

# Direct Electrochemical Determination of Glyphosate at Copper Phthalocyanine/Multiwalled Carbon Nanotube Film Electrodes

Fernando C. Moraes,<sup>a</sup> Lucia H. Mascaro,<sup>a</sup> Sergio A. S. Machado,<sup>b</sup> Christopher M. A. Brett<sup>c\*</sup>

<sup>a</sup> Departamento de Química, Universidade Federal de São Carlos – C.P. 676, 13560-970 São Carlos, SP, Brazil

<sup>b</sup> Instituto de Química de São Carlos, Universidade de São Paulo C.P. 780, 13560-970, São Carlos, SP, Brazil

<sup>c</sup> Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-535 Coimbra, Portugal

\*e-mail: brett@ci.uc.pt; tel/fax: +351-239835295

Received: December 17, 2009

Accepted: January 20, 2010

## Abstract

A copper phthalocyanine/multiwalled carbon nanotube film-modified glassy carbon electrode has been used for the determination of the herbicide glyphosate (Gly) at  $-50$  mV vs. SCE by electrochemical oxidation using differential pulse voltammetry (DPV). Cyclic voltammetry and electrochemical impedance spectroscopy showed that Gly is adsorbed on the metallic centre of the copper phthalocyanine molecule, with formation of Gly-copper ion complexes. An analytical method was developed using DPV in pH 7.4 phosphate buffer solution, without any pretreatment steps: Gly was determined in the concentration range of  $0.83$ – $9.90$   $\mu\text{mol L}^{-1}$ , with detection limit  $12.2$   $\text{nmol L}^{-1}$  ( $2.02$   $\mu\text{g L}^{-1}$ ).

**Keywords:** Copper phthalocyanine, Carbon nanotubes, Glyphosate, Electrochemical impedance spectroscopy, Differential pulse voltammetry, Nanotubes

DOI: 10.1002/elan.200900614

## 1. Introduction

Glyphosate (Gly) is a systemic, nonselective and broad-spectrum herbicide, being one of the most widely used in agriculture worldwide [1]. Gly, [*N*-(phosphonomethyl) glycine], has an action mechanism based in the inhibition of the enzyme 5-enolpyruvylshikimate 3-phosphate synthase, that acts directly on the biosynthesis of amino acids such as tryptophan, phenylalanine and tyrosine, which are fundamental to the development of plants [2].

Despite the fact that the toxicity of Gly in humans is very low [3], due to the fact that it is a small, very polar, molecule and has a high solubility in water, the indiscriminate use of Gly in many countries can cause considerable environmental impact. Thus, the development of analytical procedures for the monitoring of glyphosate has gained increasing importance.

Most of the analytical methods employed for the determination of Gly have been based on chromatographic techniques using different detection systems [4, 5]. In general, such analytical methodologies are not suitable for “in field” application nor for continuous monitoring. They often require several sample preparation steps, including extraction and clean-up procedures, in order to obtain a final extract fully compatible with chromatographic determination. These techniques also usually generate a large amount of waste containing organic solvents, which makes the procedure more complicated and expensive.

Electrochemical methods present the advantages of relatively low cost, high sensitivity, easy operation, potentiality for miniaturization and automation, and the ability to

construct simple, portable devices for fast screening purposes and for field/on-site monitoring. Up until now, the electrochemical detection of glyphosate has been indirect since Gly itself is not electroactive at accessible potentials and multistep procedures need to be devised or special adsorption strategies identified, such as modification of platinum electrode surfaces by silver carbonate sol [6]. Some of these indirect methods describe Gly detection via hydrolysis of the amino groups present in the herbicide molecule to form *N*-nitroso groups, in nitrous acid media; the nitroso groups are easily reduced and can be determined by voltammetric techniques [7, 8].

Other methodologies achieve the electrochemical detection of Gly through the use of copper electrodes [9, 10]. In this case, the Gly molecules’ functional groups – such as amino, carboxyl and phosphonate – bond to copper ions forming coordination compounds [11]. This strong coordinated interaction occurs in solutions of pH close to neutral [12]. The soluble complex formed, Gly-Cu<sup>2+</sup>, has electroactive copper ions and so the amount of Gly can be determined, in this indirect way, by using voltammetric techniques [13]. However, time has to be spent in the hydrolysis step and in surface pre-treatment of the metallic copper electrode, in order to generate available copper ions on the electrode surface, and promote the formation of the electroactive complex. Thus, the use of copper organometallic compounds, such as copper phthalocyanine, immobilized on suitable substrates, such as carbon nanotubes, would be an interesting alternative strategy for the electrochemical determination of glyphosate.

Carbon nanotubes (CNTs) have been extensively investigated for electroanalytical applications [14–16] due to their unique structure and physical properties. The excellent electrical conductivity, large surface area, significant mechanical strength, surface chemical reactivity and pore structure make CNTs attractive materials for electroanalysis. Since CNTs can easily be adsorbed on the surface of glassy carbon electrodes, they have been studied extensively for a large variety of applications, particularly for solid-state chemical and biological sensors [17, 18].

Metallophthalocyanine complexes (MPc) are recognized for their excellent electrocatalytic activity for many reactions, which is highly dependent on the central metal atom (as well as on substituents in the case of aza-macrocyclic compounds) [19]. It is known that amino-substituted metallophthalocyanine complexes can be covalently linked to CNTs via amide bond formation [20] while nonsubstituted MPc complexes are noncovalently adsorbed onto CNTs via  $\pi$ – $\pi$  interactions. It has been observed that phthalocyanine-CNT complexes have the excellent catalytic properties of phthalocyanines without losing any of the electronic properties of carbon nanotubes [21].

In the study reported here, MWCNT act as substrate to adsorb copper phthalocyanine and this electrocatalytic system was employed, to our knowledge for the first time, for the direct oxidative detection of glyphosate using differential pulse voltammetry (DPV).

## 2. Experimental

### 2.1. Apparatus and Procedures

Differential pulse voltammetry (DPV) experiments were performed using a model PGSTAT40 Autolab electrochemical system (Metrohm Autolab, Utrecht, Netherlands) coupled to a personal computer and controlled with GPES 4.9 software. The electrochemical cell was assembled with a conventional three-electrode system: glassy carbon electrode (3.0 mm diameter) modified with multi-walled carbon nanotubes (GC/MWCNT) or glassy carbon electrode modified with multi-walled carbon nanotubes plus copper phthalocyanine (GC/MWCNT/CuPc), a saturated calomel electrode (SCE) as reference and a Pt wire as auxiliary electrode. All experiments were carried out at room temperature ( $25 \pm 1^\circ\text{C}$ ).

A  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> stock solution of glyphosate (99.8% purity, Sigma-Aldrich, Germany), was prepared daily in purified water. Aliquots of this stock solution were diluted in aqueous electrolyte solution for the voltammetric experiments. Solutions of sodium phosphate buffer (PB) of ionic strength 0.1 mol L<sup>-1</sup> were used in all experiments as supporting electrolyte, and were prepared using analytical grade reagents and purified water from a Millipore Milli-Q system (conductivity  $< 0.1 \mu\text{S cm}^{-1}$ ).

The DPV measurements for constructing the Gly calibration curves were performed using optimized parameters (see Section 3.2): an amplitude of 100 mV, step potential of

2 mV, a pulse interval of 200 ms and a sampling time of 20 ms, in 0.1 mol L<sup>-1</sup> of PB (pH 7.4). Electrochemical impedance spectroscopy (EIS) data were obtained using a PC-controlled Solartron 1250 Frequency Response Analyzer coupled to a Solartron 1286 Electrochemical Interface using ZPlot 2.4 software (Solartron Analytical, UK), scanning from 65 kHz to 100 mHz frequency range with 10 mV amplitude sinusoidal perturbation, and 10 data points per frequency decade. The impedance spectra were recorded within the potential range for the glyphosate oxidation process, in 0.1 mol L<sup>-1</sup> PB (pH 7.4) containing  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> of glyphosate stock solution.

### 2.2 Preparation of the Electrodes

First, 1.0 g of MWCNT (90% purity, Sigma-Aldrich) synthesized by thermal chemical vapor deposition, was mixed with 500 mL of a 1:3 (v/v) mixture of HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> and boiled for 12 h, in order to remove most of the metallic impurities and promote CNT functionalization. The MWCNT was then filtered through a 0.45  $\mu\text{m}$  Millipore Nylon filter membrane. The resulting functionalized MWCNT were continuously washed using distilled water until the pH of the filtrate was neutral and were then dried overnight in a vacuum oven at 120 °C.

Prior to modification, the glassy carbon electrode surface was polished with 0.5  $\mu\text{m}$  alumina slurry, rinsed thoroughly with ultrapure water, sonicated 3 min in acetone and 3 min in water, and dried in air. For MWCNT, a mass of 2.0 mg of MWCNT was dispersed in 1.0 mL dimethylformamide (DMF) for 20 min using ultrasonic stirring. For MWCNT/CuPc, 2.0 mg of treated MWCNT plus 1.0 mg of CuPc (Sigma-Aldrich) was dispersed by ultrasonic stirring for 20 min in 1.0 mL of DMF. A 10  $\mu\text{L}$  aliquot of one or the other dispersion was placed as a droplet on the GC electrode surface and the solvent was then left to evaporate at room temperature. DMF was used because it was found to be more compatible with the hydrophobic nature of the GC surface than other solvents (ethanol, acetone etc.) and led to a more homogeneous film.

## 3. Results and Discussion

### 3.1. Electroactivity of GC/MWCNT/CuPc Electrode for Direct Glyphosate Oxidation

The studies of Gly oxidation on GC, GC/MWCNT and GC/MWCNT/CuPc electrodes were carried out by differential pulse voltammetry (DPV) with optimized parameters determined by maximization of peak current signal: amplitude of 100 mV, step potential of 2 mV and effective scan rate of 10 mV s<sup>-1</sup> in 0.1 mol L<sup>-1</sup> PB (pH 7.4), both in the absence and presence of 1.0 mmol L<sup>-1</sup> of Gly. The results obtained are presented in Figure 1. At the GC/MWCNT electrode an oxidative process was observed, both in the presence and absence of Gly in solution, with peak potential

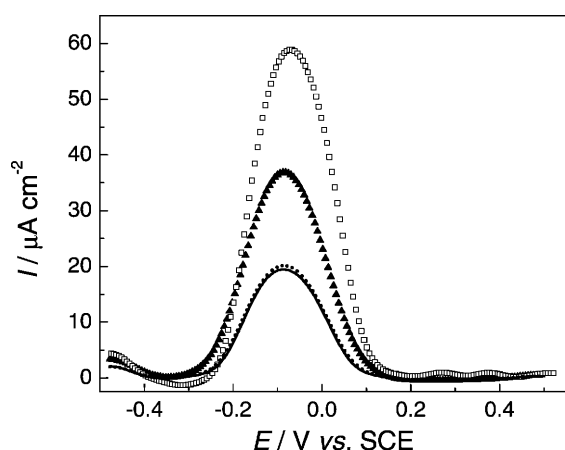


Fig. 1. Differential pulse voltammograms, in 0.1 mol L<sup>-1</sup> PB (pH 7.4) for the electrodes: GC/MWCNT in absence of Gly (—), GC/MWCNT in the presence of 1.0 mmol L<sup>-1</sup> Gly (·····), GC/MWCNT/CuPc in the absence of Gly (▲) and GC/MWCNT/CuPc in the presence of 1.0 mmol L<sup>-1</sup> Gly (□). DPV parameters: 100 mV amplitude, 2 mV step potential.

close to -70 mV vs. SCE; this was associated with functional groups, such as carbonyl or carboxyl, on the functionalized carbon nanotube surface [22].

The DPV response of the GC/MWCNT/CuPc electrode in the absence of Gly, reveals an oxidative process close to -50 mV, similar to that discussed above for the GC/MWCNT electrode. However, besides the oxidation of the functionalized carbon nanotube surface, De Wael et al. [23] report the occurrence of another anodic electrochemical process, at approximately -50 mV, due to the oxidation of Cu(I) to Cu(II) in the phthalocyanine ring. These authors showed [23] that the peak current values increased with the number of voltammetric cycles, since Cu(I) is formed during the potential scanning.

The addition of Gly to the electrolyte leads to a significant increase in the peak current of the oxidation process. This increase is probably due to the interaction between the glyphosate molecule and the copper ions present in the metallic centre of the copper phthalocyanine molecules. Such a behaviour is in agreement with that discussed by Coutinho et al. [12] who showed that the strong interaction between Gly and copper ions forms a stable complex and allows the detection of Gly by indirect electrochemical methods, based on the Cu(I)/Cu(II) couple.

The dependence of the peak current and potential of the oxidation of the Gly-CuPc complex on electrolyte pH was studied by DPV in the pH range from 6.0 to 9.0 in different phosphate buffer solutions (ionic strength 0.1 mol L<sup>-1</sup>) containing 1.0 mmol L<sup>-1</sup> glyphosate. The results obtained

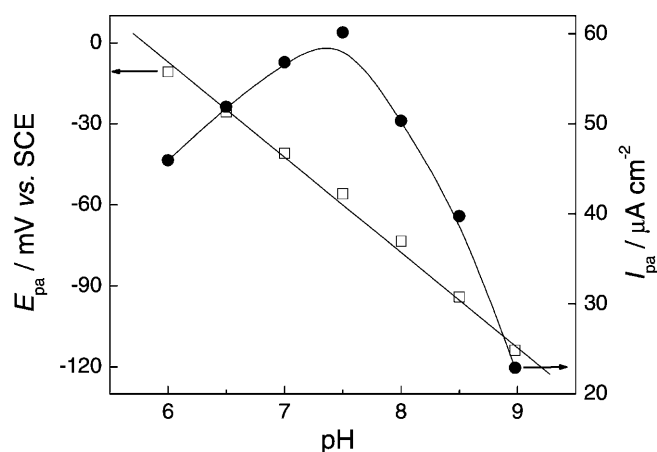


Fig. 2. Effect of pH on the peak potential (□) and peak current (●) for Gly oxidation at the GC/MWCNT/CuPc film electrode using 0.1 mol L<sup>-1</sup> PB electrolyte containing 1.0 mmol L<sup>-1</sup> Gly.

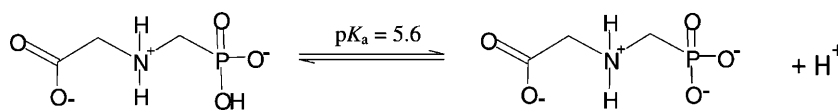
are presented in Figure 2, in the form of plots showing the DPV peak current ( $I_{pa}$ ) and peak potential ( $E_{pa}$ ) as a function of pH.

The variation of  $E_{pa}$  with pH shows that an increase in pH causes a shift in the peak potential towards more negative values, the experimental value of the slope of the plot of  $E_{pa}$  vs. pH being 32 mV per pH unit. This suggests, from the corresponding Nernst equation, the involvement of two electrons for each proton in the electrochemical oxidation process.

The plot of  $I_{pa}$  vs. pH has a maximum value at pH 7.4 decreasing sharply for both higher and lower pH values. Sprankle et al. [24] reported that Gly presents a sequence of equilibria with acid dissociation constants ( $pK_a$ ): 2.0, 2.6, 5.6 and 10.6. Near pH 7.4, most of the functional groups present in the Gly molecule, the carboxylate and phosphonate groups, are deprotonated, as shown in Scheme 1. These functional groups coordinate strongly with transition metals [25], thus stabilizing the Cu(I) species. At pH 7.4 the peak current showed the highest response and was thus selected for subsequent experiments using the GC/MWCNT/CuPc film electrode.

The effect of scan rate on the peak current on the GC/MWCNT/CuPc electrode was also investigated. There is a linear relationship between the anodic current peak and the scan rate in the range between 5 and 100 mV s<sup>-1</sup>, which can be described by the equation  $I_{pa} = 0.121 + 0.125 v$  ( $I_{pa}$  in  $\mu A$  and scan rate in mV s<sup>-1</sup>,  $r = 0.992$ ), which reflects the control of the electrochemical process by adsorbed species.

Electrochemical impedance spectroscopy experiments were performed to investigate the possibility of Gly adsorption on the electrode surface. Impedance spectra



Scheme 1. Equilibrium and dissociation constant of the herbicide glyphosate.

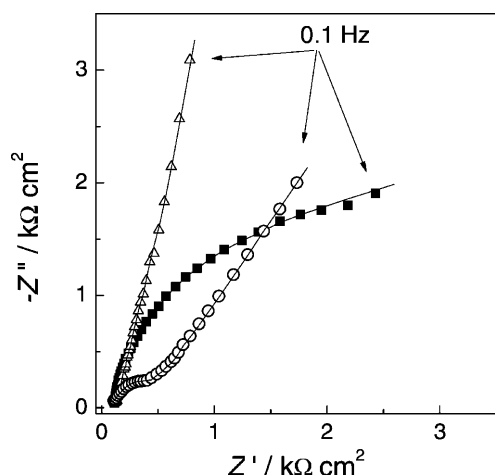


Fig. 3. Complex plane impedance spectra at GC/MWCNT/CuPc film electrode in: ( $\Delta$ ) 0.1 mol L<sup>-1</sup> PB (pH 7.4), ( $\blacksquare$ ) 0.1 mol L<sup>-1</sup> PB (pH 7.4) containing 1.0 mmol L<sup>-1</sup> Gly and ( $\circ$ ) 0.1 mol L<sup>-1</sup> PB (pH 7.4) after 10 cycles in 1.0 mmol L<sup>-1</sup> Gly. The solid lines show fitting to the equivalent circuit described in the text.

were recorded in 0.1 mol L<sup>-1</sup> of PB (pH 7.4) (blank solution), 0.1 mol L<sup>-1</sup> of PB (pH 7.4) containing 1.0 mmol L<sup>-1</sup> of Gly and in 0.1 mol L<sup>-1</sup> of PB (pH 7.4) after ten successive cyclic voltammograms between  $-0.5$  and  $+0.5$  V vs. SCE in a solution containing 1.0 mmol L<sup>-1</sup> of glyphosate. Impedance spectra were recorded at  $-70$  mV vs. SCE, the oxidation peak potential of Gly. In Figure 3 are presented impedance spectra as complex plane plots for the GC/MWCNT/CuPc electrode in these three situations. An equivalent electrical circuit with a cell resistance,  $R_{\Omega}$ , in series with a parallel combination of a constant phase element, CPE, and a charge transfer resistance,  $R_{ct}$ , was used to fit the spectra. The CPE was found to be necessary because of the heterogeneous nature of the electrode surface, expressed through the exponent  $\alpha$ , where  $\alpha = 1$  represents a perfectly smooth and uniform surface.

In blank electrolyte, the sloping straight-line can be considered as a nonideal capacitor, which is a characteristic of double layer charging on a nonhomogeneous surface [26]; in this case  $R_{ct}$  was removed from the fitting circuit. The fitting obtained values for CPE and  $\alpha$  were  $1.55 \mu\text{F cm}^{-2} \text{s}^{\alpha-1}$  and 0.85 respectively.

With the addition of 1.0 mmol L<sup>-1</sup> of Gly to the electrolyte, the spectrum presented a semicircle at high to medium frequencies, characteristic of a charge transfer reaction, and a straight line at low frequencies, corresponding to diffusion control. The values calculated by fitting were  $0.68 \text{ k}\Omega \text{ cm}^2$  for  $R_{ct}$ ,  $2.72 \mu\text{F cm}^{-2} \text{s}^{\alpha-1}$  for CPE and 0.82 for  $\alpha$ . Calculation of the apparent standard rate constant of the reaction from  $R_{ct}$  according to  $k_{app} = RT/F^2 R_{ct} c$  [27] leads to the value of  $3.55 \times 10^{-4} \text{ cm s}^{-1}$ , where  $c$  is the glyphosate concentration (in mol cm<sup>-3</sup>) and  $R$ ,  $T$  and  $F$  have their usual meanings.

Following ten potential cycles in the presence of Gly, an impedance spectrum of GC/MWCNT/CuPc was recorded in PB without Gly. Significant differences were observed in the spectra after exposure of the electrode to Gly solution. The

values calculated by fitting were  $10 \mu\text{F cm}^{-2} \text{s}^{\alpha-1}$  for CPE, 0.84 for  $\alpha$  and  $4.75 \text{ k}\Omega \text{ cm}^2$  for  $R_{ct}$ . The increase in the CPE and  $R_{ct}$  values can be attributed to saturation of the available electrode sites by glyphosate molecules. These results are in agreement with the scan rate study, confirming a surface-confined process.

### 3.2. Optimization of Experimental Parameters for Glyphosate Oxidation on the GC/MWCNT/CuPc Film Electrode

To maximize the DPV analytical signal, the effects of experimental parameters (film composition, pulse amplitude and potential step height) were studied at the GC/MWCNT/CuPc film electrode, in 0.1 mol L<sup>-1</sup> PB, at pH 7.4, containing 1.0 mmol L<sup>-1</sup> of Gly.

The effect of the composition of the MWCNT/CuPc film on the DPV profiles at the GC/MWCNT/CuPc electrode was evaluated in experiments in 0.1 mol L<sup>-1</sup> PB (pH 7.4) electrolyte solution containing 1.0 mmol L<sup>-1</sup> Gly, as shown in Figure 4. In such studies the amount of MWCNT (1.0 mg per mL of suspension) was kept constant and the quantity of CuPc was varied from 0.25 to 2.0 mg per mL of suspension.

The peak current values increase up to 1.0 mg of CuPc in the film. For larger amounts of CuPc a decrease in the peak current was found. In previous work [16, 28] it was observed that cobalt phthalocyanine has poor adhesion to the surface of glassy carbon electrodes. Thus, the decrease in the analytical signal may be due to the instability of the MWCNT/CuPc film on glassy carbon electrode surfaces. Larger proportions of CuPc result in electrode assemblies which are unsuitable for analytical use. The best film was obtained from the suspension ratio: 1.0 mg of MWCNT, 1.0 mg of CuPc and 1.0 mL of DMF solvent.

The influence of DPV voltammetric parameters was also investigated. First, the pulse amplitude was varied in the range of 10–100 mV, at a constant step potential of 2 mV,

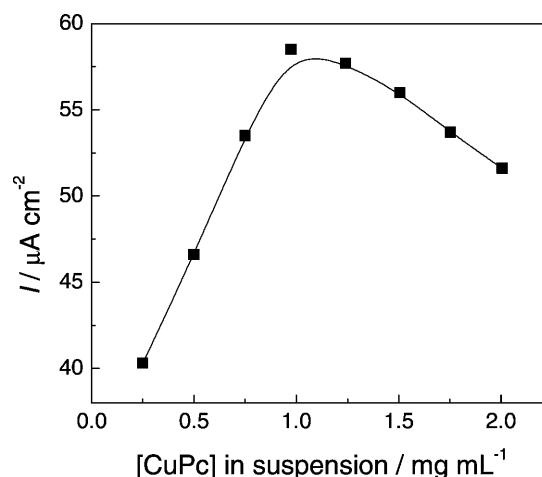


Fig. 4. Effect of the CuPc concentration in the CNT suspension on the Gly oxidation peak current, in 0.1 mol L<sup>-1</sup> PB (pH 7.4), containing 1.0 mmol L<sup>-1</sup> Gly, with the optimised DPV parameters.

effective scan rate  $10 \text{ mV s}^{-1}$ . In such conditions,  $I_{\text{pa}}$  increased with increasing amplitude. For amplitude values as high as  $100 \text{ mV}$ , no deformation of the peak shape was observed, such as an increase in peak width. Hence,  $100 \text{ mV}$  was chosen as the DPV amplitude.

Fixing the amplitude at  $100 \text{ mV}$ , the effect of potential step increment was studied, in the range of  $1\text{--}10 \text{ mV}$ , keeping the effective scan rate constant at  $10 \text{ mV s}^{-1}$ . For potential steps greater than  $2 \text{ mV}$ , deformation of the voltammetric profile was observed and the current peak decreased in height. Hence a  $2 \text{ mV}$  potential step increment was selected.

### 3.3. Analytical Curve for Glyphosate

DPV experiments were carried out in triplicate using the optimized experimental parameters in order to obtain an analytical curve for the determination of Gly at the GC/MWCNT/CuPc film electrode, see Figure 5. The analytical curve shown in the Inset of Figure 5 has a linear response in the range of  $0.83\text{--}9.90 \mu\text{mol L}^{-1}$ , according to:

$$I (\mu\text{A cm}^{-2}) = (0.54 \pm 0.05) (\mu\text{A cm}^{-2}/\mu\text{mol L}^{-1}) + (6.14 \pm 0.09) [\text{Gly}] (\mu\text{mol L}^{-1})$$

with a correlation coefficient of  $0.9994$  ( $n = 7$ ). The  $LOD$  of  $12.2 \text{ nmol L}^{-1}$  ( $2.02 \mu\text{g L}^{-1}$ ) was determined using a  $3\sigma/\text{slope}$  ratio, where  $\sigma$  is the standard deviation of the mean value for 10 voltammograms of the blank, determined according to IUPAC recommendations, as stated in [29].

The method yielded values for the  $LOD$  lower than those required for the environmental monitoring of glyphosate in surface water by many government agencies, as reported by IUPAC [30]. Depending on the legislation, the maximum

permitted residue levels in such matrices can vary from  $50.0$  to  $1.0 \mu\text{g L}^{-1}$  of glyphosate.

Comparing the detection limit of  $12 \text{ nmol L}^{-1}$  at the GC/MWCNT/CuPc film electrode with other electroanalytical methods, there is a significant improvement in relation to the indirect determinations of Gly using metallic copper electrodes of  $30.0 \mu\text{mol L}^{-1}$  ( $5.07 \text{ mg L}^{-1}$ ) [9] and  $0.35 \mu\text{mol L}^{-1}$  ( $59 \mu\text{g L}^{-1}$ ) [10]. Higher sensitivity was also observed at the GC/MWCNT/CuPc film electrode, which can be attributed to the efficiency of the electron transfer between the modified electrode and Gly due to the relatively high rate constant for the oxidation process.

### 4. Conclusions

Carbon nanotubes on glassy carbon electrode substrates were used to attach copper phthalocyanine, making use of the unique properties of CNTs such as high specific surface area and strong adsorptive ability. This assembly was shown to be efficient in the detection of the herbicide glyphosate. Differential pulse voltammetry was used to investigate the mechanism of oxidation. Cyclic voltammetry and electrochemical impedance spectroscopy studies showed the adsorption of glyphosate on the GC/MWCNT/CuPc film electrode surface, by complexation, at neutral pH, between functional groups in the Gly molecule and phthalocyanine copper ions.

Differential pulse voltammetry yielded values for the  $LOD$  lower than those required for environmental control for glyphosate in surface waters and demonstrates that the electrochemical sensor described here can be used to analyze and monitor glyphosate in natural samples directly and in real time.

### Acknowledgements

Financial support from *CNPq* (SWE Proc. 201494/2008-6) Brazil, and for the scholarship to FCM and from *Fundação para a Ciência e Tecnologia* (FCT), Portugal, projects PTDC/QUI/65255/2006 and PTDC/QUI/65732/2006, POCI (co-financed by the *European Community Fund FEDER*), and *CEMUC* (Research Unit 285), is gratefully acknowledged.

### References

- [1] L. A. Castle, D. L. Siehl, R. Gorton, P. A. Patten, Y. H. Chen, S. Bertain, H. Cho, N. Duck, J. Wong, D. Liu, M. W. Lassner, *Science* **2004**, *304*, 1151.
- [2] F. Rubio, L. Veldhuis, S. Clegg, F. Fleeker, J. Hall, *J. Agric. Food Chem.* **2003**, *51*, 691.
- [3] U.S. Environmental Protection Agency (EPA), <http://www.epa.gov/iris/subst/0057.htm>, (accessed on December 08, 2009).
- [4] N. F. Zelenkova, N. G. Vinokurova, *J. Anal. Chem.* **2008**, *63*, 871.

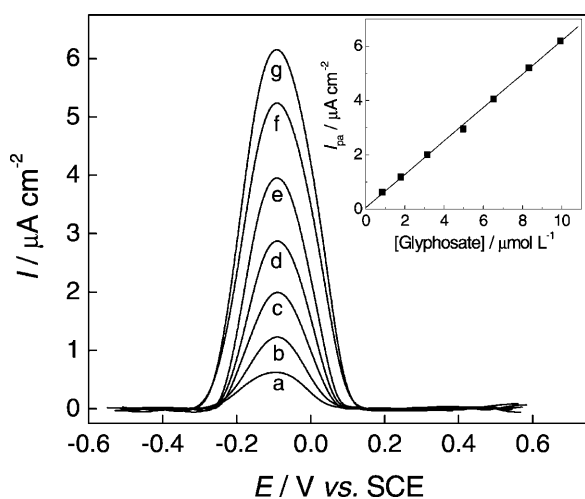


Fig. 5. Differential pulse voltammograms at the GC/MWCNT/CuPc film electrode, after background subtraction of the response in the absence of Gly, using the optimized DPV parameters; Gly concentrations in  $\mu\text{mol L}^{-1}$ : (a)  $0.83$ , (b)  $1.66$ , (c)  $3.32$ , (d)  $4.97$ , (e)  $6.62$ , (f)  $8.26$  and (g)  $9.90$ . Inset: linear dependence of peak current with Gly concentration.

- [5] I. Hanke, H. Singer, J. Hollender, *Anal. Bioanal. Chem.* **2008**, *391*, 2265.
- [6] M. A. Méndez, M. F. Suárez, M. T. Cortés, V. M. Sarria, *Electrochem. Commun.* **2007**, *9*, 2585.
- [7] W. F. Smyth, P. Watkiss, J. S. Burmicz, H. O. Hanley, *Anal.-Chim. Acta* **1975**, *78*, 81.
- [8] R. F. Teófilo, E. L. Reis, C. Reis, G. A. da Silva, L. T. Kubota, *J. Braz. Chem. Soc.* **2004**, *15*, 865.
- [9] E. V. Sierra, M. A. Méndez, V. M. Sarria, M. T. Cortés, *Quim. Nova* **2008**, *31*, 220.
- [10] A. F. Garcia, M. C. Rollemberg, *Quim. Nova* **2007**, *30*, 592.
- [11] E. Morillo, C. Maqueda, M. Bejarano, L. Madrid, T. Undabeytia, *Chemosphere* **1994**, *28*, 2185.
- [12] C. F. B. Coutinho, L. H. Mazo, *Quim. Nova* **2005**, *28*, 1038.
- [13] C. F. B. Coutinho, M. O. Silva, S. A. S. Machado, L. H. Mazo, *Appl. Surf. Sci.* **2007**, *253*, 3270.
- [14] Q. J. Wan, X. W. Wang, F. Yu, X. X. Wang, N. J. Yang, *J. Appl. Electrochem.* **2009**, *39*, 785.
- [15] A. Salimi, B. Kavosi, R. Hallaj, A. Babaei, *Electroanalysis* **2009**, *21*, 909.
- [16] F. C. Moraes, M. F. Cabral, S. A. S. Machado, L. H. Mascaro, *Electroanalysis* **2008**, *20*, 851.
- [17] F. C. Moraes, S. T. Tanimoto, G. R. Salazar-Banda, S. A. S. Machado, L. H. Mascaro, *Electroanalysis* **2009**, *21*, 1091.
- [18] H. Ma, L. Zhang, Y. Pan, K. Zhang, Y. Zhang *Electroanalysis* **2008**, *20*, 1220.
- [19] J. Costamagna, G. Ferraudi, B. Matsuhira, M. Campos-Vallette, J. Canales, M. Villagra'n, J. Vargas, M. J. Aguirre, *Coord. Chem Rev.* **2000**, *196*, 125.
- [20] G. de la Torre, W. Blau, T. Torres, *Nanotechnology* **2003**, *14*, 765.
- [21] X. Wang, Y. Liu, W. Qiu, D. Zhu, *J. Mater. Chem.* **2002**, *12*, 1636.
- [22] C. A. Thorogood, G. G. Wildgoose, A. Crossley, R. M. J. Jacobs, J. H. Jones, R. G. Compton, *Chem. Mater.* **2007**, *19*, 4964.
- [23] K. De Wael, K. Peeters, D. Bogaert, H. Buschop, L. Vincze, A. Adriaens, *J. Electroanal. Chem.* **2007**, *603*, 212.
- [24] P. Sprankle, W. F. Meggitt, D. Penner, *Weed Sci.* **1975**, *23*, 229.
- [25] V. Subramaniam, P. E. Hoggard, *J. Agric. Food Chem.* **1988**, *36*, 1326.
- [26] W. G. Pell, A. Zolfaghari, B. E. Conway, *J. Electroanal. Chem.* **2002**, *532*, 13.
- [27] E. Sabatani, I. Rubinstein, *J. Phys. Chem.* **1987**, *91*, 6663.
- [28] F. C. Moraes, L. H. Mascaro, S. A. S. Machado, C. M. A. Brett, *Talanta* **2009**, *79*, 1406.
- [29] Analytical Methods Committee, *Analyst* **1987**, *112*, 199.
- [30] D. J. Hamilton, Á. Ambrus, R. M. Dieterle, A. S. Felsot, C. A. Harris, P. T. Holland, A. Katayama, N. Kurihara, J. Linders, J. Unsworth, S. S. Wong, *Pure Appl. Chem.* **2003**, *75*, 1123.