was carried out. The results of these analyses are given in Table 2.

Table 2. DPASV determination in natural waters containing 50 µg L⁻¹ mercury(II) (added)

Sample (place)	Hg content found (µg L ⁻¹)	R.S.D. (%) (n = 7)
River water		
Paraná River, Sao Paulo State	49	3.4
Tiete River, Sao Paulo State	52	4.1
Sea Water		
Santos Beach, Sao Paulo State	46	3.9
Ubatuba Beach, Sao Paulo State	48	3.2

Both water samples were made 50 µg L⁻¹ in mercury (II), assuming that the original content of these ions was negligible compared to the concentration that was spiked in. The mercury was determined by the DPASV method (standard addition technique) already described.

The responses of the mercury peaks in both river and sea water samples were essentially the same size. The

procedure of successive additions was applied for both solutions of samples, and it was observed that linear calibration plots had practically the same slopes. These observations and results have confirmed that the DPASV method reported in this paper can be used for practical analysis. This method can also be used as a relatively simple and quick method to determine mercury(II) in polluted and industrial waste water.

Conclusions

SiATD has been shown to be an effective solid-phase selective sorbent for Hg(II) and can also be applied in the preparation of a chemically modified carbon paste electrode (CMCPE). Formation of a stronger metal-to-sulphur donor atom bond accounts for the high affinity shown by SiATD for Hg(II) on basis of the Pearson hard-soft acid/base rule.

The carbon paste electrode modified by SiATD shows two peaks; one cathodic peak at about 0.0 V and other anodic peak at 0.30 V scanning the potential from -0.2 to 0.8 V (0.05 mol L⁻¹ KNO₃ vs. Ag/AgCl). The anodic peak at 0.30 V presents a excellent selectivity for Hg(II) ions in presence of foreign ions. The detection limit was estimated as 5 µg L⁻¹. The precision of determination is satisfactory for the respective concentration level. As it is well known in electrochemistry, if the anodic and cathodic peaks are separated by a potential range of 60 mV/n, the reaction is considered reversible.

The carbon paste electrode modified by SiATD proved to be a simple and selective sensor for the determination of mercury(II) in the trace concentration range. The considerable sensitivity and selectivity towards mercury(II) can also be useful for routine analysis.

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