



# 1-Furoylthiourea-Sonogel-Carbon electrodes: Structural and electrochemical characterization

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## ABSTRACT

A new type of sensor based on Sonogel-Carbon materials modified with 1-(2-furoyl)-3-(1-naphthyl)thiourea is presented to be used as an amperometric sensor for metals. Different percentages of modifier were tested in order to optimise the structural and mechanical properties, as well as the electrochemical behaviour.

Scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (EDS), Fourier transform-infrared spectroscopy (FTIR), single crystal X-ray diffraction (XRD) and powder XRD were used for the structural characterization of these electrodes. The 1-(2-furoyl)-3-(1-naphthyl)thiourea did not modify significantly the structural and mechanical properties of the Sonogel-Carbon electrodes, being similar to other modifications carried out previously in these materials. For the study of the electrochemical response, anodic stripping differential pulse voltammetry (ASDPV) was employed, optimising other parameters of measurement such as pH of the buffer, potential and accumulation time and pulse amplitude. The electrochemical response of the modified electrodes improved significantly with respect to the non-modified electrode, giving good signals and acceptable detection limit.

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## 1. Introduction

Thiourea and its derivatives (N-benzoyl-N'-2-nitro-4-methoxy-phenylthiourea [1], N-methylthiourea, N-ethylthiourea, N,N'-dimethylthiourea [2], N-alkyl and N,N'-dialkyl-N'-acyl(aryl)thiourea [3], and tetramethylthiourea [4], amongst others) are reported as a versatile family of ligands appropriate for forming complexes with transition (e.g. Ni(II), Cu(II/I), Co(III), Zn(II), Ag(I), Cd(II), Pt(II), Pd(II), Au(III), Rh(III), Re(III), Tc(III)) and post-transition (e.g. Pb(II), Sb(III), Bi(III)) metallic ions. It is well known that the coordination chemistry of such derivatives is much more varied than that of simple thiourea. Thus, the physicochemical properties of their metal complexes are more marked, resulting in a number of potentially interesting technical and analytical applications [3]. The 1-furoylthioureas family has been tested, with promising results, as ionophores in ion selective electrodes [5], and as heavy metal complexing modifiers incorporated in carbon paste electrodes (CPE) [6,7].

In bibliography, many devices have been recently described to determine heavy metals by using voltammetric techniques. Differ-

ent supporting electrodes were employed with multiple configurations: hanging mercury drop electrode [8–10], mercury film glassy carbon [11], nanocrystalline boron-doped diamond electrode [12], stannum film electrode [13], bismuth film-modified gold electrodes [14], bismuth-sputtered electrodes [15], bismuth-modified zeolite doped carbon paste electrodes [16], Nafion/2,2'-bipyridyl/bismuth composite film-coated glassy carbon electrodes [17], bismuth film-modified edge plane pyrolytic graphite electrodes [18], multiwalled carbon nanotubes-Nafion-bismuth-modified glassy carbon electrodes [19], Nafion/multiwalled carbon nanotube modified glassy carbon electrodes [20], organofunctionalized SBA-15 nanostructured silica modified carbon paste electrodes [21] and sol-gel electrodes [22–24], among others.

The Sonogel-Carbon electrodes have been previously studied and described by our group in many of their aspects: the manufacture; the electrochemical behaviour of the basis material [25,26]; their use as electrochemical sensor, including other possible modifiers [27–32]; their use as biosensors [33–35] and the structural characterization of the material and of the electrodes based on them [28,36].

In this paper, a new electrochemical sensor based on Sonogel-Carbon materials modified with 1-(2-furoyl)-3-(1-naphthyl)thiourea is described. An optimisation study of the percentage of modifier into the material has been carried out in

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order to get the best mechanical properties and electrochemical response. Besides, a study of the electrochemical behaviour of the sensor and its response versus an environmental pollutant has been explored. Cd(II) was selected as benchmark analyte since it possesses great affinity by sulphurated species, such as 1-furoylthiourea derivatives (FTHD).

For the electrochemical study, several chemical and instrumental parameters, such as pH of the buffer solution, potential and accumulation time and pulse amplitude have been investigated in order to establish their influence.

For the structural study, scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (EDS), Fourier transform-infrared spectroscopy (FTIR), single crystal X-ray diffraction (XRD) and powder XRD have been employed. All these techniques have been used previously in the study of the Sonogel-Carbon materials with and without modifiers [28,34,36], having shown their effectiveness to characterize these materials.

## 2. Material and methods

### 2.1. Reagents and materials

Methyltrimethoxysilane (MTMOS) and HCl were from Merck (Darmstadt, Germany). Britton–Robinson 0.04 M buffer solution was prepared with boric acid, orthophosphoric acid and acetic acid; sodium hydroxide was used to obtain the pH of measurement (pH 4). All these chemicals were from Merck. All reagents were of analytical grade or higher and used as received without further purification. Graphite powder natural, high purity, –200 Mesh, 99.9999% (metal basis), was from Alfa-Aesar (Johnson Matthey GmbH, Germany). Nanopure water was obtained by passing twice-distilled water through a Milli-Q system ( $18\text{ M}\Omega\text{ cm}^{-1}$ , Millipore, Bedford, MA). KBr for the IR spectroscopy was from Panreac (Panreac, Barcelona, Spain). Glass capillary tubes, i.d. 1.15 mm, were used as the bodies for the composite electrodes. 1-(2-furoyl)-3-(1-naphthyl)thiourea was synthesized as previously reported by Otazo-Sánchez et al. [5], and then re-crystallized twice in ethanol.

### 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 ( $25 \pm 1^\circ\text{C}$ ). The counter electrode was a platinum wire, and a silver/silver chloride/KCl (3 M) electrode was used as reference electrode. The composite-filled glass capillary tubes were used as working electrode.

The synthesis of the Sonogel-Carbon was carried out sonicating with a high power ultrasonic generator, SONICATOR 3000, from MISONIX (MISONIX, Inc. Farmingdale, NY, USA) (equipped with a 13-mm titanium tip), that provides a maximum power of 600 W.

Scanning electron microscopy (SEM) studies were carried out on a QUANTA 200 (FEI Company, Hillsboro, Oregon, USA) operating at 20 kV and equipped with a Microanalyzer (EDAX) to perform energy dispersive spectroscopy (EDS).

The analysis by Fourier transform-infrared spectroscopy (FTIR) were carried out using a NICOLET 20SXB (NICOLET, Warwick, UK), with the software OMNIC v1.1. Pellets were prepared by mixing the samples with KBr. Measurements were carried out at room temperature.

The single crystal X-ray diffraction studies were developed on an X8-Apex (Bruker AXS, S.r.l., Milan, Italy), 3.0 kW KRISTALLOFLEX 760-80, equipped with a 4-circle KAPPA goniometer.

The powder X-ray diffraction studies were carried out on a PHILIPS (Koninklijke Philips Electronics N.V., Amsterdam, The Netherlands) powder diffractometer, 3 kW. The goniometer was a PHILIPS PW 1820, with a high temperature chamber AP HTK-10.

With respect to the electrochemical study, the instrumental parameters for carrying out anodic stripping differential pulse voltammetry (ASDPV) were as follows: pulse amplitude 100 mV, pulse repetition time 0.6 s, scan rate  $60\text{ mV s}^{-1}$ , and a pre-treatment at  $-1.2\text{ V}$  for 5 min. The potential range was from  $-1.2$  to  $0.8\text{ V}$ . Measurements were carried out under  $\text{N}_2$  atmosphere when it was required.

### 2.3. Electrode preparation procedure and electrochemical renewal

To prepare the Sonogel-Carbon, a mixture of 500  $\mu\text{L}$  of MTMOS and 100  $\mu\text{L}$  of 0.2 M HCl was insonated for 5 s; next, 0.5 g of graphite powder were added and dispersed homogeneously in the sonosol obtained, as optimised previously [28].

Several minutes after beginning the gelification process of the sonosol, the capillary tubes were filled with the synthesized material to obtain the electrode as described elsewhere [26].

The Sonogel-Carbon-1-furoylthiourea material was obtained by addition of different amounts of 1-(2-furoyl)-3-(1-naphthyl)thiourea (Fig. 1) into the sonosol phase of the basis material. The added amounts gave place to different percentages of modification of the basis material: 15, 18, 20, 22 and 25% (w/w). The electrodes prepared were dried under room conditions, which provide enough humidity for the gelification process.

An electrochemical renewal after each measurement was carried out. The experimental procedure can be described as follows: 25 ml of buffer solution were poured in the electrochemical cell placed in the VA 663 Stand of Metrohm with the aim of performing the cleaning step. This pre-treatment consists of applying an accumulation potential of 1.2 V during 300 s, with a subsequent sweeping from  $-1.2$  to  $0.8\text{ V}$ . This procedure is repeated three times, in order to cancel any residue of the analyte(s) that could have been adsorbed in the surface of the electrode because of previous determinations. The last sweep is considered as the register of the background for the subsequent measurement.

## 3. Results and discussion

The FTHD have the advantages of simple synthesis and purification methods, and their low solubility in water. According to results reported by some of us, some of them can preconcentrate Cd(II) from aqueous solution to the surface of the modified CPE by forming complexes with this ion and greatly increasing the sensitivity of its determination. However, it was also found that 1-furoyl-3-monosubstituted thioureas always gave better results than 1-furoyl-3,3-disubstituted thioureas [6,7]. Although both of them display a larger double bond character of the C=S with a lower nucleophilic character of the sulphur atom than others 1-furoylthioureas [37,38], it seems that the steric factor determines the formation and the stability of the complex.

In previous studies, the electrochemical devices obtained by the modification of the Sonogel-Carbon material with three different 1-furoyl-3-monosubstituted thioureas: 1-furoyl-3-phenylthiourea, 1-furoyl-3-benzylthiourea and 1-(2-furoyl)-3-(1-naphthyl) thiourea, were tested [39]. The good electrochemical behaviour in terms of greater signal to noise ratio, shape and intensity of the peaks, reproducibility and a wide operative linear range of concentrations for the determination of Cd(II) in water samples was obtained for the 1-(2-furoyl)-3-(1-naphthyl)thiourea. That is why we decided to work with this thiourea derivative as modifier

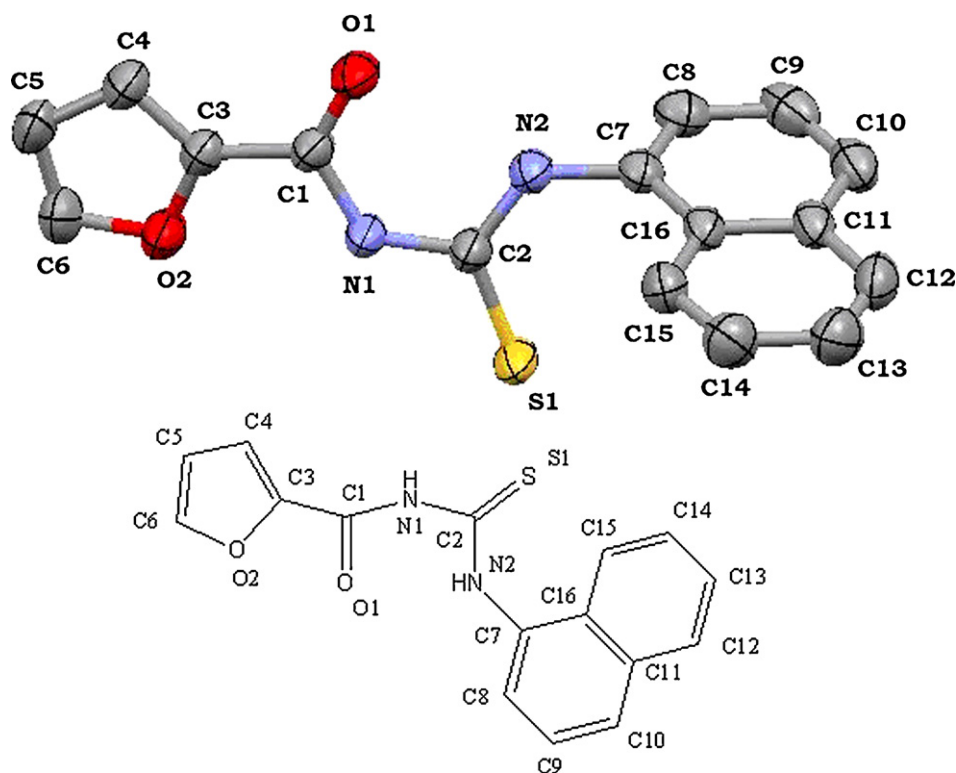


Fig. 1. 2D and 3D molecular structure of 1-(2-furoyl)-3-(1-naphthyl)thiourea.

into the Sonogel-Carbon electrodes. Fig. 2 shows anodic stripping differential pulse voltammograms corresponding to 1-(2-furoyl)-3-(1-naphthyl)thiourea-modified and unmodified electrodes, in absence and presence of Cd(II).

All modified Sonogel-Carbon materials synthesized using the different percentages of modifier, showed high homogeneity and appropriate compactness. These properties allowed the filling of the capillary tubes that serve as supporting bodies to the electrodes. Moreover, their mechanical properties, after the drying step, were similar than those showed by the unmodified Sonogel-Carbon materials.

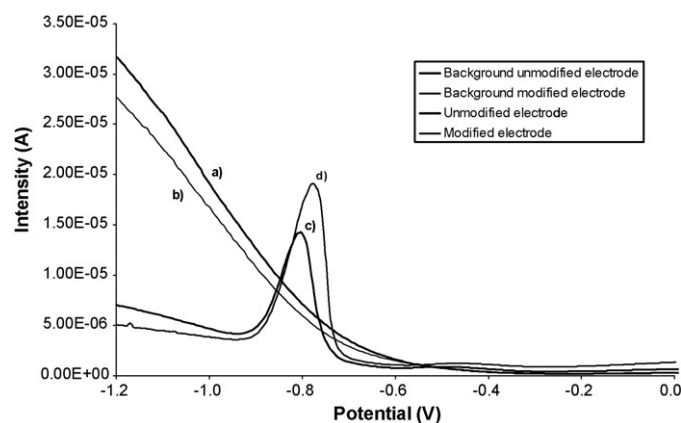


Fig. 2. Voltammograms corresponding to: (a) background of the unmodified Sonogel-Carbon electrode; (b) background of the 1-(2-furoyl)-3-(1-naphthyl)thiourea-modified Sonogel-Carbon electrode; (c)  $0.5 \text{ mg l}^{-1}$  of Cd(II) measured with the unmodified Sonogel-Carbon electrode; and (d)  $0.5 \text{ mg l}^{-1}$  of Cd(II) measured with the 1-(2-furoyl)-3-(1-naphthyl)thiourea-modified Sonogel-Carbon electrode. Conditions of measurement: Britton–Robinson buffer solution pH 4; accumulation potential  $-1.2 \text{ V}$ ; accumulation time 300 s; pulse amplitude  $100 \text{ mV}$ ; percentage of modifier 18% (for the modified electrodes).

### 3.1. Electrochemical study

ASDPV was used for the electrochemical studies. Only one of the different percentages of modifier used in the manufacturing step of the material, 18% of 1-(2-furoyl)-3-(1-naphthyl)thiourea, gave good results versus Cd(II), obtaining reproducible and symmetrical signals with intensity values higher than those obtained with electrodes modified with other percentages (see Table 1).

Once the best percentage of modifier was selected, the study of other measurement parameters was carried out using Cd(II) as benchmark analyte into the voltammetric cell.

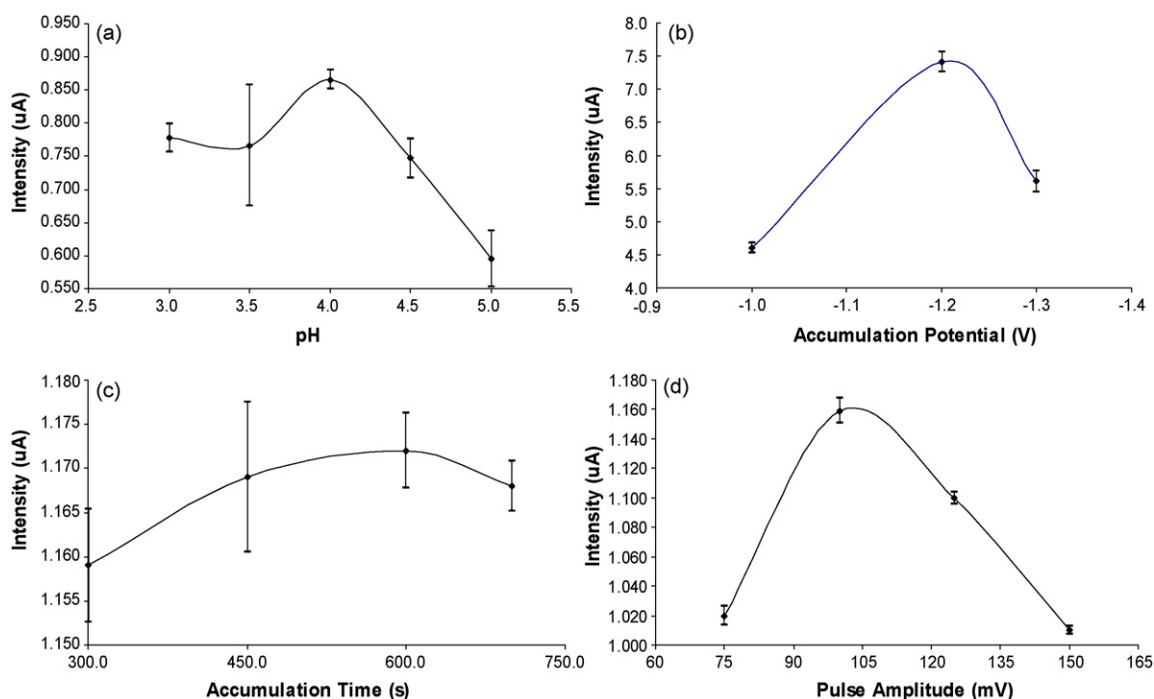
#### 3.1.1. Effect of pH

The influence of pH on the determination of Cd(II) was investigated. The buffer solution used was Britton–Robinson. The original pH of this solution was 2.85, and was increased to the tested values with sodium hydroxide. The pH values tested were 3, 3.5, 4, 4.5 and 5. An increase of peak current was observed at first, reaching a maximum value around pH 4 (see Fig. 3a). The continuous increase of pH led to a decrease of peak current and a broadening of the signal, which is due to the hydrolysis of Cd(II). Furthermore, the 1-furoylthioureas and their derivatives can slowly dissolve in basic solution due to the acidity of the amidic proton NH, and lose their ability of complexing Cd(II).

Table 1

Peak intensity obtaining for the different percentages of modification with 1-(2-furoyl)-3-(1-naphthyl)thiourea versus  $0.1 \text{ mg l}^{-1}$  of Cd(II).

	Potential (V)	Intensity ( $\mu\text{A}$ )
15%	-0.819	0.438
18%	-0.819	1.177
20%	-0.807	0.955
22%	-0.801	0.682
25%	-0.777	0.484



**Fig. 3.** Study of optimisation of the electrochemical parameters: (a) pH; (b) accumulation potential; (c) accumulation time; and (d) pulse amplitude. Conditions of measurement: Britton–Robinson buffer solution; Cd(II) concentration = 0.1 mg l<sup>-1</sup>.

### 3.1.2. Effect of accumulation potential and accumulation time

Accumulation potential and accumulation time are two important parameters in any electrochemical technique using preconcentration step, in our case ASDPV technique. The preconcentration is done by cathodic deposition at a controlled time and potential. According to bibliography, deposition potential must be about 0.3–0.5 V more negative than the peak potential. In our case, Cd(II) peak potential is around -0.8 V, and the effect of accumulation potential was studied in the range from -1.0 to -1.3 V; for less negative potential values the effect of accumulation is negligible, whereas for more negative values superficial interferences can occur on the electrode surface [40].

The peak height for Cd(II) increased when more negative accumulation potentials were applied, until a maximum value was obtained at -1.2 V, decreasing the peak height value for higher (more negative) accumulation potentials (see Fig. 3b).

With respect to the accumulation time, the results show that the peak height depends on the contact time of the electrode with the solution where the analyte has been added; this time must be selected according to the concentration level of the metal ion, usually from 0.5 to 20 min [40]. A typical behaviour for an accumulation process was found in our study, i.e., peak height increases with the preconcentration time up to the stabilization of the signal. From the results obtained, 5 min was selected as the best interval time; although higher accumulation times led to slightly higher values of peak height, 5 min was chosen as a compromise between sensitivity and time analysis (see Fig. 3c).

### 3.1.3. Effect of pulse amplitude

The improvement in selectivity and the measure sensitivity attained depend on a proper choice of the pulse amplitude. From the point of view of the selectivity, pulse amplitude should be as small as possible, whereas the measure sensitivity increases up to a certain value with increasing pulse amplitude. The effect of this parameter was studied over the range 75–150 mV. The peak height increased with the pulse amplitude (see Fig. 3d). The peak width and the residual current also increased with increasing pulse ampli-

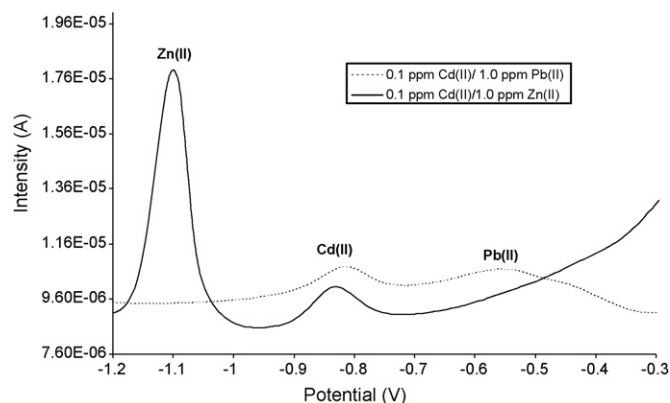
tude, and thus a distortion in the shape and symmetry of the signal was found. As compromise between sensitivity and selectivity, a value of 100 mV was chosen due to the peak height (maximum value) and well-defined signals.

After obtaining the best values for the parameters influencing on the electrochemical behaviour of our device, the conditions for electrochemical measurements were fixed as follows: Britton–Robinson buffer solution of pH 4; accumulation potential -1.2 V; accumulation time 300 s; pulse amplitude 100 mV; percentage of modifier 18%.

### 3.1.4. Effect of other ions

The influence of Pb(II), Cu(II), Zn(II) and Hg(II) on Cd(II) peak current was also evaluated at 10:1 interferent:analyte mass ratio. Zn(II) and Hg(II) do not interfere the determination of Cd(II) (see some examples in Fig. 4).

The presence of Pb(II) and Cu(II) interfere significantly by suppressing the Cd(II) signal up to 40%, because they form complexes



**Fig. 4.** Voltammograms corresponding to the interferences of Pb(II) and Zn(II) in the determination of Cd(II): 10:1 interferent:analyte mass ratio. The experimental conditions are: Britton–Robinson buffer solution pH 4; accumulation potential -1.2 V; accumulation time 300 s; pulse amplitude 100 mV; percentage of modifier 18%.



with the modifier and prevent the complex formation and accumulation of Cd(II) at the electrode surface. Although Zn and Hg also form complexes with the 1-furoylthioureas, in the tested cases they did not interfere, due to their peak potentials are far from this one for Cd(II), and accumulations conditions are not favourable for their preconcentration. Peak potential for Pb(II) signal is near to that of Cd(II), and overlapping is also observed.

### 3.1.5. Calibration graph and detection limit

The sensitivity of the method was studied by recording differential pulse anodic stripping voltammograms at different Cd(II) concentrations. For the 1-(2-furoyl)-3-(1-naphthyl)thiourea-modified Sonogel-Carbon electrode a calibration plot was obtained in the range from 0.001 to 0.05 mg l<sup>-1</sup>. The linear regression equation was  $I_{pa} (\mu A) = 0.025 + 11.951 [Cd(II)] (mg l^{-1})$ , with a correlation coefficient of 0.9999. The detection limit calculated [41] as the signal of the blank plus three times its standard deviation was 0.8  $\mu g l^{-1}$ ; for the unmodified electrode the value obtained was 47  $\mu g l^{-1}$ . The results obtained for the detection limit show that the ligand has greater sensitivity toward Cd(II). This fact is consistent with the results previously reported for the complexes of this ligand with cadmium chloride [6,7].

The relative standard deviation was found to be 3.9% for ten determinations of 0.1 mg l<sup>-1</sup> Cd(II) in the experimental conditions previously optimised. The results indicate that the 1-(2-furoyl)-3-(1-naphthyl)thiourea-modified Sonogel-Carbon electrode has good reproducibility.

When comparing our values with other reported in literature, some of us have used other electrochemical device, such as a carbon paste electrode modified with different thioureas derivatives: 1-furoyl-3-p-(tetradecylphenyl)thiourea and 1-furoyl-3-bencyl-3-phenylthiourea [6,7], to determine the same analyte (Cd(II)), finding the following limits of detection: 0.06 and 3  $\mu g l^{-1}$ , respectively. Moreover, in the last years, other authors

have reported the electrochemical stripping analysis of Cd(II) using different modifiers for carbon paste electrodes, such as bismuth-powered, carbamoylphosphonic acid, organofunctionalized amorphous silica, diacetyldioxime, polycyclodextrin and N-p-chorophenylcinnamohydroxamic acid (references can be found in [7]). The detection limits for these carbon paste modified electrodes were in the range from 1.1 to 220  $\mu g l^{-1}$ , with relative standard deviations from 2.6 to 6.5%. Hence, our device has improved significantly the detection limits existing until now, offering the second best result with an acceptable relative standard deviation value.

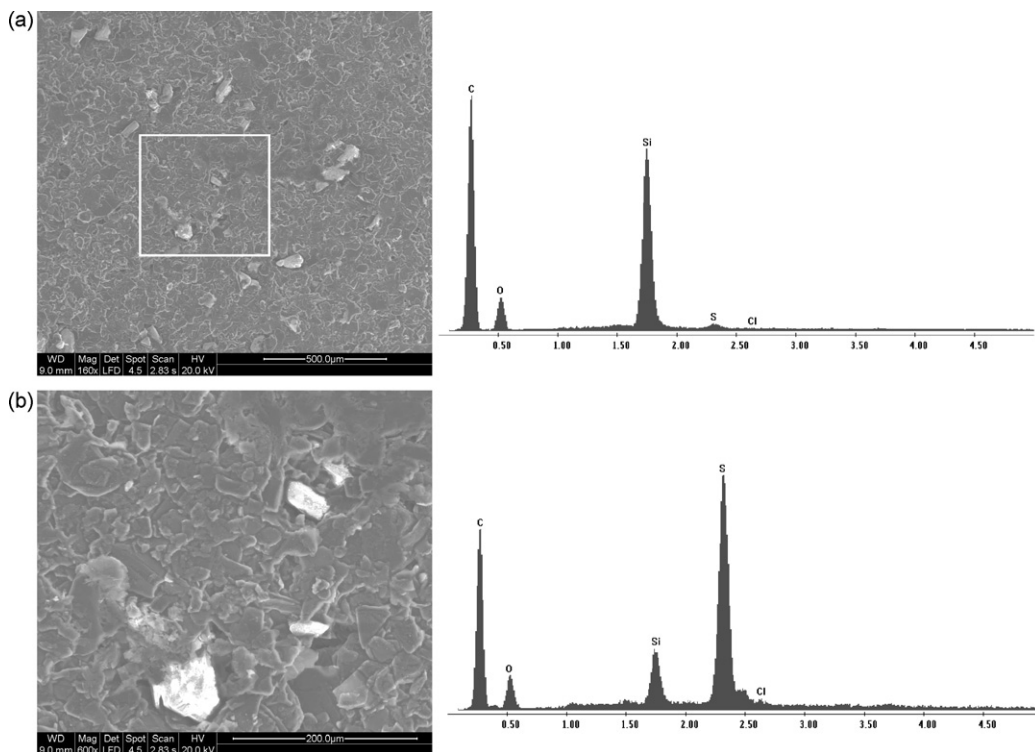
### 3.2. Characterization of the 1-furoylthiourea-modified Sonogel-Carbon materials by SEM, EDS, FTIR and XRD

The structural characterization of the 1-furoylthiourea-modified Sonogel-Carbon materials was performed, once the best formulation (18% of modifier with respect to the carbon weight) for 1-furoylthiourea-modified Sonogel-Carbon electrodes was optimised, and in order to corroborate the electrochemical studies.

#### 3.2.1. SEM and EDS

For each sample, the SEM and EDS studies were performed on the same equipment and at the same time, as mentioned in Section 2.

The 25 samples for SEM and EDS techniques were distributed as follows: 1-(2-furoyl)-3-(1-naphthyl)thiourea-modified Sonogel-Carbon material at the five different percentages in five different ways: polished electrode not used; polished electrode and used; non-polished electrode; and monolithic shapes with two faces, external (face dried in contact with the lab environment) and internal (face dried in contact with the drying recipient: polypropylene). Each face constituted one way of characterization.



**Fig. 5.** SEM micrographs and EDS spectra for a Sonogel-Carbon electrode modified with 1-(2-furoyl)-3-(1-naphthyl)thiourea: (a) general vision of the electrode surface with EDS beam focused on the Sonogel-Carbon material and (b) magnification of the same surface (square) with EDS beam focused on a shining particle, corresponding to 1-(2-furoyl)-3-(1-naphthyl)thiourea.

As SEM studies were carried out at low vacuum, it was not necessary a previous step of coating the samples with gold. The micrographs were taken at 20 kV.

In all cases, it can be observed the presence of non-conductive particles (shining particles in the micrographs) in the samples surface of the modified Sonogel-Carbon materials. Fig. 5 shows an example for a Sonogel-Carbon electrode modified with 18% of 1-(2-furoyl)-3-(1-naphthyl)thiourea. The particles on the surface of the material can be attributed to 1-furoylthioureas, due to the presence of sulphur in the EDS spectrum, besides carbon, oxygen and silicon, main components of the Sonogel-Carbon materials. The presence of chlorine corresponds to remaining traces of the acid catalysts (HCl) used for the Sonogel-Carbon synthesis, as discussed elsewhere [28].

A particularity, observed previously in the Sonogel-Carbon material, and not too marked in the 1-furoylthioureas modified Sonogel-Carbon materials is the volume contraction suffered by the Sonogel-Carbon materials in the drying step. This contraction has been previously described and exclusively depends on the formulation of the Sonogel-Carbon (quantity and type of graphite used)

and the drying time [28]. In this case, the new materials do not show a great volume contraction; therefore there is not an important separation between material and capillary tubes. However, the appearance of minor erosion can be observed: the formation of holes and fissures on the surface of the used electrode, since the electrodes have been continually used for a long time.

### 3.2.2. FTIR

As reported previously [28], FTIR technique was employed to characterize structurally the Sonogel-Carbon materials. The main purpose of using FTIR was to test whether the modification of this basis material with the 1-(2-furoyl)-3-(1-naphthyl)thiourea had caused some structural changes in it. This fact would be undesirable since the electrochemical application of this electrode might be affected in a dramatic way. That is why FTIR spectra for the 1-(2-furoyl)-3-(1-naphthyl)thiourea and the Sonogel-Carbon material modified with this thiourea were recorded (see Fig. 6).

In the FTIR spectrum for the 1-(2-furoyl)-3-(1-naphthyl)thiourea-modified Sonogel-Carbon material, some bands belonging to Sonogel-Carbon materials without modifi-

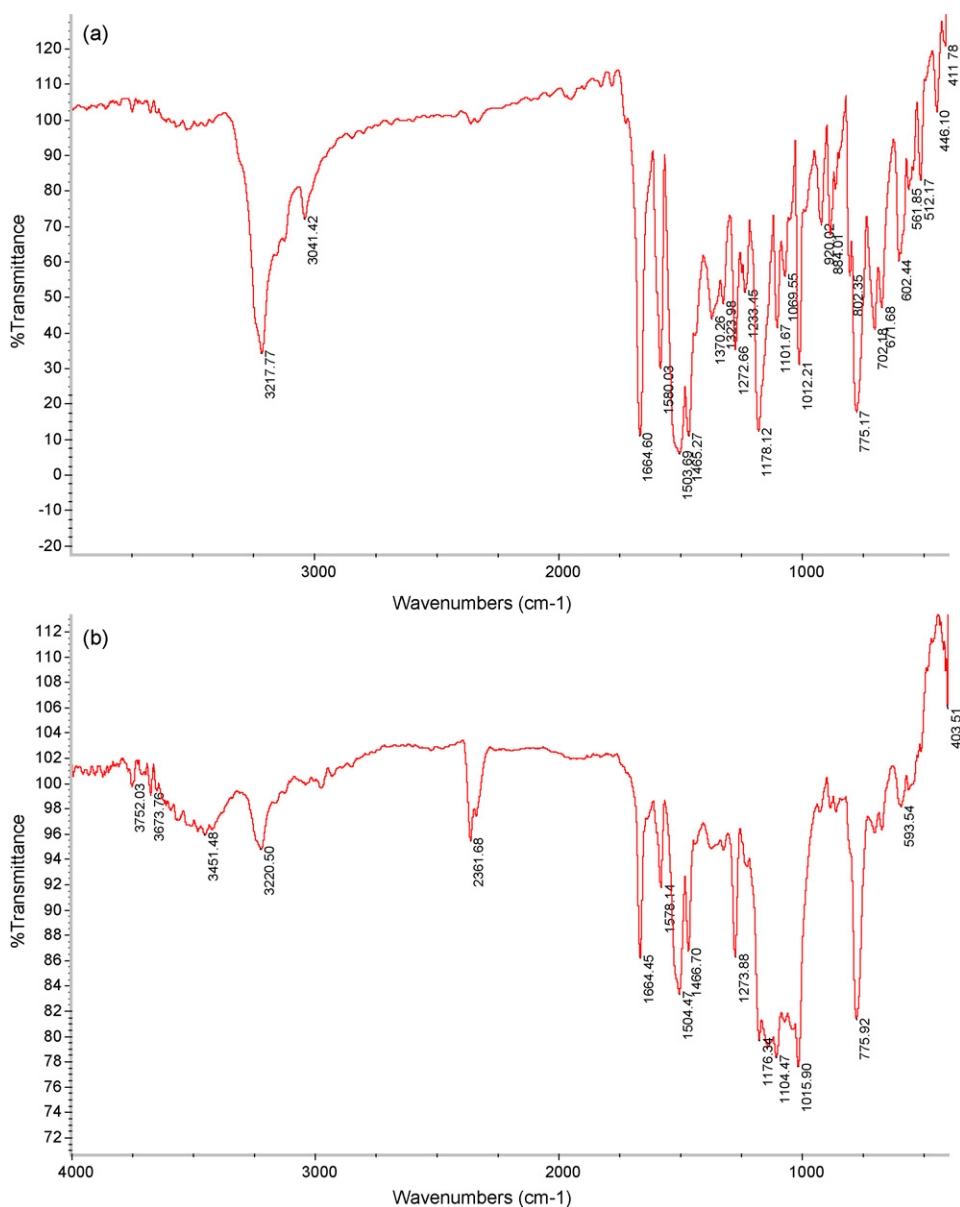


Fig. 6. FTIR spectra for: (a) 1-(2-furoyl)-3-(1-naphthyl)thiourea, and (b) Sonogel-Carbon-1-(2-furoyl)-3-(1-naphthyl)thiourea.

cation can be identified: the bands corresponding to Si–O–Si, Si–O stretching; they constitute a set of bands in the interval  $1125\text{--}1026\text{ cm}^{-1}$ ; the most frequent bands appear at  $1094, 1091, 1084, 1069, 1037$  and  $1029\text{ cm}^{-1}$ , according to the bibliography [42,43]; and the band that appears on  $770\text{ cm}^{-1}$ , belonging to Si–CH<sub>3</sub>, Si–C stretching; among others.

Among the bands corresponding to 1-furoylthiourea, the bands attributed to the C–S bending vibration, although a bit displaced, ( $1000\text{--}900\text{ cm}^{-1}$ ), and the bands corresponding to the aromatic ring ( $\sim 1600\text{ cm}^{-1}$ ) can be observed. The bands corresponding to N–C–N bonds can not be observed because the registered spectra have not arrived until the region of IR where they appear.

### 3.2.3. Single crystal and powder XRD

With respect to the results obtained after the single crystal and powder XRD measurements, Fig. 7 shows the diffractograms corresponding to three different samples: (a) 1-(2-furoyl)-3-(1-naphthyl)thiourea (single crystal XRD), (b) 1-(2-furoyl)-3-(1-naphthyl)thiourea-modified Sonogel-Carbon material (powder

XRD), and (c) Sonogel-Carbon without modifications (powder XRD).

The peaks of the thiourea that appear in the first diffractogram (a) can be appreciated in the diffractogram corresponding to the modified material (b), but their intensity is very low, if we compare it with the peaks belonging to the graphite (corresponding to a hexagonal configuration) that appear in the second and third diffractograms (b and c). It can be also appreciated the smallest intensity of these peaks in the diffractogram of the modified material (b), compared with the no-modified one (c). This difference is due to the decrease of the quantity of graphite in the case of the modified material which would change in the range from 82 to 100%.

Moreover, the single crystal XRD characterization of the 1-(2-furoyl)-3-(1-naphthyl)thiourea gave us crystal information similar to that described previously by Duque et al. [44]: monoclinic structure, lattice parameters, etc.

## 4. Conclusions

As conclusion we can say that the presence of 1-(2-furoyl)-3-(1-naphthyl)thiourea does not affect significantly the structure of our basis material.

The electrochemical studies using ASDPV showed its good electrochemical behaviour, giving well-defined voltammetric peaks, with high values of peak current, when tested versus the benchmark ion.

The structural characterization showed similar results that previous studies made with the Sonogel-Carbon materials with and without modifiers. The 1-furoylthiourea did not modify significantly the structure of these materials. In the FTIR studies, the bands corresponding to the functional groups of the 1-furoylthiourea were assigned, as well as the bands corresponding to the basis material: Sonogel-Carbon. With respect to the XRD characterization, the bands corresponding to the 1-furoylthiourea were also indexed and the crystalline structure information obtained was similar to the information reported in literature.

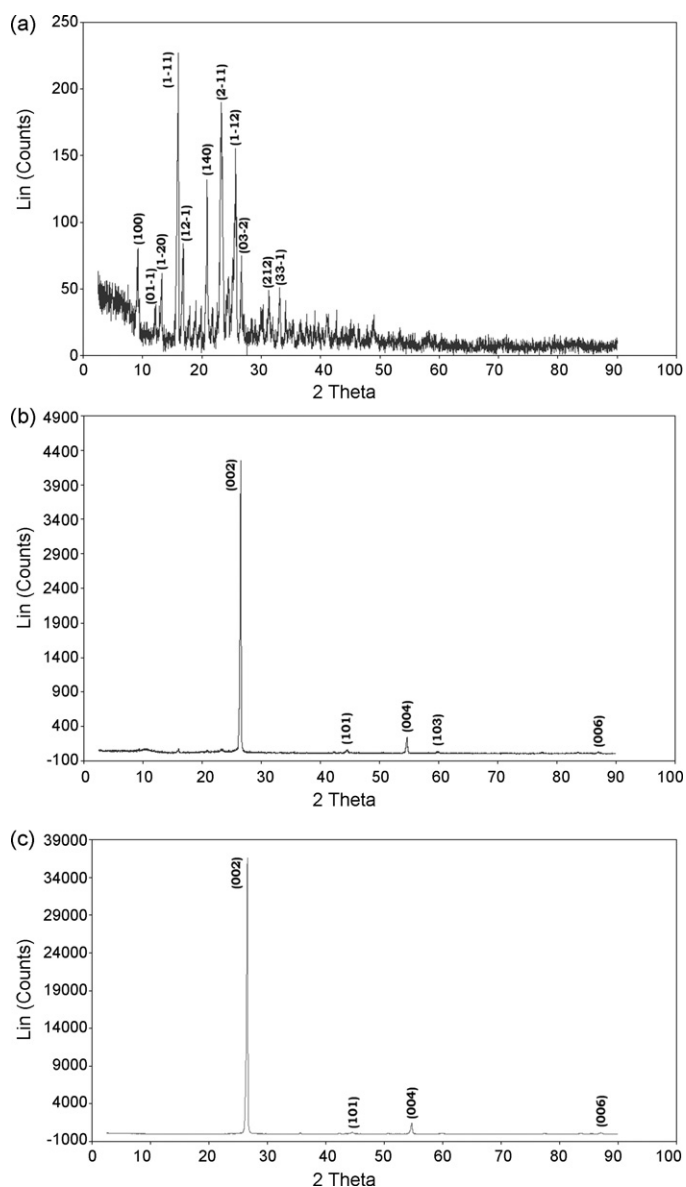
The studies with SEM and EDS showed similar results to those described in previous papers. However, one advantage of the modified electrodes reported here consists of suffering from fewer problems due to volume contraction and erosion before and after their use. These techniques have also allowed us to identify small and not conductive particles in the surface of the samples (1-furoylthiourea-Sonogel-Carbon materials); these particles correspond to the 1-furoylthiourea added as modifier. The presence of these particles in the surface of the electrodes is responsible of the good electrochemical behaviour of the sensor device versus the benchmark ion.

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**Fig. 7.** Diffractograms corresponding to three different samples: (a) 1-(2-furoyl)-3-(1-naphthyl)thiourea, (b) Sonogel-Carbon-1-(2-furoyl)-3-(1-naphthyl)thiourea and (c) Sonogel-Carbon without modifications.

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