**Full Paper**

# Study of the Responses of a Sonogel-Carbon Electrode Towards Phenolic Compounds

*M$^a$ del Mar Cordero-Rando, Ignacio Naranjo-Rodríguez, José M$^a$ Palacios-Santander, Laura M$^a$ Cubillana-Aguilera, José Luis Hidalgo-Hidalgo-de-Cisneros**

Departamento de Química Analítica, Universidad de Cádiz, Polígono Río San Pedro, Apartado 40, 11510, Puerto Real, Cádiz, Spain
*e-mail: jluis.hidalgo@uca.es

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**Abstract**

The electrochemical behavior of a sonogel-carbon electrode towards nine phenolic compounds (chloro-, nitro- and alkyl-phenols) was studied; one of them (4-chloro-3-methylphenol) was used to evaluate characteristics of the electrode, such as accumulation and cleaning procedure of the electrode surface, reproducibility of the measurements, and influence of time from fabrication on electrochemical response. A polyethyleneglycol-modified sonogel-carbon electrode was found to improve the electrochemical response towards the analyte. A linear relationship between peak height and concentration in the range 0.005 – 0.5 mg $L^{-1}$ was obtained, with a detection limit of 2.8 μg $L^{-1}$. The studies of electrochemical parameters, as well as interferences, are also included.

**Keywords:** Sonogel-carbon electrode, Phenolic compounds, Differential pulse voltammetry, Polyethyleneglycol-modified electrode

## 1. Introduction

The use of sol-gel chemistry to produce electrical conducting matrixes based on graphite gave as a result the carbon ceramic electrodes, CCEs [1, 2]. The incorporation of graphite to the sol-gel precursors has given rise to malleable materials that can take any configuration. These materials allow making sensors with chemical and/or biological modifications, renewable surface and relative chemical inertness towards several solvents.

Nowadays there is a great interest in the developing and application of new graphite-based sol-gel electrodes, with the aim to have alternatives to other solid electrodes [3 – 6]. Following this idea, we have proposed a procedure to yield solid carbon composite materials for the preparation of sol-gel electrodes using sonocatalysis. By means of the direct application of high-energy ultrasound to the sol-gel precursors in acidic media, hydrolysis is carried out for a short time and without the presence of alcoholic solvents. The mixture of the sonogel obtained with spectroscopic grade graphite leads to a new type of sol-gel electrodes: the sonogel-carbon electrodes [7 – 10].

The sonogel-carbon electrodes show the general good properties of the other CCEs. Besides, in comparison with other carbon electrodes, they exhibit especially favorable electrochemical properties. Moreover, the electrodes show direct response towards a large group of organic compounds and several metallic ions. Thanks to these properties, and their stability, these electrodes show good characteristics to be used as electrochemical sensors.

On the other hand, phenols are compounds of the greatest interest from an environmental point of view [11, 12]. Phenol and its derivatives are between the more widely used chemicals in industry [13 – 15]. Consequently phenols have been found as air, water and soil pollutants. The seriousness of the environmental pollution by phenols is due to the high toxicity of many substituted phenolic compounds for living creatures [16]. For these reasons, phenols are included in the Priority Lists of all environmental agencies, and numerous procedures have been developed for their study [17 – 19].

In this article, nine phenols have been used to prove the good behavior of a sonogel-carbon electrode. They were chosen as follows: four chlorophenols (2-chlorophenol; 4-chloro-3-methylphenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol), four nitrophenols (2-nitrophenol; 4-nitrophenol; 2-methyl-4,6-dinitrophenol; picric acid) and one alkylphenol (2,4-dimethylphenol). 4-Chloro-3-methylphenol was considered as the proof analyte. The results show the good properties of this type of electrodes to be used as detectors.

## 2. Experimental

### 2.1. Reagents and Materials

Methyltrimethoxysilane (MTMOS) was from Merck (Darmstad, Germany) and HCl was from Panreac (Barcelona, Spain). Boric acid, ortho-phosphoric acid, acetic acid and sodium hydroxide for Britton-Robinson buffer solution were from Merck. Polyethyleneglycol (PEG, MW 550) was from Aldrich (Milwaukee, WI). All reagents were of analytical grade or higher, and used as received without further purification. Graphite powder (spectroscopic grade RBW) was from SGL Carbon (Ringsdorff, Germany).

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Nanopure water was obtained by passing twice-distilled water through a Milli-Q system (18 MΩ · cm, Millipore, Bedford, MA). Pollutants tested in this work (2,4-dimethylphenol, picric acid, 4-nitrophenol, 2-nitrophenol, 2-methyl-4,6-dinitrophenol, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, pentachlorophenol, 2,4-dichlorophenol,) were of analytical grade, and purchased from Merck, Panreac, Fluka, (Buchs, Switzerland), Riedel (Seelze, Germany) or Supelco (Bellefonte, Pennsylvania).

Pollutant stock solutions (500 mg $L^{-1}$) were prepared in ethanol (Merck); working solutions were prepared daily by diluting with ethanol.

Glass capillary tubes, i.d. 1.15 mm, were used as the bodies for the composite electrodes.

### 2.2. Instrumentation

All the electrochemical measurements were performed with an AutoLab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat interfaced with a personal computer, using the AutoLab software GPES for waveform generation and data acquisition and elaboration. The experiments were carried out in a single compartment three-electrode cell, at room temperature ($25 \pm 1\,^{\circ}$C), and under nitrogen atmosphere. The counter electrode was a platinum wire and a silver/silver chloride/3 M KCl electrode was used as the reference. The composite-filled glass capillary tubes were used as the working electrode.

A 600-Watt Model, 20 kHz ultrasonic processor (Kontes, Dusseldorf, Germany) equipped with a 13 mm titanium tip was used. The ultrasonic processor was enclosed inside a sound-proof chamber during operation.

Scanning electron microscopy (SEM) studies were carried out on a JSM 820 instrument (JEOL, Japan) operating at 30 keV and equipped with a Microanalyzer AN/10000.

Differential pulse voltammetry (DPV) was the electrochemical technique applied to study the behavior of the sonogel-carbon electrodes. For the study of pollutants, DPV was carried out from 0 to $\pm 1.25$ V depending on the nature of the process to be studied (reduction or oxidation process). Other instrumental parameters for DPV were as follow: pulse amplitude $\pm 100$ mV, pulse repetition time 0.2 s, scan rate 25 mV $s^{-1}$, and a pretreatment at 0 V during 120 s.

### 2.3. Procedures

#### 2.3.1. Electrode Preparation Procedure

To prepare the sonogel-carbon, 500 μL of MTMOS and 100 μL of 0.2 M HCl were mixed and then insonated during 5 seconds; next, 1 g of graphite powder was added and homogeneously dispersed in the sonosol obtained. By applying ultrasonic cavitation to favor the sol-gel process to begin, we have avoided the use of alcoholic solvent and reduced drastically the time needed to get an unique phase; the mixture was insonated during 5 seconds to promote cavitation and thus hydrolysis. The complete procedure has been described previously [8].

For the sonogel-carbon electrode modified with PEG, 12.5 μL of a 5 : 2 w/w $H_2O$ : PEG solution were added to the sonosol obtained according to the previous procedure. The addition of more than 12.5 μL of a 5 : 2 w/w $H_2O$ : PEG solution resulted in an excessive time for the composite solidification, and yielded a fragile and easily breakable material. Smaller amounts of PEG solution lead to lower peak currents.

#### 2.3.2. Procedure for the Study of Pollutants

Nine phenolic compounds were studied by DPV with the sonogel-carbon electrode. A concentration of 1 mg $L^{-1}$ was used for the pollutants. All measurements were carried out in a pH 4 Britton-Robinson buffer solution. The DPV procedure described above was applied for this study.

#### 2.3.3. Procedure for the Study of Variables

For the study of each variable, the procedure consisted of: 1) selecting a value of the variable and registering the Britton-Robinson buffer at pH 4 as background; 2) adding 0.5 mg $L^{-1}$ of 4-chloro-3-methylphenol in cell and homogenizing the solution with magnetic stirring; 3) applying the accumulation conditions; 4) registering; 5) cleaning the electrodes thoroughly with water; 6) changing the cell, using another one which contains only the buffer solution and applying a cleaning treatment (− 0.5 V for 2 min), repeating the treatment if it is necessary; 6) changing the cell again and repeating the procedure.

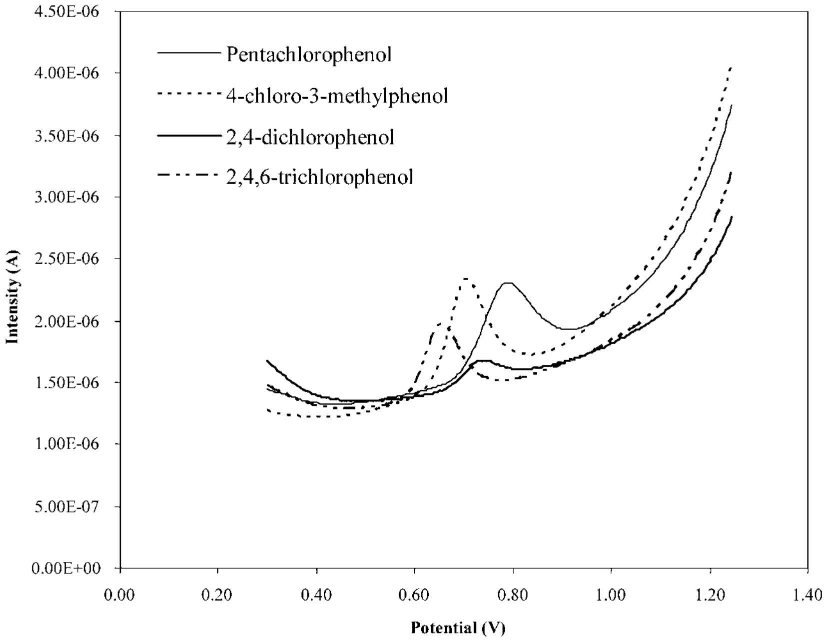
Calibration and study of interferences were carried out under the operating conditions obtained through the study of variables: a sonogel-carbon electrode modified with PEG as working electrode; Britton-Robinson buffer at pH 4 as supporting electrolyte; accumulation time, 600 s; accumulation potential, 0 V; pulse amplitude, 125 mV; pulse repetition time, 0.8 s.

## 3. Results and Discussion

### 3.1. Study of Pollutants

The response of a sonogel-carbon electrode towards nine phenolic compounds (picric acid, 2,4-dinitrophenol, 4-nitrophenol, 2-nitrophenol, 2-methyl-4,6-dinitrophenol, 2,4,6-trichlorophenol, pentachlorophenol, 2,4-dichlorophenol, 4-chloro-3-methylphenol) was studied. The individual signals for these compounds in the oxidation range are shown in Figure 1. A concentration of 1 mg $L^{-1}$ was used for all the pollutants. No signal was obtained for picric acid.

Nitrophenols were also studied in the reduction range (Fig. 2); chloro and methyl phenols showed no signal in this range. Picric acid and 2-methyl-4,6-dinitrophenol yielded characteristic signals, with several peaks due to the nitro groups present in the molecules. The peak heights obtained



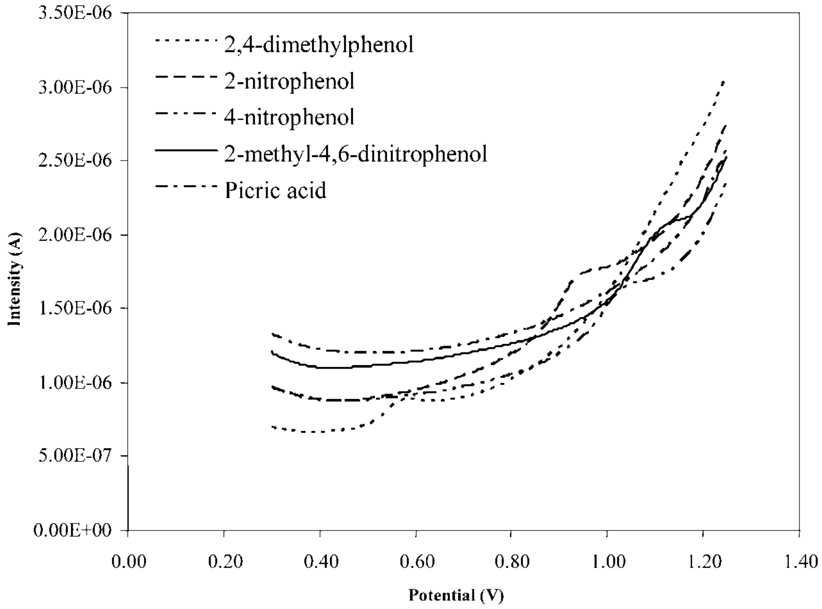


Fig. 1. Oxidation signals for the phenolic compounds in a Britton-Robinson buffer of pH 4 at a concentration of 1 mg $L^{-1}$. Pretreatment 0 V during 120 s; pulse amplitude 100 mV; pulse repetition time 0.2 s; scan rate 25 mV $s^{-1}$.

for 4-nitrophenol and 2-nitrophenol were smaller than those obtained for these compounds when other carbon electrodes are used [20, 21]; however, it must be taken into account that this electrochemical procedure is not optimized for the measurements of 4-nitrophenol and 2-nitrophenol.

Figure 3 shows the oxidation signal of a solution in which all the pollutants are present at the same concentration, 1 mg $L^{-1}$. The best defined signal appears at a peak potential of about 0.74 V, and can be considered the sum of the clorophenols present in the solution.

With the aim of carrying out a complete study of the behavior of the sonogel-carbon electrode towards an organic pollutant, one of the species tested was chosen for subsequent studies. 4-Chloro-3-methylphenol was the analyte selected, due to the sensitivity and good definition of its electrochemical signal.

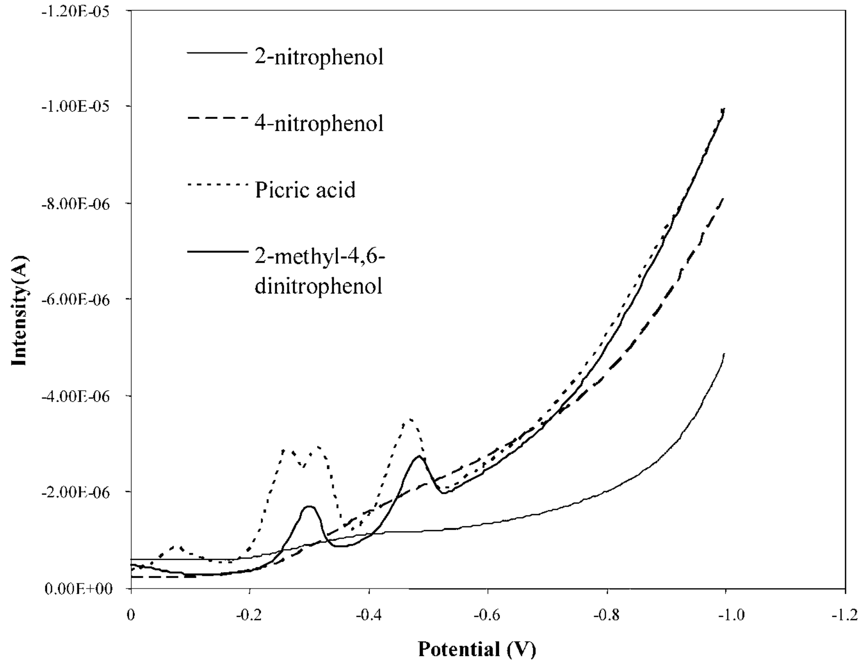


Fig. 2. Reduction signals for the nitrophenols in a Britton-Robinson buffer of pH 4 at a concentration of 1 mg $L^{-1}$. Pretreatment 0 V during 120 s; pulse amplitude $-100$ mV; pulse repetition time 0.2 s; scan rate 25 mV $s^{-1}$.

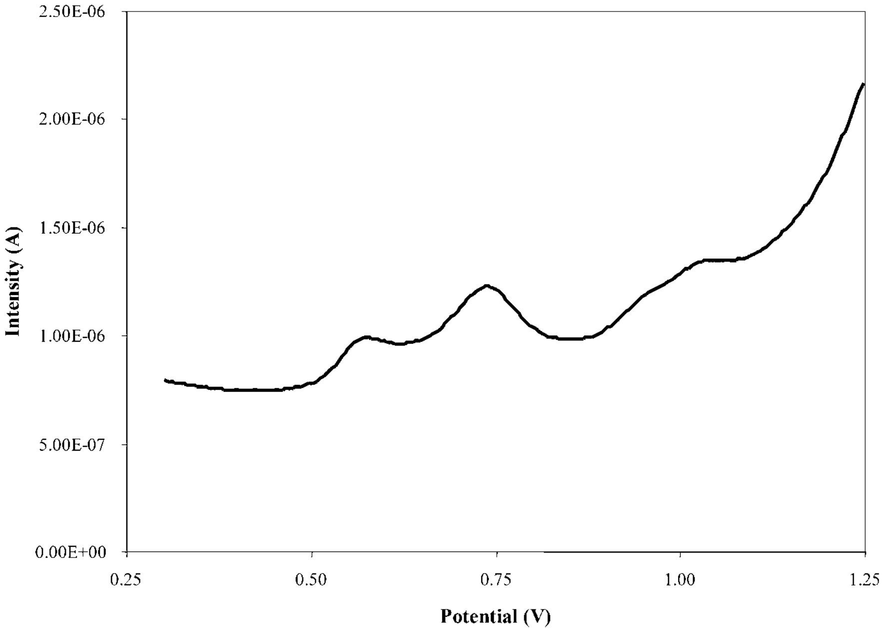


Fig. 3. Oxidation signal of a solution in which all pollutants are at a concentration of 1 mg $L^{-1}$ for each pollutant in a Britton-Robinson buffer of pH 4. Pretreatment 0 V during 120 s; pulse amplitude 100 mV; pulse repetition time 0.2 s; scan rate 25 mV $s^{-1}$.

## 3.2. Renewal of the Electrode Surface

As a previous step to the electrochemical study of 4-chloro-3-methylphenol, we carried out a comprehensive study about the renewal of the surface of the sonogel-carbon electrode, and the reproducibility of the measurements after a cleaning procedure. The study was carried out by using mechanical and electrochemical renewal. Tests were done for the same electrode and for different sonogel-carbon electrodes.

### *3.2.1. Mechanical Renewal*

In this case, three different sonogel-carbon electrodes were used. Four measurements were made for each sonogel-carbon electrode, renewing their surface before each measurement according to the described procedure. Neither considering each electrode independently nor comparing the results of all the electrodes, an acceptable reproducibility was obtained after several mechanical renewals. Relative standard deviations obtained were between 13 and 41% [8].

### *2.3.2. Electrochemical Renewal*

Two different procedures were applied to carry out the electrochemical renewal of the active surface: a) consecutive sweeps between 0.8 and – 0.2 V; b) the application of a potential of – 0.5 V for 120 s.

In the first method, and after the electrochemical measurement of the analyte, the active surface of the electrode was washed with Milli-Q water, the electrode was immersed in the cleaning solution, and then the electrochemical renewal was applied. Figure 4A shows the voltammogram of the analyte solution and the signals obtained after electrochemical cleaning of the electrode surface carrying out sweeps between 0.8 and – 0.2 V in the buffer solution. There was an evidence of a decrease of the 4-chloro-3-methylphenol peak height. Three cycles of sweeps are considered sufficient to obtain a clean surface. A larger effectiveness in the cleaning procedure was possible by using five cycles of sweeps.

The last step consisted of verifying if the electrode continues being active and its capablity of detecting the analyte with reproducibility. After registering 4-chloro-3-methylphenol in a second sweep, the peak height was lower than that obtained before applying this kind of electrochemical renewal (70% of its initial value). This seems to imply that these measurement conditions do not provide reproducibility.

The second possibility of electrochemical renewal consisted of applying a fixed potential of – 0.5 V for 2 min with magnetic stirring. After applying electrochemical cleaning, a voltammogram of the buffer solution is recorded to check the absence of electrochemical signal, and thus that the electrode surface is clean. Voltammograms shown in Figure 4B confirm that this method is successful. The results obtained carrying out a new measurement of the analyte show an excellent reproducibility for peak height.

For 4-chloro-3-methylphenol, it was plain that the best method was the electrochemical renewal applying a fixed potential of – 0.5 V during 2 min. This is the method used to clean the electrode surface in the determination of our analyte.

## 3.3. Accumulation Study on the Electrode Surface

The accumulation of 4-chloro-3-methylphenol on the surface of the sonogel-carbon electrode was studied. As has been described in the Experimental section, to establish the accumulation time, the electrode was immersed into the solution containing the pollutant for different periods of time. The results show that a sorption process over the electrode surface occurs and the peak height depends on the contact time of the electrode with the solution where the analyte has been added.

A typical behavior for a sorption process was found, i.e., peak height increases with the preconcentration time up to the stabilization of the signal. From the results obtained, ten minutes was selected as the interval time in which the sorption process was stabilized.

Peak height was found to clearly decrease with the increase of the accumulation potential. 0 V was the potential that provided the highest peak height. For this reason, the value used in the following tests was an accumulation potential of 0 V for 10 min.

The next assay consisted of studying the peak height reproducibility under the optimized conditions. The results (relative standard deviation value of 0.5% for $n = 9$) indicate that the cleaning treatment is valid and the application of a 10 min accumulation step at a potential of 0 V leads to very good reproducibility in the peak height measurements.

## 3.4. Temporary Evolution of Peak Currents for Sonogel-Carbon Electrodes

As is known, a gel has a dynamic structure because the polimerization reactions continue, even after the gelification point; thus, it is reasonable to think that peak intensities will vary with time.

A stable analytical response is essential for a sensor. It is then necessary to search strategies for getting good stability. Polyethyleneglycol, PEG, has been used to stabilize electrochemical signals [22, 23], due to the formation of microchannels that increase the electrode response.

In this paper, a study of the evolution of the voltammetric responses for 4-chloro-3-methylphenol was performed. Two electrode sets were used: six sonogel-carbon electrodes and six sonogel-carbon electrodes modified with PEG. All the electrodes were prepared the same day; but all them were not tested the same day; the first measurements were carried out 24 h after their fabrication. New electrodes were included in the study during 30 days. Results obtained are shown in Figure 5.

As observed, the peak current of the first measurement increases asymptotically with respect to the time passed from the fabrication of the electrode. In previous studies, we demonstrate the stability of the background signal after at least 42 days; so, the changes observed in presence of 4-chloro-3-methylphenol can be attributed to the interaction between the analyte and the working electrode.

All electrodes decrease their peak currents with respect to the first measurement, reaching a steady value after several days. The time for stabilization does not seem very different from one to another electrode. Apparently, neither the presence of PEG nor the time passed from the fabrication of the electrode affect the time for getting stability.

In the first measurement, the peak current for unmodified electrodes is always higher than that obtained using

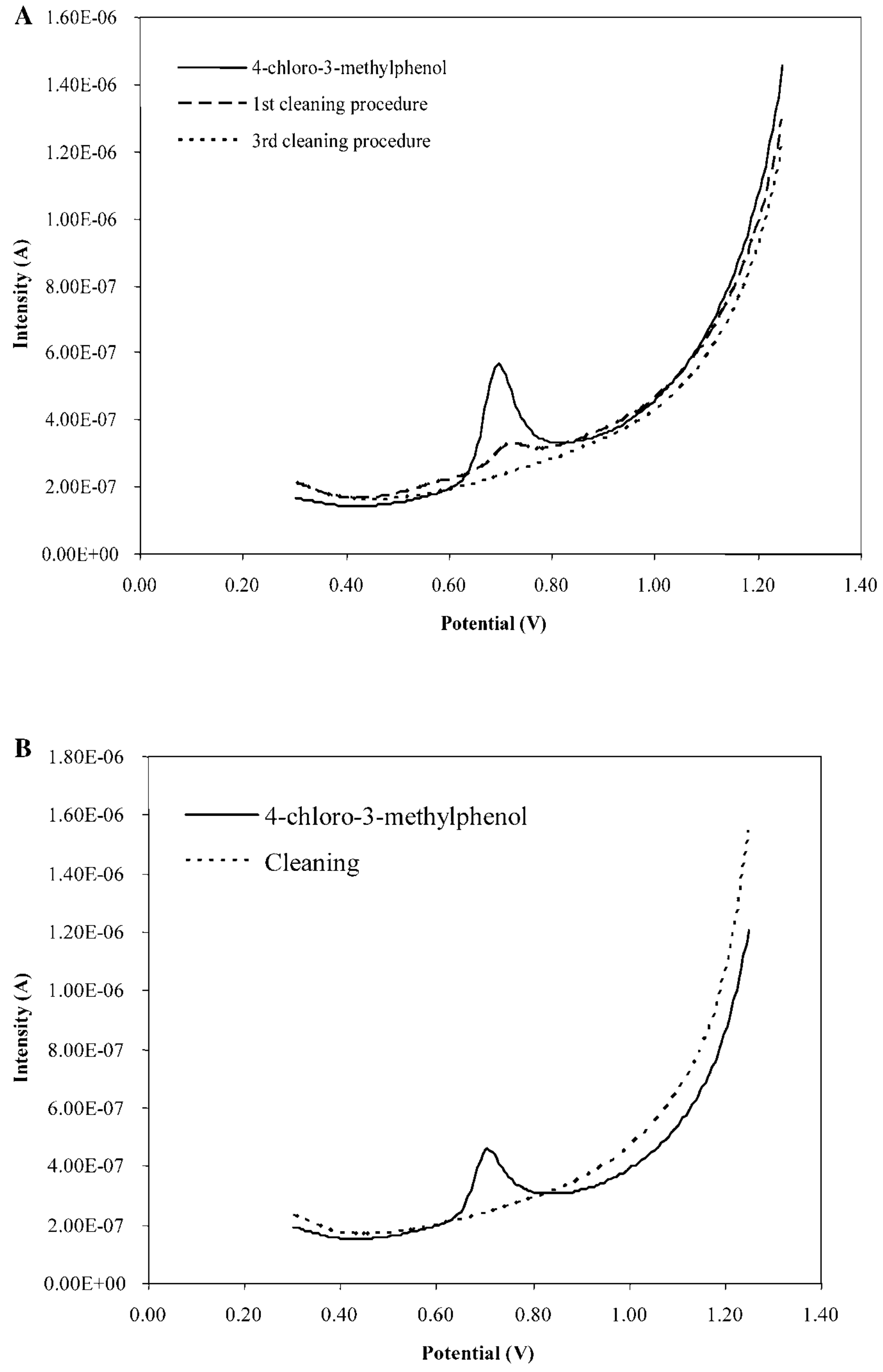


Fig. 4. Analyte (—) and the signals obtained after A) an electrochemical cleaning procedure between 0.8 and −0.2 V (one cycle – – –; three cycles -----); or B) after an electrochemical cleaning procedure by applying a potential of −0.5 V during 2 min (-----). Britton-Robinson buffer of pH 4 at a concentration of 0.5 mg L$^{-1}$; pulse amplitude 100 mV; pulse repetition time 0.2 s; scan rate 25 mV s$^{-1}$.

modified electrodes. As a result, the presence of PEG stabilizes the signal at higher values of peak currents.

After these studies, several questions arise that could be resolved with the use of structural analytical techniques. So, the presence of PEG seems to cause less structural changes in the gel, since the peak current decrease is not as pronounced as when PEG is not present. The highest value, in general, of the final peak currents in presence of PEG can justify its use, although the stabilization process does not seem to decrease in time.

To answer these questions, an unused sonogel-carbon electrode modified with PEG was studied by SEM. Figure 6 shows the images obtained for the surface of the electrode before polishing (A), after polishing using the method described previously (B), and after maintaining the surface immersed in water with magnetic stirring for several days (C

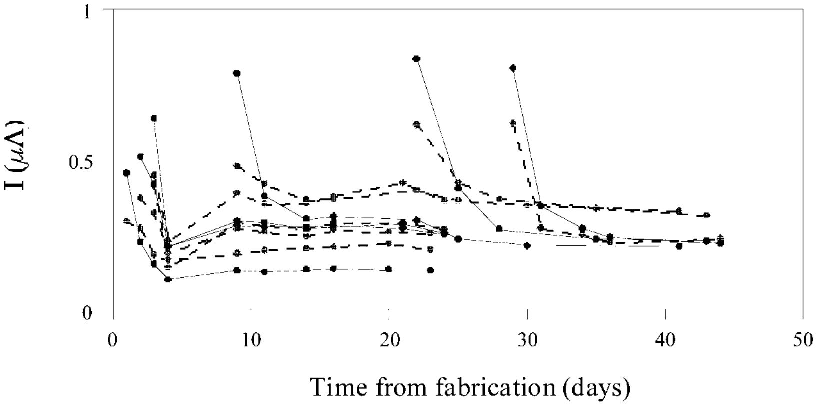


Fig. 5. Variation of peak height with time from fabrication for an unmodified Sonogel- Carbon electrode (——), and for a sonogel-carbon electrode modified with PEG (– – –) in a Britton-Robinson buffer of pH 4 at a 4-chloro-3-methylphenol concentration of 0.5 mg $L^{-1}$. Pretreatment 0 V during 600 s; pulse amplitude 100 mV; pulse repetition time 0.2 s; scan rate 25 mV $s^{-1}$.

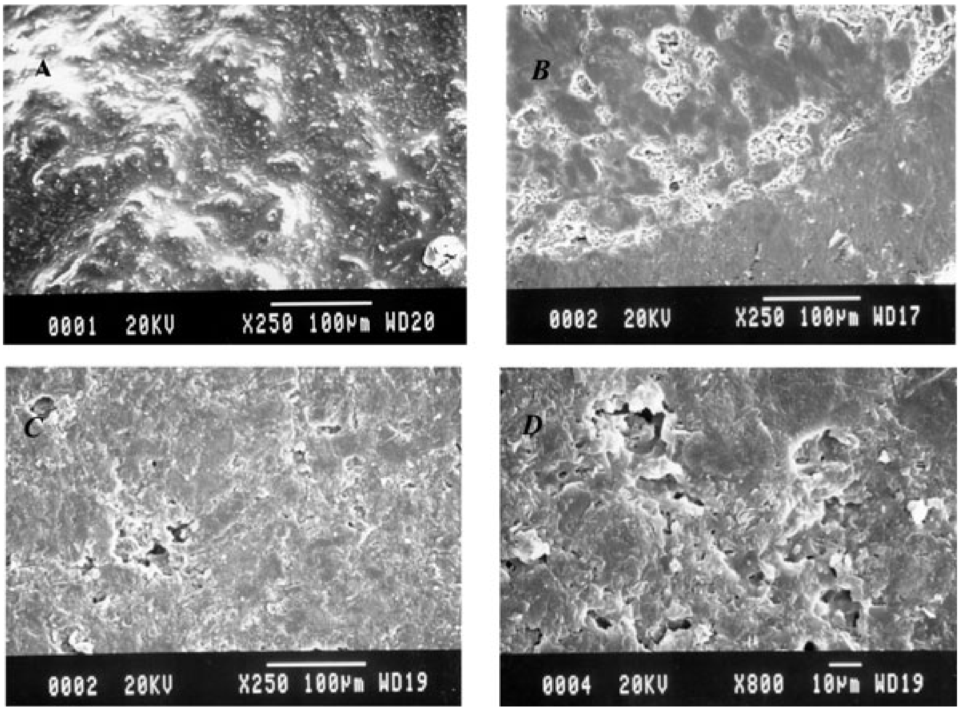


Fig. 6. SEM micrographs of the surface of a PEG-modified sonogel-carbon electrode: A) before polishing, B) after polishing, C) after maintaining the electrode immersed in water for several days with magnetic stirring, and D) like C but with a × 800 magnification.

and D) with the objective of solving partially the PEG, causing the formation of microchannels in the electrode, as described in [22]. After polishing the surface (from A to B), it is evident the porosity of this material. Comparing B and C micrographs, it is observed that after immersing the electrode in water for several days, the porosity increases because of the solvation of PEG in the aqueous media. The canalization of the material is more evident in the micrograph D (higher resolution). For this reason, the presence of PEG explains that the stabilization of peak currents at higher values, given for the modified electrodes, is a consequence of the increasing of their canalization and, therefore, of the electrochemically active surface.

With respect to the stability of the sonogel-carbon electrode and its continuous use, the response of the electrode reaches a steady state after several days, and remains with a reproducible response for a longtime. We have carried out a study of the response of a sonogel-carbon electrode toward phenolic compounds and mixtures of them; an unique electrode was used for all the measurements of the individual analytes and for all the mixtures of analytes [24], and only electrochemical renewal was used to clean the electrode surface. Thus, we can assume that these electrodes are suitable for continuous use.

### 3.5. Reproducibility for a Polyethyleneglycol-Modified Electrode

One of the PEG-modified electrodes employed in the temporary evolution study was selected to evaluate the reproducibility of its response versus 4-chloro-3-methylphenol using electrochemical renewal. The measurements were carried out for several days until 14 measurements were obtained. The values showed a constant response of the electrode and so confirms the reproducibility of the measurement. The relative standard deviation was 2.5%.

A similar study was carried out using mechanical renewal of the electrode surface. The same procedure used so far was applied. The reproducibility obtained with electrochemical renewal was much better than that obtained with mechanical renewal (relative standard deviation of 6.7% for mechanical renewal). Nevertheless, it is necessary to note that mechanical renewal involves higher values of intensities and, therefore, more sensitivity, with a mean peak height value of 0.9 μA versus a value of about 0.4 μA for electrochemical renewal. This is because mechanical renewal implies a real generation of a new surface, whereas it does not occur when electrochemical renewal is used; in consequence, after a mechanical renewal, the peak height value should be comparable with the first measurement obtained with an unused electrode, whereas after an electrochemical cleaning the peak height values should be comparable with the values once stabilization is reached.

### 3.6. Calibration Plot and Detection Limit

In order to establish a calibration plot, electrochemical measurements of different 4-chloro-3-methylphenol concentrations were carried out using the experimental parameters previously optimized.

For each concentration the measurements were taken twice; the calibration plot included the arithmetic means of the peak heights obtained. The relationship between peak height and the concentration was evaluated in the range from 0.005 to 0.5 mg $L^{-1}$. An intercept of $6.93 \pm 3.58$ nA, a slope of $839.17 \pm 16.49$ nA L $mg^{-1}$ (95% significance level), and a correlation coefficient of 0.999 were obtained.

The detection limit was considered as the concentration whose intensity value equals the blank intensity plus three times the standard deviation of the blank; for the determination limit ten times the standard deviation of the blank was used [25]. The detection limit obtained (2.8 μg $L^{-1}$) is satisfactory and even the determination limit is situated in the range of μg $L^{-1}$, with a value of 9.3 μg $L^{-1}$.

According to previous results in the study of phenols with carbon electrodes, the stability of the sonogel-carbon electrodes is superior than for other carbon electrodes, and the detection limit obtained for 4-chloro-3-methylphenol was better than those described in the papers [20, 21, 26, 27].

Some tests were carried out for spiked drinking water samples; 4-chloro-3-methylphenol concentrations of 0.1 and 0.25 mg $L^{-1}$ were used. The results show recoveries of 97.8 and 98.9%, respectively, for three measurements of each concentration. In all cases electrochemical renewal was used as cleaning procedure, giving relative standard deviations for the repeated measurements of 3.0 and 2.2% for 0.1 and 0.25 mg $L^{-1}$ 4-chloro-3-methylphenol concentrations.

A study of the response of a sonogel-carbon electrode versus binary mixtures of 4-chloro-3-methylphenol with the other eight phenols was carried out. As expected, according to Figure 1, strong interferences were observed for chlorophenols, as well as for alkylphenol; no interferences were observed for nitrophenols because of the wide separation among the peak potentials of these compounds and the reference compound. The use of a previous chromatographic step or the use of chemometric techniques should allow the resolution of a mixture of phenols. Results are shown in Table 1.

Table 1. Effect of organic species on the determination of 4-chloro-3-methylphenol at a concentration of 0.5 mg $L^{-1}$.

| Interferent | Interferent:analyte mass ratio | Deviation (%) |
|---|---|---|
| Pentachlorophenol | 2:1 | >100 |
| | 1:1 | 69.7 |
| 2,4,6-Trichlorophenol | 1:1 | 36.5 |
| | 0.5:1 | −10.7 |
| 2,4-Dichlorophenol | 1:1 | 62.8 |
| 2,4-Dimethylphenol | 1:1 | −67.1 |
| | 0.5:1 | n.i. [a] |
| 2-Nitrophenol | 2:1 | −21.0 |
| | 1:1 | n.i. [a] |
| 4-Nitrophenol | 2:1 | n.i. [a] |
| 2-Methyl-4,6-dinitrophenol | 2:1 | n.i. [a] |
| Picric acid | 2:1 | n.i. [a] |

[a] n.i.: no interference was observed.

Pentachlorophenol gave a very high interference on 4-chloro-3-methylphenol signal; in addition, the cleaning procedure was very much difficult, due to the interaction of pentachlorophenol over the electrode surface.

For 2,4-dimethylphenol, the separation between peak potentials (about 130 mV) gave as a result two peaks, but with high negative deviation on analyte signal; however, for a 0.5:1 interferent:analyte concentration ratio a deviation lower than 5% was obtained.

## 4. Conclusions

The sonogel-carbon electrodes show electrochemical response towards phenolic compounds, in oxidation and/or reduction range according to their chemical structure.

The existence of a typical process of adsorption for 4-chloro-3-methylphenol over the electrode surface is patent.

However, mechanical or electrochemical cleaning can be used to renew the active surface of the electrode, although electrochemical renewal provides better reproducibility.

The peak heights evolve according to the time passed from the fabrication of the electrode and all of them reach a steady value; polyethyleneglycol-modified electrodes stabilize their intensities at higher values than those that do not contain polyethyleneglycol. The responses of the stabilized electrodes show a good reproducibility.

Scanning electron microscopy (SEM) micrographs show that the presence of PEG notably increases the canalization in the sonogel-carbon material, due to the partial solubilization of PEG, with the subsequent formation of microchannels, what might explain the mentioned difference between the current intensities.

According to previous results obtained by our research group in the study of phenols with carbon electrodes, the electrochemical behavior of the sonogel-carbon electrodes is better than that obtained for other carbon and sol-gel electrodes; the stability of the sonogel-carbon electrodes, as well as the detection limit obtained for 4-chloro-3-methylphenol, compare well with any other carbon electrode [8, 19–21]. Properties such as good mechanical properties, physical rigidity and a constant surface activity allow a good behavior of sonogel-carbon electrodes as electrochemical sensors.

## 5. Acknowledgements

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