

New Pb²⁺ Carbon Paste Electrode based on Organically Modified Silicate and its Square Wave Anodic Stripping Voltammetric Response for Pretreated Gasoline Samples

William S. Cardoso,^a Teresa Cristina Oliveira da Fonseca,^b
Aldaléa L. B. Marques^c and Edmar P. Marques^{*,d}

^aDepartamento de Química e Biologia, Universidade Estadual do Maranhão,
Cidade Universitária Paulo VI, CP 09, 65055-970 São Luís-MA, Brazil

^bCentro de Pesquisas e Desenvolvimento Leopoldo Américo Miguez de Melo - CENPES -
PETROBRAS, 21941-915 Rio de Janeiro-RJ, Brazil

^cDepartamento de Química Tecnológica and ^dDepartamento de Química, Universidade Federal do
Maranhão, Av. dos Portugueses s/n, 65085-580 São Luis- MA, Brazil

Este trabalho descreve um procedimento analítico para a determinação de íons chumbo (II) por voltametria de redissolução anódica de onda quadrada em amostra de gasolina pré-tratada e a avaliação de um eletrodo de pasta de carbono modificada com um material híbrido inorgânico-orgânico (aminopropil preso a uma rede de sílica (APSil) obtido *via* a rota sintética sol-gel) como um sensor eletroquímico. As condições ótimas de análise dos íons Pb²⁺ foram as seguintes: a composição de APSil na pasta de carbono foi 40% (em massa); o pH da solução de deposição igual a 1,8; o potencial de acumulação igual -0,7 V vs. Ag/AgCl e o tempo de deposição de 600 s. No estudo de interferentes observou-se que somente a espécie Cu²⁺, presente em concentração cinco vezes maior interferiu significativamente na resposta de redissolução.

An analytical procedure for determining Pb²⁺ by square wave anodic stripping voltammetry in pretreated gasoline sample is described and a carbon paste electrode modified with a inorganic-organic hybrid material (aminopropyl linked to the silica network (APSil) obtained by the sol-gel method) was evaluated as an electrochemical sensor. The optimum conditions for the analysis of Pb²⁺ ions were presented as follows: composition of APSil on the carbon paste electrode 40% (wt.%); deposition solution of pH 1.8; accumulation potential of -0.7 V vs. Ag/AgCl and deposition time of 600 s. Interference studies indicated that only Cu²⁺, at a 5-fold excess, interfered drastically on the stripping response of Pb²⁺.

Keywords: inorganic-organic hybrid, lead determination, stripping voltammetry, carbon paste electrode

Introduction

Many heavy metals ions are found at several products related to the industry of the petroleum, for example gasoline, diesel oil. Their presence, even in low concentrations can affect petroleum processing and impose economical setbacks to the petroleum industry¹ as well as to the environment.² Presence of trace metals in fuels is usually undesirable causing decomposition and poor performance of fuel, corrosion of engine and formation of sediments.³ Therefore, it is necessary to develop analytical techniques capable of detecting trace levels of these metal ions in fuel

matrices. Several techniques have been employed for such purpose.⁴⁻¹⁰ However, electrochemical methods such as anodic stripping voltammetry is one of the most favorable for determination of traces of numerous metals, including Pb²⁺,^{11,12} due its simplicity, relative low cost, fast analysis and good performance in terms of detectability, selectivity and accuracy.

Anodic stripping voltammetry (ASV) presents two principal steps: reducing metal ions to zero valence at the electrode surface, and oxidizing the reduced species while sweeping a positive potential (stripping). The reduction step enables analyte preconcentration at the working electrode, improving sensitivity of the ASV methods.¹³ Chemically modified electrodes using hybrid materials

*e-mail: edmarmarques@superig.com.br

(nanocomposites), obtained by combination of silica and groups containing N, S or O, offer new approaches for the development of improved stripping voltammetric methods.

In this work, the preparation of hybrid material by the sol-gel reaction of 3-aminopropyltriethoxysilane (APTES) and tetraethylorthosilicate (TEOS) is presented. The use of this material to modify carbon paste and the application of the APSil modified carbon paste electrode for the determination of Pb²⁺ by square-wave ASV is evaluated.

Experimental

Reagents and solutions

Metal standard solutions were prepared by diluting standard stock solution (1000 mg L⁻¹) (atomic absorption spectrometric grade, Merck). All other reagents were of analytical grade purity and used without further purification. High purity de-ionized water was used to prepare the solutions from a Nanopure water system (NANOPURE Infinity, Barnstead model). Nitrogen gas (99.999%) was used for purging oxygen in a solution. The pH was adjusted to the desired values by adding controlled amounts of 0.1 mol L⁻¹ NaOH solution in the pH range from 1.0 to 5.0. All measurements were performed at a temperature of 25 ± 2 °C.

Preparation of hybrid material

The xerogel of hybrid nanocomposite (APSil) was prepared according to the following procedure: a solution containing 40.0 mL of TEOS (0.088 mol) and ethanol (TEOS/ethanol 1:1 v/v) was prepared, and added 1.9 mL of 0.75 mol L⁻¹ HCl aqueous solution. The mixture was stirred for 3 h at 343 K. The resulting solution was allowed to cool to room temperature and then 130.0 mL of ethanol and 5.6 mL of 0.93 mol L⁻¹ HCl aqueous solution were added and stirred for 2 h. Then, 5.2 mL of APTES (0.022 mol) was added dropwise, and the formed gel was diluted by further addition of 150.0 mL of ethanol with vigorous stirring at room temperature for 2 h. Finally, the solution was carefully heated at 333 K until complete evaporation of solvents. The xerogel was ground to a fine powder, and then it was exhaustively washed with ethanol in a Soxhlet apparatus (8 h) and, as final step, immersed in demineralized water. The xerogel was filtered and dried in an oven at 323 K. For the sake of brevity, the hybrid material will hereafter be designated as APSil.

Spectroscopic measurements

In order to characterize the APSil infrared spectra from pressed KBr pellets containing 1% (wt.%) of

material were obtained using a spectrophotometer Bomen Hartmann and Braun, MB series with 4 cm⁻¹ resolution and 50 cumulative scan.

Electrochemical measurements

All the electrochemical measurements were performed using an Autolab PGSTAT 30 potentiostat-galvanostat apparatus. All the experiments were carried out in an electrochemical cell filled with 10.0 mL of 0.1 mol L⁻¹ HNO₃ aqueous solution (pH 1.8). A platinum wire (auxiliary electrode), a saturated Ag/AgCl reference electrode, and a carbon paste electrode (area of 0.21 cm²) modified with APSil as a working electrode were employed. The modified carbon paste was prepared by hand-mixing graphite powder and APSil in a 40:60 ratio (wt.%) with a small amount of liquid hydrocarbon (used as binder) to obtain a uniform paste. The paste was introduced into a cavity with 0.1 cm of depth, in contact with a platinum disc having an area of 0.3 cm² fused to a glass tube.

Analytical procedure

The electrochemical measurement consisted of accumulation Pb²⁺ at -0.7 V vs. Ag/AgCl for 600 s, then the square wave stripping voltammograms were recorded from -0.70 to -0.4 V after 10 s quiescence (frequency: 50 Hz, step potential: 0.3 mV, pulse: 0.075V). The solutions were not degassed during this stage of the experiment.

Digestion of gasoline sample in closed system

The digestion of common gasoline sample was carried out at a microwave MULTIWAVE oven of the Anton Paar with high pressure according following program in Table 1. Each sample of gasoline (300 mg) was digested with a combination of 4.0 mL concentrated HNO₃ and 2.0 mL of hydrogen peroxide. After the high pressure vessel was completely cooled, the digestion solution was diluted to 25.0 mL with deionized and ultrapure water. This procedure was also repeated for the blanks.

Results and Discussion

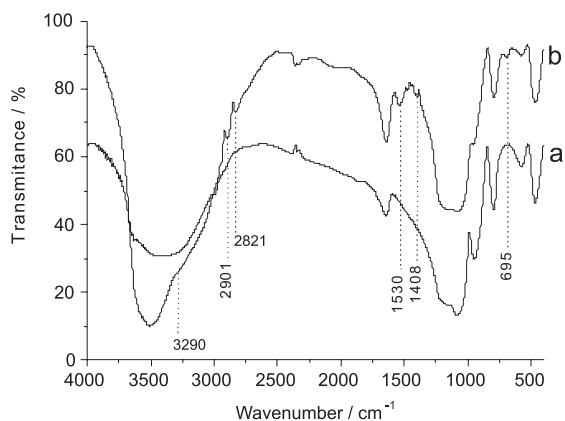
Characterization of APSil using infrared spectroscopy

FTIR spectra of silica powder before and after reaction with APTES showed considerable changes associated to the inorganic-organic hybrid material formation. It was clear appearance of primary amine stretch. Figure 1 shows FTIR spectra of silica, obtained from hydrolyze

Table 1. Heating program with microwave radiation

Step	Power (w)	time (min)	Ventilation
1	500	10	1
2	1000	10	1
3	0	15	3

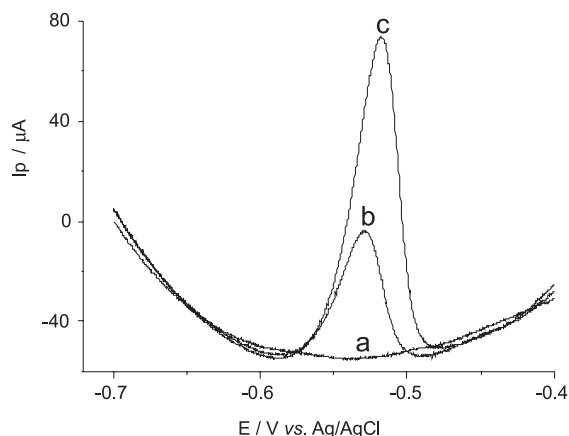
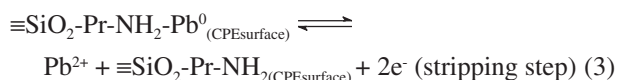
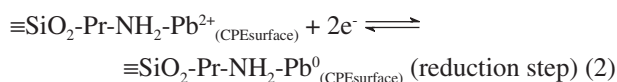
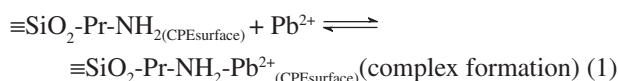
and condensation reactions of TEOS (Figure 1a) and APSIL formation (Figure 1b). The characteristic Si–O–Si bands at 1200, 1079, 948 e 791 and 465 cm^{-1} are related with the condensed silica network and it can be seen at both spectra.¹⁴⁻¹⁷ In Figure 1b, a weak band at 695 cm^{-1} attributed to the N–H stretching mode confirms incorporation of amino group to the silica network.¹⁵⁻¹⁷ Another absorption band at 1530 cm^{-1} , which can be assigned to the symmetric $-\text{NH}_3^+$ bending vibration is observed due a part of amino group to be protonated by residual silanol groups during synthesis of hybrid material.¹⁸ A very weak intensity band at 1408 cm^{-1} is ascribed to the deformation mode of COO^- produced from reaction between CO_2 present in air and aminopropil group on silica matrix.¹⁶ Still in Figure 1b, in the higher frequency region, the presence of aminopropil groups was corroborated by presence of two weak bands at 2821 and 2901 cm^{-1} attributed to the symmetric and asymmetric stretching vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ groups, respectively.^{15,17} There is a weak absorption band around 3290 cm^{-1} which appears as a small shoulder superimposed with a broad side band, which can be attributed to the stretching vibration mode of NH_2 groups.^{16,17} The infrared spectrum of the APSil is consistent with the spectrum of the similar material reported in the literature.¹⁶⁻²³ This result confirms that the target hybrid nanocomposite was successfully synthesized in this work.

**Figure 1.** FTIR spectra of (a) SiO_2 and (b) APSil.

Electrochemical measurements

Typical square wave voltammograms obtained using recommended procedure specified in section analytical

procedure are shown in Figure 2. No electrochemical process is observed on bare carbon paste electrode surface (Figure 2a) even after application of a deposition potential, but when the APSil modified carbon paste was used, one anodic peak was observed at $-0.53 \text{ V vs. Ag/AgCl}$ (Figure 2b). The intensity of this peak increased proportionally with the concentration of Pb^{2+} in the electrochemical cell (Figure 2c). Lead could be reconcentrated in the APSil carbon paste modified electrode and the possible mechanism involved may be described by the following reactions:^{14, 24, 25}

**Figure 2.** Square wave voltammograms obtained in $0.1 \text{ mol L}^{-1} \text{HNO}_3$ aqueous solution at carbon paste electrode: (a) Bare electrode in $7.0 \times 10^{-7} \text{ mol L}^{-1} \text{Pb}^{2+}$ aqueous solution, (b) modified with APSil in $7.0 \times 10^{-7} \text{ mol L}^{-1} \text{Pb}^{2+}$ aqueous solution, (c) modified with APSil in $1.0 \times 10^{-6} \text{ mol L}^{-1} \text{Pb}^{2+}$ aqueous solution. After deposition for 600 s at pH 1.8, deposition potential: $-0.7 \text{ V vs. Ag/AgCl}$.

Effect of carbon paste composition

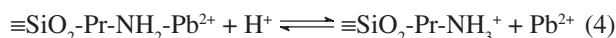
According to the equation 1 the efficiency of modified carbon paste electrode towards accumulation of Pb^{2+} on electrode surface is based on the complex formation between metal ion and APSil. Therefore, quantitative estimation of APSil in the carbon paste was studied. Six different modified carbon paste compositions (10, 20, 30, 40, 50 and 60% APSil (wt.%)) were tested. The maximum current was obtained when the APSil composition in the paste was 40%. Higher concentration of APSil ($\geq 50\%$) decreased the peak current significantly because in this

case an additional amount of modifier, in the carbon paste, increased the resistance of electrode, thus the peak current decreased.

Effect of pH

The influence of the pH using 0.1 mol L⁻¹ HNO₃ aqueous solution on the preconcentration of Pb²⁺ was studied at the pH range from 1.0 to 5.0. The pH was adjusted with 0.1 mol L⁻¹ NaOH aqueous solution. The results showed that the anodic peak current is strongly dependent of the pH value, it decreased abruptly with increasing pH up to 4.5 and then remained close to zero in pH range 5. The maximum peak current is generated at pH 1.0. The pH 1.8 was chosen instead pH 1.0 to avoid work at boundary condition.

APSil has properties that accredit it to be an electronic insulating, so the voltammetric detection of the previously accumulated Pb²⁺ implies a desorption process.²⁴ According to the study of effect of pH, a strongly acidic medium was selected as better suitable for desorption described by following reaction:



Stronger acidic medium favors Pb²⁺ leaching out from the APSil at the electrode/solution interface and consequently improvement voltammetric detection.

Effect of deposition potential

The dependence of the anodic current peak on the deposition potential was studied over the range of -0.9 to -0.5 V vs. Ag/AgCl. As it can be depicted from Figure 3 the highest peak current was obtained when the initial potential was set at -0.7 V vs. Ag/AgCl. At this negative overpotential, a fast reduction of Pb²⁺ takes place.

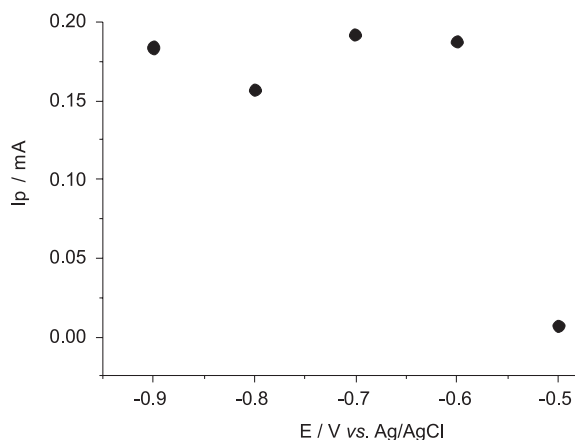


Figure 3. Effect of deposition potential on the anodic peak current. Same conditions as Figure 2.

Therefore, the potential of -0.7 V was chosen as the most suitable for lead determination.

Effect of accumulation time

As for any technique voltammetric employing a preconcentration step, the choice of accumulation time has a significant importance on the stripping peak response.²⁶ In Figure 4, the effect of varying deposition time on anodic peak current using the APSil modified carbon paste electrode is shown for an aqueous solution containing 1.0 × 10⁻⁵ mol L⁻¹ Pb²⁺. The anodic current peak increased linearly with increasing deposition time from 60 to 720 s. For higher deposition times, the anodic current decreases, indicating there was attainment of equilibrium between the bound Pb²⁺ specie on the electrode surface and the ions in solution. In order not to extend accumulation time, it was decided that 600 s were an adequate period of time for voltammetric measurements of Pb²⁺. The optimum conditions for the analysis of Pb²⁺ are summarized in the Table 2.

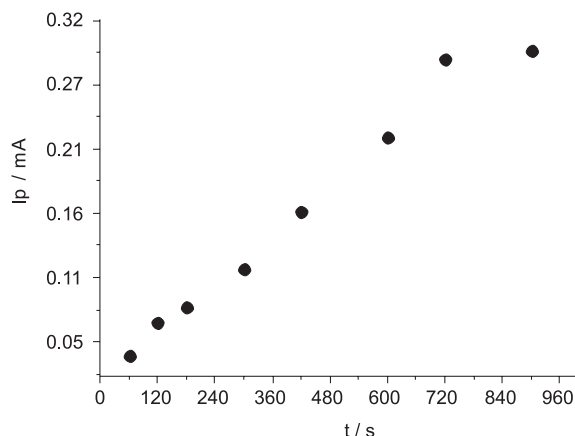


Figure 4. Effect of accumulation time on the square wave stripping voltammetric peak current. Same conditions as Figure 2.

Table 2. Optimum conditions for the analysis of Pb²⁺ using APSil modified carbon paste electrode

Effect	Optimum condition
Carbon paste composition	40% (wt.%)
pH	1.8
Deposition potential	-0.7 V vs. Ag/AgCl
Accumulation time	600 s

Effect of other ions

The selectivity of the APSil modified carbon paste electrode towards Pb²⁺ was studied by testing different metal ions as potential interferents (in mol L⁻¹) using the

same procedure optimized for Pb^{2+} determination. The experimental results are presented in Table 3. Most of the ions studied had only a little effect on the anodic peak current intensity of Pb^{2+} , such as Ca^{2+} , Fe^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Na^{2+} (up to 100-fold excess); Zn^{2+} (up to 50-fold excess) and Mg^{2+} (up to 25-fold excess). Only Cu^{2+} at a 5-fold excess interfered drastically the stripping response for Pb^{2+} , causing a decrease of 44.4% in voltammetric peak current. However, when the recommended procedure was applied to the determination of Pb^{2+} using equal amount of Cu^{2+} no interference was observed. Cu^{2+} interferes significantly by decreasing the Pb^{2+} signal, because there is a strong competition between both metals for complex formation with APSil on the carbon paste electrode surface.²⁵

Table 3. Change in SWASV peak current of $1.0 \times 10^{-5} \text{ mol L}^{-1} \text{ Pb}^{2+}$ in the presence of other ions

Interfering ion	Concentration (mol L^{-1})	Change of current (%)
Ca^{2+}	1.0×10^{-3}	-1.76
Fe^{2+}	1.0×10^{-3}	+2.42
Cd^{2+}	1.0×10^{-3}	+8.19
Co^{2+}	1.0×10^{-3}	+0.67
Ni^{2+}	1.0×10^{-3}	-3.12
Na^{+}	1.0×10^{-3}	+1.77
Zn^{2+}	5.0×10^{-4}	+4.80
Mg^{2+}	2.5×10^{-4}	-2.87
Cu^{2+}	5.0×10^{-5}	-44.4
Cu^{2+}	2.0×10^{-5}	-7.41
Cu^{2+}	1.0×10^{-5}	+0.01

Determination of Pb^{2+} in pretreated gasoline sample

The concentration of lead in pretreated gasoline sample was determined by the standard addition method. Solutions of known concentrations (over the range of 2.0×10^{-7} to $1.4 \times 10^{-6} \text{ mol L}^{-1}$) of Pb^{2+} were added to the pretreated gasoline sample. Representative square wave anodic

stripping voltammograms at different concentrations of Pb^{2+} under optimum conditions are shown in Figure 5. The anodic peak current increased linearly with increasing concentration up to $1.4 \times 10^{-6} \text{ mol L}^{-1}$ of Pb^{2+} (inserted Figure.) and its linearity was described by the equation: $I_p \text{ (mA)} = 2.6 (\pm 1.4) + 3.3 (\pm 0.2) \times 10^7 [\text{Pb}^{2+}] \text{ (mol L}^{-1}\text{)}$ with linear correlation coefficient equal to 0.990. A limit of detection was found to be $3.8 \times 10^{-8} \text{ mol L}^{-1}$ ($7.9 \mu\text{g L}^{-1}$) as a signal/noise ratio of 3.

Table 4 presents summary of the results obtained from three determinations of Pb^{2+} in pretreated gasoline samples. The precision of results was checked by the reproducibility of voltammetric analysis results and relative standard deviation was 2.1%. These observations shows that the carbon paste electrode modified with APSil can be used for Pb^{2+} determination in pretreated gasoline sample.

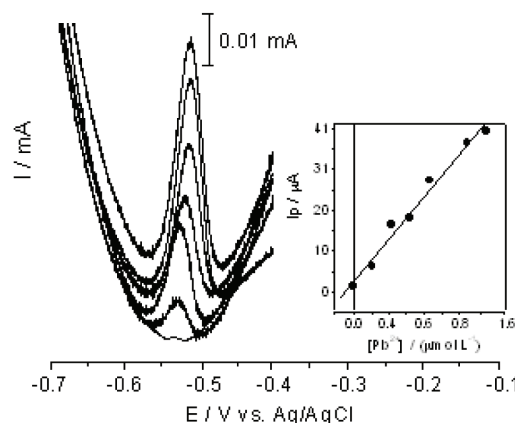


Figure 5. Square wave anodic stripping voltammograms of Pb^{2+} accumulated on APSil modified carbon paste electrode (40% (wt.%) in pretreated gasoline sample, pH 1.8. After addition of $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ Pb}^{2+}$ standard solution aliquots (mL): 20, 40, 60, 80, 120 and 140. Preconcentration time 600 s. Deposition potential $-0.7 \text{ V vs. Ag/AgCl}$. Inserted Figure: Plot I_p vs. $[\text{Pb}^{2+}]$.

Conclusion

The experimental results presented in this work showed that carbon paste electrode modified with hybrid composite

Table 4. Determination of Pb^{2+} in pretreated gasoline sample by square wave anodic stripping voltammetry. Digestion of gasoline in closed system

Parameters	Pretreated gasoline samples		
	Sample 1	Sample 2	Sample 3
Linear coefficient	0.74 ± 1.1	1.59 ± 1.2	2.58 ± 1.4
Slope	$(1.9 \pm 0.16) \times 10^7$	$(2.01 \pm 0.17) \times 10^7$	$(3.25 \pm 0.18) \times 10^7$
r	0.991	0.990	0.990
n	5	6	7
$[\text{Pb}^{2+}] \text{ (mg L}^{-1}\text{)*}$	0.27	0.28	0.28

*Correction of dilution factor (df): df = 100, for the sample 1 and df = 50, for the samples 2 and 3.

APSil (aminopropyl linked to the silica network obtained by the sol-gel method) has specific properties that enables it to be used such as simplicity of electrode preparation, ability of aminopropyl groups to adsorb Pb²⁺ from aqueous solution in acid medium (pH 1.8 using HNO₃ solution) and high stability. These conditions revealed satisfactory analytical performance and better suitable for desorption process becoming the electrode as a useful device for Pb²⁺ determination by square wave stripping voltammetry. Under optimum conditions, the method developed to measure Pb²⁺ in pretreated gasoline sample is very promising presenting a satisfactory linear response, a wide linear range, good limit of detection (3.8×10^{-8} mol L⁻¹ (7.9 mg L⁻¹)). The procedure is not interfered significantly by other metal ions and its reproducibility of voltammetric analysis results was excellent with relative standard deviation of 2.1%.

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