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Notes

Preconcentration and Determination of Mercury(II) at a Chemically Modified Electrode Containing 3-(2-Thioimidazolyl)propyl Silica Gel

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A mercury-sensitive chemically modified graphite paste electrode was constructed by incorporating modified silica gel into a conventional graphite paste electrode. The functional group attached to the (3-chloropropyl) silica gel surface was 2-mercaptoimidazole, giving a new product denoted by 3-(2-thioimidazolyl)propyl silica gel, which is able to complex mercury ions. Mercury was chemically adsorbed on the modified graphite paste electrode containing 3-(2-thioimidazolyl)propyl silica (TIPSG GPE) by immersion in a Hg(II) solution, and the resultant surface was characterized by cyclic and differential pulse anodic stripping voltammetry. One cathodic peak at 0.1 V and other anodic peak at 0.34 V were observed on scanning the potential from –0.1 to 0.8 V (0.01 M KNO_3; $v = 2.0$ mV s^{-1} *vs.* Ag/AgCl). The anodic peak at 0.34 V show an excellent sensitivity for Hg(II) ions in the presence of several foreign ions. A calibration graph covering the concentration range from 0.02 to 2 mg L^{-1} was obtained. The detection limit was estimated to be 5 μg L^{-1}. The precision for six determinations of 0.05 and 0.26 mg L^{-1} Hg(II) was 3.0 and 2.5% (relative standard deviation), respectively. The method can be used to determine the concentration of mercury(II) in natural waters contaminated by this metal.

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Introduction

The chemical modification of electrodes is a field of growing interest in analytical chemistry. In electrochemistry, several researchers have demonstrated that chemically modified electrodes possess distinct advantages over conventional electrodes in numerous application areas including electrocatalysis, electrochemical sensors and preconcentration.[1-7]

One important matrix used for modification of graphite is a functionalized silica gel with organic[8] and inorganic compounds[9-11] in view of the well known chemical stability and preconcentration of electroactive species.

Recently, Dias Filho and his coworkers have described the preparation, characterization and uses of silica gel with functional organic materials such as 2-mercaptoimidazole groups covalently bonded on its surface.[12-18]

In a second part of these studies, we will describe the adsorptive properties of graphite paste electrodes modified with a silica gel surface chemically functionalized with 2-mercaptoimidazole and their use as selective preconcentration agents for mercury(II) ions. The organic compound, 2-mercaptoimidazole, was incorporated in the silica gel surface by reaction with (3-chloropropyl) silica gel,[13,17] resulting in the product 3-(2-thioimidazolyl)propyl silica gel (TIPSG), which was employed as the electrode surface modifier. This organic compound (2-mercaptoimidazole) belonging to soft base group has strong affinity for soft acids such as mercury(II) and a lower affinity for borderline acids (Cu^{2+}, Zn^{2+} and Pb^{2+}), the extraction behavior of which has been reported previously.[17]

Considerable attention has been devoted to the determination of Hg(II) in environmental samples, since Hg(II) and organomercury compounds are very harmful for most living organisms even in very low concentrations.[19] Mercury in various forms constitutes a serious environmental pollutant;[20,21] hence there is the need for its detection and determination, particularly at trace levels.

Mercury, which is used in gold mines, has contaminated rivers, poisoned fish stocks and now threatens the population; for instance, extraction techniques used in gold mining cause over 130 metric tons of mercury to be spilled annually in the Amazon Brazilian. Mercury contamination and large-scale destruction of aquatic ecosystems have become the focal points of environmental concerns.

Since a number of sensitive reactions of organic compounds with Hg(II) are known, chemically modified carbon paste[22-25] and glassy carbon electrodes[26,27] have been recently used to determine Hg(II) by differential pulse anodic stripping voltammetry (DPASV), often in connection with an accumulation step.

The chemical stability and selectivity of this functional group on the silica gel surface combined with electrochemical response permits its preconcentration and determination in a single step. The voltammetric measurements are preceded by chemical deposition of the analyte at the electrode surface *via* selective reaction with a specific surface modifier. In addition,

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the proposed method can be applied in the mercury removal in industrial effluents through a chromatographic column, because the adsorption process occurs in open circuit also.

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 behavior of TIPSG-GPE was monitored by cyclic voltammetry and differential pulse anodic stripping voltammetry (DPASV) techniques. A three-electrode cell involving a TIPSG-GPE as the working electrode, a Ag/AgCl combination as the reference electrode, and a Pt-wire as the auxiliary electrode were used for all investigations.

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-thioimidazolyl)propyl groups (TIPSG) was prepared according to the literature.[13,17]

Construction of the TIPSG-GPE

The chemically modified graphite paste electrodes were prepared by thorough mixing of graphite powder (Aldrich), 35% (w/w) Nujol oil (Aldrich) and silica gel functionalized with 3-(2-thioimidazolyl)propyl in proportions of 3, 6, 9, 12, 15, 18 and 21% (w/w), respectively. The electrode body was prepared 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 (i.d. 3 mm up to a height of 3.0 cm) 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.

Procedure

Electrode conditioning. Fresh TIPSG-GPE surfaces were conditioned by exposure to a 1.0 mg L^{-1} mercury solution at pH 3.0, adjusted with HNO_3, 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 cyclic voltammetry and differential pulse anodic stripping voltammetry (DPASV) was recorded over the range –0.1 to 0.8 V in 0.01 mol L^{-1} KNO_3 solution. The electrode was then rinsed for 2 min in 0.02 mol L^{-1} KCN solution with open circuit. The KCN solution removes the Hg(II) completely by complexing it with CN^- ions, recovering the active sites for mercury ions. This conditioning cycle was repeated five times for each new TIPSG-GPE surface. This way, one electrode surface can be used several times by just being cleaned in KCN between the measurements.

Determination of mercury. The TIPSG-GPE 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 pH value was kept in the range 2.0 – 5.0, adjusted with HNO_3. The electrode is then removed from the preconcentration solution, washed with water, dried with absorbent paper and placed in the measurement cell containing a of 0.01 mol L^{-1} KNO_3 as supporting electrolyte solution. Any time that has elapsed between the preconcentration step and the measurement steps is not relevant. The diffusion process of Hg(II) observed into the solution can be neglected, because mercury forms a fairly strong complex on the surface of the adsorbent, and therefore no significant desorption is possible in the studied conditions.[13,17] In this step, voltammograms were then recorded over the potential range –0.1 and 0.8 V. In these experiments several supporting electrolytes were tested and for every step the modified electrode was washed with supporting electrolyte and then cleaned with KCN as in the conditioning step.

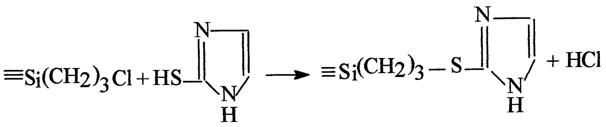
Determination of mercury(II) in natural waters

The standard addition method was used in the analysis of the ion Hg(II) of the spiked samples. The mercury was determined by the DPASV technique. Successive additions of known concentrations of Hg(II) were introduced into the reference solution of 25 mL sample of river or seawater already described to obtain the dependence between the current intensity and the concentration of Hg(II) (calibration plot). Finally, the current intensities of the spiked water samples containing mercury were compared with a calibration plot obtained for the reference solution.

Results and Discussion

Properties of the TIPSG-GPE

The preparation and the properties of the material used in the fabrication of the graphite paste electrode GPE were studied by Dias Filho and Gushikem.[13,17] The reaction which describes the preparation this material can be represented by the following equation:



TIPSG

where $\equiv Si(CH_2)_3Cl$ is the chloropropyl silica gel. The site of bonding of the 2-mercaptoimidazole molecule to the matrix is possible at both the heterocyclic nitrogen atom and the exocyclic sulfur atom. Their results favored the S atom, as shown in the equation above.

The complexation of mercury at the surface electrode is achieved by direct coordination with the ligand acting as monodentate[17] involving the sulfur atom of the product of the above reaction, 3-(2-thioimidazolyl)propyl silica gel. In neutral pH, the coordination can occur simultaneously through nitrogen and sulfur atoms, while at lower pH, only the sulfur atom is available. In acidic media the protonation of the nitrogen atom moiety group occurs; this is responsible for the coordination of the metal ion.

Optimization of experimental conditions

In order to establish the most suitable conditions for retention of mercury on the TIPSG-GPE, we examined several characteristics. Figure 1 shows a repetitive cyclic voltammogram of Hg(II) solution in the potential range –0.1 to 0.8 V *vs.* Ag/AgCl; two peaks were observed. However, the cathodic wave peak, around 0.1 V (the reduction current for Hg(II) accumulated in the TIPSG-GPE, is irregular, it changes its form in each cycle and shifts to the more negative potentials. This shift is ceased immediately after four continuous cycles.

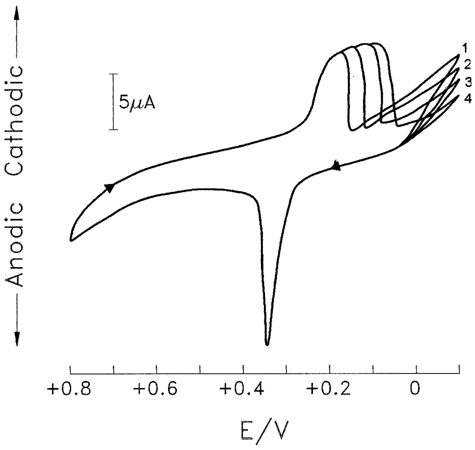


Fig. 1 Cyclic voltammogram of mercury obtained at a carbon paste electrode modified with 15% of TIPSG: 1 – 4 cycles. [Hg], 4.2 mg L^{-1}; 0.01 mol L^{-1} KNO_3; *v*, 20 mV s^{-1}.

This behavior could be tentatively attributed to the species of Hg(I) such as Hg_2^{2+} present in the sample. Such species are sorbed onto the electrode surface, possibly after new cycles in the potential range –0.1 to 0.8 V *vs.* Ag/AgCl during the reduction step causing a peak sharp deformation. On the stripping process, just before the voltammetric measurements and after the cleaning step (tested by electrochemical methods described above), the electrode was moved to another solution. As there are no Hg(II) ions in the stripping solution, the reduction of soluble Hg(II) can be excluded. The anodic wave peak verified at 0.34 V is well-defined and does not change during the cycles. This peak is due to oxidation of the overall mercury species. The separation of peaks ($\Delta E_p = E_{pa} - E_{pc}$; where E_{pa} and E_{pc} is anodic and cathodic peak respectively) for the modified electrode in the presence of mercury species was more than 0.15 V (to first cycle), indicating an irreversible process. This separation peak (0.15 V) could be attributed to the insulator nature of matrix silica (enhance electrode resistance). The electrode process is then irreversible; the anodic peak was therefore further investigated for analytical purposes. After the accumulation step made with open circuit, the electrode was placed in the voltammetric cell with the supporting electrolyte and a potential of –0.1 V was applied at the beginning of the scan. When the potential scan reaches the value of 0.34 V, an anodic peak is produced, owing the oxidation of mercury (Eq. (1)).

$$Hg^0 \longrightarrow Hg^{2+} + 2e^- \qquad (1)$$

Since the anodic peak at 0.34 V is sharp enough to be used for the determination of Hg(II), the procedure including reduction of the accumulated Hg(II) is recommended.

The scan rate that started immediately after the connection of the electrodes used in the differential-pulse voltammetry was 2 mV s^{-1}.

For anodic stripping, several alkaline salts were tested (KNO_3, KCl, KSCN, KI, KNO_2, and KBr). The best developed peaks were recorded in 0.01 mol L^{-1} KNO_3. This medium allows the reduction and the anodic stripping to be done in a single electrolyte without decreasing the sensitivity; moreover, the determination may be carried out in the presence of dissolved oxygen. This was confirmed by comparison of the results obtained in nitrogen atmosphere.

The influence of the pH solution on the accumulation of Hg(II) was examined in the concentration range 0.07 – 0.7 mg L^{-1}. The signal increases with decreasing acid concentration (Fig. 2) until pH 4 and then decreased slightly in this studied concentration range. To achieve maximum selectivity of mercury uptake, we chose the pH value of 3.0. It was observed that at pH 3.0 the method shows a better tolerance to interfering ions.

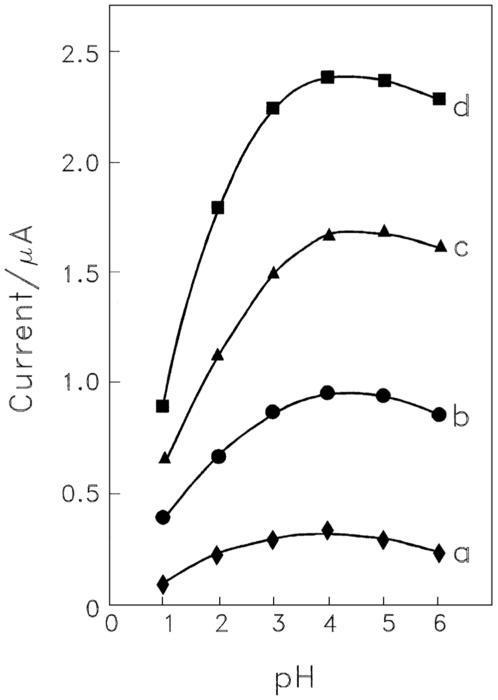


Fig. 2 Dependence of the anodic peak current of Hg(II) on the pH of the preconcentration solution of Hg(II). Differential pulse anodic stripping voltammetry with 2 mV s^{-1} scan rate, 50 mV amplitude and 10 min preconcentration time. Hg(II) concentration; a, 0.07; b, 0.3; c, 0.5; d, 0.7 mg L^{-1}. Details of the preconcentration/medium-exchange/electrochemical measurement aregiven in the Experimental section.

The effect of the amount of functionalized silica gel on the accumulation of Hg(II) was investigated by altering the weight ratio of modified silica gel to graphite powder in carbon paste. For a 0.5 mg L^{-1} Hg(II) solution the peak current increased with an increasing amount of functionalized silica gel up to 15%, and then remained constant and decreased above 18%. This might be related to the destruction of the mechanical integrity of the paste. It is thought that electron transfer at modified graphite paste electrode 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 15%, so that the peak current was constant. A modified graphite paste electrode with 15% functionalized silica gel was used for most of this work.

Several "cleaning" solutions were evaluated. The best cleaning efficiency and reproducibility were obtained with 0.02 mol L^{-1} KCN.

A final parameter expected to be of primary importance to the Hg(II) preconcentration was the length of time allowed for the deposition process to take place. In all three cases, the deposition process was relatively rapid, with 70 – 90% of the final response generated within the first 5 min of exposure. Compared to previously reported rates of uptake of metal ions at various CMGPE surfaces, the present process was fast.[22-25] The greatest increase in current occurred in the first 10 min and this

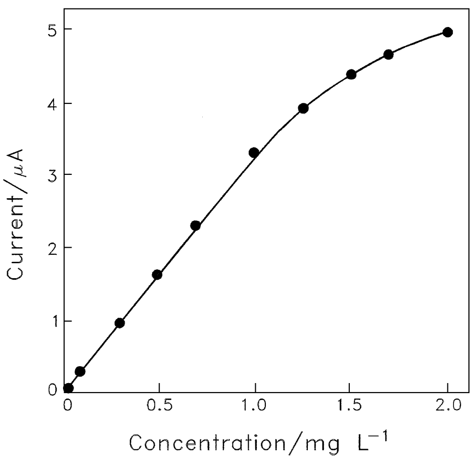


Fig. 3 Calibration graph of current *versus* mercury concentration. Other conditions as in Fig. 2.

time was chosen for the preconcentration step.

Calibration graph, precision, and detection limit

The calibration graph of current intensity *vs.* mercury concentration in the range 0.02 – 2.0 mg L^{-1} in a mixture of 0.01 mol L^{-1} KNO_3 solution for a preconcentration time of 10 min is shown in Fig. 3. The calibration graph was linear over the range 0.02 – 1.0 mg L^{-1} Hg(II) and obeys the straight-line equation:

$$I\ (\mu A) = 3.37[Hg(II)] - 0.045$$

with a correlation coefficient of 0.998. For points between 1.0 and 2.0 mg L^{-1}, the plot shows non-linear behavior, which requires the use of a calibration graph in this concentration range.

The reproducible accumulation and effective cleaning were illustrated by the precision obtained for a series of six repetitions ($n = 6$), with 0.05 and 0.26 mg L^{-1} Hg(II) during a continuous 59-min period. Such series yielded relative standard deviations of 3.0 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 µg L^{-1} mercury(II) by means of 4:1 current-to-noise ratio in connection with the optimization of the various parameters involved and using the highest-possible analyzer sensitivity. This value is higher than that for the determination of mercury by ICP-AES or AAS, often in connection with a preconcentration step[28-33] or by some special stripping voltammetric techniques.[34-36] However, the detection limit is lower and the concentration range with a linear response is wider than those obtained with other CMGPEs[22-25] and near one obtained for a glassy carbon electrode.[26] For instance, the detection limits for the determination of Hg(II) on the carbon paste electrode modified with clay,[22] diphenylcarbazone,[23] diphenylcarbazide,[24] humic acid,[23] are 10, 10, 1, 0.1 µg L^{-1}, respectively, and for a glassy carbon electrode modified with polypyrrole derivative[26] the limit is 2 µg L^{-1}.

Influence of foreign ions and speciation

The selectivity of the chemically modified carbon-paste electrode containing silica gel functionalized with 2-mercaptoimidazole 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), Tl(I), Te(IV), Fe(II) and Fe(III). These ions were chosen either because they have been reported to show some complexation tendencies with the 3-(2-thioimidazolyl)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-thioimidazolyl) propyl silica gel. The interference of some anions and organic compounds has 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) present in distinct excess (10-fold). A 100-fold excess of Zn(II), Co(II), Pb(II), Cu(II), Ni(II), Mn(II), Cd(II), Bi(III), Tl(I), Te(IV), Fe(II) and Fe(III), a 1000-fold excess of SO_4^{-2}, NO^{-2}, F^- and a 500-fold excess of Cl^- had no influence on the determination of 0.1 mg L^{-1} Hg(II) at pH 3, adjusted with HNO_3, for 10 min preconcentration. In practice, thousand-fold excesses were able to be tolerated before the Hg(II) quantification began to be affected. In this cases, no new redox waves indicative of formation and carry-over of the interferents were observed; rather, a gradual suppression (*e.g.*, a 30% decrease for a 1000-fold interferent level) of the Hg signal became evident. 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 10:1 ([Ag]/[Hg]), as usually occurs in the voltammetric determination of mercury in the presence of silver. A 15-fold excess of Ag(I) produced a >30% increase in Hg(II) response under the same preconcentration conditions that had been employed above for the other interferents. In the presence of EDTA, cysteine, thiourea, SO_3^{-2}, $S_2O_3^{-2}$ and CN^-, the mercury peak almost disappears. 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 in the analysis of natural waters. In comparison, different from the method described by Sousa,[35] the lower conductivity of functionalized silica due its insulator nature, does not intervene in the mercury determination. The electrode is capable of measuring Hg(II) bound in labile (halide, sulfate and hydroxide) complexes. Methyl mercury compounds and Hg(I) can also be determined with this electrode.

Determination of Hg(II) in natural waters

The determination of Hg(II) was carried out in both river and sea water. However, as expected, this method is not sensitive enough to determine the concentration of Hg(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}).[36] 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 1.

Both water samples were made 100 µg L^{-1} in Hg(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, and the difference between the results in Table 1 can probably be explained as due to the effect of the different organic and inorganic constituents

Table 1 DCASV determination in natural waters containing 100 μg L^{-1} mercury(II) (added)

Sample (place)	Hg content found/μg L^{-1}	RSD (n = 6), %
River water		
Pinheiros River (Sao Paulo State)	105	3.9
Tiete River (Sao Paulo State)	108	4.5
Sea water		
Santos Beach (Sao Paulo State)	96	3.5
Ubatuba Beach (Sao Paulo State)	98	3.2

in each matrix. 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; its application would, however, be limited to heavily polluted water systems.

Conclusions

The graphite paste electrode modified by TIPSG show two peaks: one cathodic peak at –0.1 V and one anodic peak at 0.34 V, on scanning the potential from –0.1 to 0.8 V (0.01 M KNO_3 *vs*. Ag/AgCl). The separation of peaks (ΔE_p) is more than 0.15 V, indicating an irreversible process. The anodic peak at 0.34 V presents a excellent selectivity for Hg(II) ions in the presence of foreign ions. The detection limit was estimated as 5 μg L^{-1}. The precision of determination (n = 6) is satisfactory for the respective concentration level. Storage of the electrode in air for several weeks has no influence on its function. On the other hand, a simple preparation of working electrode (compared to either the fabrication of modified solid electrodes or the expensiveness of gold electrodes), together with the exploitation of short deposition times (in contrast to other procedures) can be advantageous. Even so, the sensitivity and selectivity towards Hg(II) can be sufficient for routine analysis.

This method is relatively easy and has proved to be a simple and selective sensor for the determination of Hg(II) in the trace concentration range, for instance in polluted and industrial waste water. An electrode surface renewal is not necessary as only a simple electrode washing is enough before each experiment.

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