

Assessment of Multiwalled Carbon Nanotube Paste Electrode for Square-Wave Adsorptive Cathodic Stripping Voltammetric (SWAdCSV) Determination of Methyl Parathion in Water Samples

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ABSTRACT

In this paper the assessment of an electrode composed by multiwalled carbon nanotube (MWCNT) dispersed in mineral oil as well as its application on the electrochemical determination of methyl parathion (MP) in environmental water samples by square-wave adsorptive cathodic stripping voltammetry (SWAdCSV) is described. The suitability of the electrode for this purpose was confirmed by comparing it to a glassy carbon electrode (GCE) and to a carbon paste electrode (CPE). A 7.1- and 3.4-fold increase of the signal, respectively, was achieved. In order to obtain the best performance of the method, significant factors were established by a factorial design and the method optimized by employing the Doehlert matrix. Based on these chemometric tools the following experimental conditions were selected: 7.95, 70 mV, 205 Hz and 0.3 mol L⁻¹, respectively, for sample pH, PA, F and BC. A study of interferences was conducted through the addition of inorganic ions NO₃⁻, SO₄²⁻, PO₄³⁻ and Mn²⁺ during MP analysis and no interference was noted. The method presented a linear range between 0.56 and 18.00 μmol L⁻¹ (r = 0.995), limit of detection (LD) of 0.15 μmol.L⁻¹ and limit of quantification (LQ) of 0.49 μmol.L⁻¹. The determination of MP on environmental spiked samples showed good recovery values and repeatability.

Keywords: electrochemical analysis, environmental sample, factorial design, total organophosphate assay

Abbreviations: BC, buffer concentration; CNT, carbon nanotube; CPE, carbon paste electrode; DP, deposition potential; DT, deposition time; F, frequency; GCE, glassy carbon electrode; HPLC, high performance liquid chromatography; LD, limit of detection; LQ, limit of quantification; MP, methyl parathion; MWCNT, multiwalled carbon nanotube; OP, organophosphate; PA, pulse amplitude; SWAdCSV, square-wave adsorptive cathodic stripping voltammetry

INTRODUCTION

Methyl parathion (MP) is an important broad-spectrum organophosphate (OP) insecticide which is the most commonly used in the class of OPs and widely used in some kinds of vegetable crops (Akhtar *et al.* 2007). Although this compound does not remain for a long time in the environment, its highly toxic potential and its mechanism of action, irreversibly inhibiting the degradation of acetylcholine, have encouraged several researchers to work on this matter in recent years (Worek *et al.* 2007).

In the field of analytical chemistry some techniques have been used to determine MP in distinct kinds of samples, namely biological, chemical and environmental (Deo *et al.* 2005). Indeed, high performance liquid chromatography (HPLC) and gas chromatography (GC) have been the techniques widely used for these purposes (Martinez *et al.* 1992; Pérez-Ruiz *et al.* 2005; Guo and Jans 2006; Liu *et al.* 2006). However, such analytical techniques commonly require high implementation and maintenance costs as well as skilled personnel. These constraints justify the search for new methods and suggest that the electrochemical analytical method for insecticide is still indispensable. Some advantages of electroanalytical methods for analysis of insecticides are simplicity, possibility of simultaneous determination, relatively low cost and high sensitivity (Bourque *et al.* 1989; Sreedhar *et al.* 1997; Al-Meqbali *et al.* 1998; El-Shahawi and Kamal 1998; Ulakhovich *et al.* 1998; Ni *et al.* 2004; Santos *et al.* 2008). Additionally, these features can

be achieved by adequate employment of electroanalytical method and the nature of the working electrode. In this sense, one of the most sensitive electroanalytical techniques is the SWAdCSV. A typical determination experiment in SWAdCSV includes two steps: an adsorptive preconcentration of analyte, which can be a metallic complex or an organic molecule onto an electrode surface, followed by square-wave cathodic stripping voltammetric detection. The adsorption step is performed at a controlled potential as it determines the adsorption efficiency. In spite of a controlled potential being used in the preconcentration step, the retention of the analyte onto the surface of the electrode does not take place by electrodeposition; instead the analyte is adsorbed by involving electrostatic attraction or hydrophobic interaction (Shubietah *et al.* 1994; Achterberg and Braungardt 1999). Generally, SWAdCSV is carried out using a hanging mercury dropping electrode (HMDE). However, efforts have been made to develop new electrodes to replace HMDE, such as CPE (Liu and Lin 2005), modified GCE (Du *et al.* 2008a, 2008b) and modified carbon nanotube (Du *et al.* 2008c). Taking into account that in SWAdCSV an adsorption step is carried out, the materials employed for building the electrodes must comprise excellent specific surface area. Thus, nanostructured materials, especially carbon nanotubes (CNTs), have received significant attention for the preparation of electrochemical sensors owing to their intrinsic properties, such as high surface area and high chemical and electrical properties. Various kinds of CNTs have been used to build novel electrodes with interest for

electroanalytical applications (Tarley *et al.* 2009). Their application in adsorptive stripping voltammetric techniques for organic molecules is especially favorable because previous studies based on solid phase extraction coupled to chromatographic techniques have shown excellent adsorption capacity for analytes of environmental interest, including phenolic compounds and insecticides (Wang *et al.* 2007; Du *et al.* 2008a). Despite their excellent features as a sensing material for building electrode (Fanjul-Bolado *et al.* 2007), the use of CNTs in adsorptive stripping voltammetric techniques is still little exploited, whereas the unique publications on this subject has focused on nucleic acids (Pedano and Rivas 2004), amitrole (Chicharro *et al.* 2005), 4-aminophenol (Huang *et al.* 2003), 2,4,6-trinitrotoluene (Wang *et al.* 2004) and reserpine (Zhang and Wu 2005).

Therefore, the aim of the present work was to assess the performance of multiwalled CNT paste electrode as a new sensing electrode for direct MP determination in water samples using SWAdCSV.

EXPERIMENTAL

Apparatus

All the electrochemical measurements were performed on a Potentiostat/Galvanostat Autolab PGSTAT12 (Eco Chemie BV, Utrecht, The Netherlands) with a conventional three electrode cell comprising a platinum wire as an auxiliary electrode, an Ag/AgCl (3 M KCl) reference electrode and the CNT paste electrode as working electrode. A GCE (Metrohm, 3.0 mm in diameter) employed as a comparative electrode was carefully polished with 0.5 μm alumina slurry on a flat surface, rinsed thoroughly with deionized water, and then sonicated immediately before using in deionized water for 2 min. The pH values were checked with a Metrohm (Herisau, Switzerland) model 827 pH Lab.

Reagents and solutions

The aqueous standard solutions were prepared with water obtained from a Milli-Q[®] purification system (Millipore, Bedford, MA, USA). In order to prevent metal contamination from laboratory glassware it was kept for 24 hrs in a 10% (v/v) HNO₃ bath. Methyl parathion (99.9%) was purchased from Sigma Aldrich Co. (Seelze, Germany), ethyl acetate (HPLC grade, 99.99%), ethanol (HPLC grade 99.99% purity). A solution of pesticide at 1.0 g L⁻¹ was prepared by dissolving 0.1 g of MP in 100 ml of ethyl acetate. Afterwards, intermediate solutions of MP were prepared daily in ethanol. The working concentration of MP was further prepared in water samples into the electrochemical cell. MWCNTs without further purification were supplied by CNTs Co., Ltd. (Yeonsu-Gu, Incheon, Korea) with > 95% purity, diameters between 10-40 nm and lengths of 5-20 μm and the mineral oil used was obtained from Aldrich (Milwaukee, USA). Graphite powder (purity 99.9%) was supplied by Aldrich. Buffer solutions (phosphate and acetate) were prepared from their respective salts (Darmstadt, Merck) without further purification. Other OP compounds used in interference studies, such as chlorpyrifos, dichlorvos and malathion were purchased from Sigma Aldrich Co. (Seelze, Germany).

Preparation of paste electrode

The CNT paste electrodes were prepared by mixing MWCNTs and mineral oil (1: 1, w/w) for about 30 min until a paste consistence was obtained. After this step, the resulting paste was carefully forced into a cavity (4.0 mm diameter; 1 mm depth) at the end of a homemade glass tube with 15 cm of length. The electrical connection was provided by a copper wire inserted in the inner hole of the tube which is connected to the MWCNT paste. The surface of the paste electrode was smoothed and rinsed carefully with Milli-Q water. Finally, prior to the electrochemical measurements, the CNT electrode was submitted to electrochemical activation, carried out by cyclic voltammetry in the potential window from -1.0 to 1.0 V (18 cycles) in 0.3 mol.L⁻¹ phosphate buffer solution, pH 7.95 (Rivas *et al.* 2007). Graphite paste electrode (1: 1, w/w) was prepared in a similar way except by electrochemical activation by

cyclic voltammetry.

Analytical procedure

The measurements of SWAdCSV were carried out in a conventional electrochemical cell with 15 mL capacity containing the CNT paste electrode, Ag/AgCl (KCl, 3.0 mol L⁻¹) reference electrode and the platinum auxiliary electrode under constant agitation in a 0.3 mol L⁻¹ phosphate buffer at pH 7.95. MP was adsorbed onto MWCNT electrode surface by applying a potential of 0.0 V for 60 sec. Afterwards, an equilibrium time of 10 sec was employed and the potential was scanned towards the cathodic region from 0.0 up to -1.0 V at unstirred solution using square-wave stripping voltammetry at a frequency of 205 Hz with pulse amplitude of 70 mV. The cathodic peak potential for MP was observed at -0.78 V vs Ag/AgCl (3 M).

Optimization procedure based on factorial design

During SWAdCSV measurements, a large number of experimental chemical and electrochemical factors might affect the result. Moreover, the factors involving electroanalytical measurements are not commonly independent. Thus, if "one-at-a-time" optimization (i.e., univariate optimization) is used, a biased interpretation of the system being studied might be obtained. Additionally, electroanalytical procedures optimized with univariate optimization approaches are less economical and require a larger number of experiments than multivariate optimization. Despite these facts, the use of multivariate optimization still has rarely been applied to electroanalytical data (Tarley *et al.* 2006; Santos *et al.* 2009). Thus, we adopted in this study a 2⁶⁻¹ fractional factorial design followed by a Doehlert matrix so that the factors that influence the SWAdCSV measurements could be optimized. The fractional factorial design was performed with the aim of establishing the degree of influence for each factor on the response and verifying the existence of interactions of two-factors. The following factors were investigated: deposition time (seconds) (DT), deposition potential (mV) (DP), frequency (Hz) (F), buffer concentration (mol L⁻¹) (BC), pulse amplitude (mV) (PA) and sample pH. The 32 assays were performed in a random order by using 10 mL of MP solution at 1.8 $\mu\text{g mL}^{-1}$ concentration. After the establishment of those significant factors on the system studied, a Doehlert matrix was employed for final optimization (Santos *et al.* 2009). All data were processed by using the Statistical package program (Version 6.0).

RESULTS AND DISCUSSION

Electrochemical behavior of methyl parathion

Fig. 1 presents the cyclic voltammetric curves obtained with multiwalled CNTs paste electrode of MP in 0.3 mol L⁻¹ phosphate buffer solution at pH 7.95. The cyclic voltammograms were recorded by scanning the potential between -0.9 V and 0.4 V. As can be seen, very well defined and quasi-reversible redox peaks were observed (Epa -0.04 V and Epc -0.29 V) and an irreversible cathodic peak at ca. -0.78 V. **Fig. 2** shows the cyclic voltammetric curves under different scan rates ranging from 50 to 500 mV s⁻¹. As observed, the redox peaks increased by increasing the scan rate and there is a linear relationship between square root of the scan rate and peak current (**Fig. 2**, inset), thus indicating that the electrode reaction is controlled by mass transport (Zhang and Dong 2004). This mechanism has been very well elucidated by literature data (Liu and Lin 2005). The irreversible cathodic peak corresponds to the reaction indicated in **Fig. 3**. Despite the irreversible reaction, it can be successfully exploited as a reaction for MP monitoring by square-wave stripping voltammetry because of the high speed at which the measurements are made.

Optimization procedure based on factorial design

The six factors, their levels and the analytical response (peak current) obtained from the 2⁶⁻¹ fractional factorial

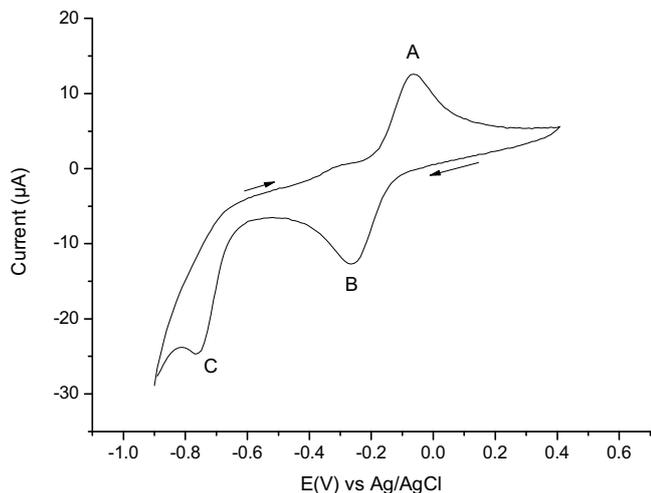


Fig. 1 Cyclic voltammogram of MP ($5.7 \mu\text{mol L}^{-1}$) on the MWCNT electrode in 0.3 mol L^{-1} phosphate buffer solution, pH 7.95 at 100 mVs^{-1} .

design, resulting in 32 experiments carried out in duplicate are shown in **Table 1**. Bearing in mind that a fractional factorial design was used, the generator matrix for this experiment was $I = \text{pH.DP.DT.F.PA.BC}$. Thus, the last column of signals (BC) was obtained by multiplying the signals from pH, DP, DT, F and PA.

The effect of factors and its interactions in the studied system was investigated by using variance analysis (ANOVA) taking into account the current peak as the analytical response. The information obtained from ANOVA can be represented in a Pareto Chart (**Fig. 4**) which is a graphical representation of ANOVA and represents the statistical significance of each experiment evaluated in the system

with a confidence interval of 95%.

As can be seen from the Pareto chart, the effect of sample pH has large influence on the analytical response with positive effect (8.91), thus indicating that the use of maximum level (pH 7.0) increases the cathodic peak current. This result is somewhat expected since the MP presents $\text{pK}_a = 7.2$ (Akthar *et al.* 2007; Fan *et al.* 2008), and naturally, the molecule is found uncharged at pH 7.0. As the MWCNT was not submitted to acid treatment previous to its use, its surface presents hydrophobic characteristics, thus making the MP adsorption easier (Simões *et al.* 2009).

The second most important factor was PA. It is known that in square-wave voltammetry, PA plays an important role on the analytical sensitivity of the method. The effect observed for this factor was found to be 7.18, thus an increase from 10 up to 25 mV led to a higher analytical signal. This behavior is consistent with the literature (Santos *et al.* 2008).

Regarding the effect of F, a negative effect was obtained (-5.31) and obviously, high values can significantly decrease the analytical signal. Such a result is attributed to the irreversible cathodic peak used for MP signal monitoring. Therefore, even using square-wave voltammetry, which possesses high speed of measurement, high values of frequency would imply decreases of peak current for an irreversible redox process (Liu and Lin 2005).

BC was the fourth most important factor in the system showing a positive effect of 3.99. The SWAdCSV measurements in the presence of high amounts of BC, i.e., high supporting electrolyte amounts are enhanced.

Besides the main effects, it is possible to note that the effects of second order interactions, mainly $FxBC$, $pHxBC$ and $pHxF$ are synergistic. This means that by changing the level of one-factor influences the effect caused by another in a positive way. In other words, by simultaneously increasing their levels, higher analytical responses can be achieved. This fact could never have been observed if a uni-

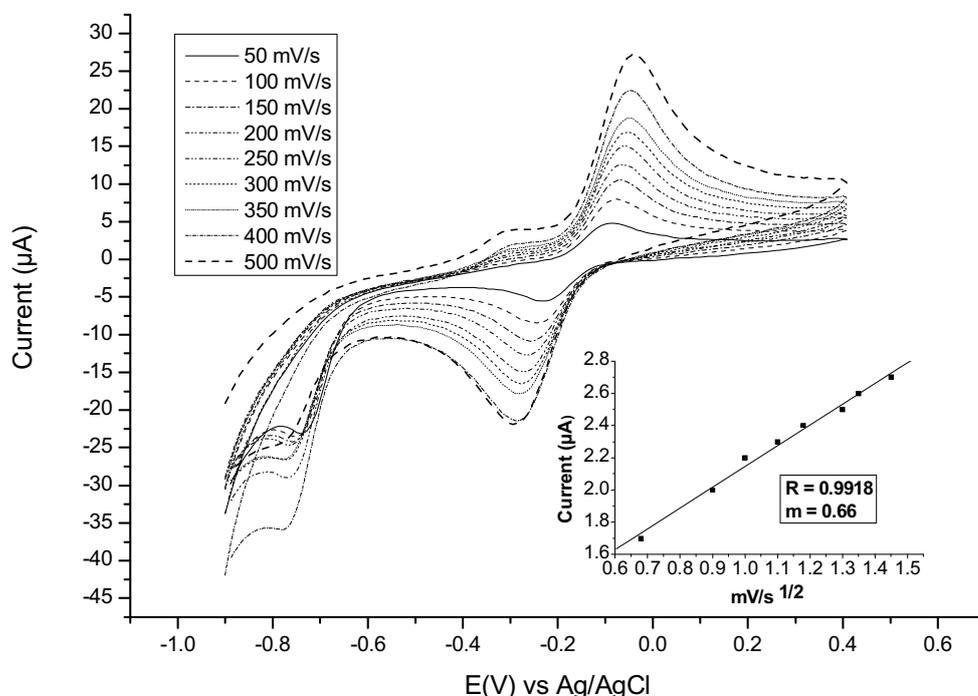


Fig. 2 Cyclic voltammograms of MP ($5.7 \mu\text{mol L}^{-1}$) scanning the potential between -0.9 V and 0.4 V, under different scan rates ranging from 50 to 500 mVs^{-1} on the MWCNT electrode in 0.3 mol L^{-1} phosphate buffer solution, pH 7.95.

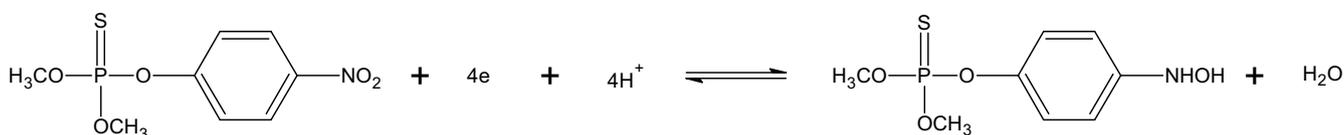


Fig. 3 Electrochemical reduction of MP.

Table 1 Factors and their respective tested levels on the 2⁶⁻¹ fractional factorial design.

Factors	Levels	
	(-) Low	(+) High
pH	4.0	7.0
Pulse amplitude (PA) (mV)	10.0	25.0
Buffer concentration (BC) ^a (mol L ⁻¹)	0.10	0.25
Frequency (F) (Hz)	100	250
Deposition potential (DP) (V)	-0.30	0.0
Deposition time (DT) (s)	20	60

Runs	pH	DP (mV)	DT (s)	F (Hz)	PA (mV)	BC (mol L ⁻¹)	Peak current (10 ⁻⁵ A)	
							1	2
							1	-
2	+	-	-	-	-	+	3.18	3.15
3	-	+	-	-	-	+	1.25	1.03
4	+	+	-	-	-	+	4.57	4.20
5	-	-	+	-	-	+	1.34	1.40
6	+	-	+	-	-	-	4.86	4.85
7	-	+	+	-	-	-	0.63	0.65
8	+	+	+	-	-	+	3.54	3.65
9	-	-	-	+	-	+	1.10	1.12
10	+	-	-	+	-	-	--	--
11	-	+	-	+	-	-	0.28	0.27
12	+	+	-	+	-	+	3.85	3.94
13	-	-	+	+	-	-	0.31	0.35
14	+	-	+	+	-	+	4.54	4.80
15	-	+	+	+	-	+	1.33	1.40
16	+	+	+	+	-	-	--	--
17	-	-	-	-	+	+	2.13	3.30
18	+	-	-	-	+	-	9.35	8.85
19	-	+	-	-	+	-	1.32	1.21
20	+	+	-	-	+	+	7.62	7.10
21	-	-	+	-	+	-	1.66	1.67
22	+	-	+	-	+	+	7.68	8.22
23	-	+	+	-	+	+	3.51	3.63
24	+	+	+	-	+	-	10.30	10.70
25	-	-	-	+	+	-	0.82	0.76
26	+	-	-	+	+	+	9.55	9.25
27	-	+	-	+	+	+	2.42	2.45
28	+	+	-	+	+	-	--	--
29	-	-	+	+	+	+	--	--
30	+	-	+	+	+	-	--	--
31	-	+	+	+	+	-	8.60	8.59
32	+	+	+	+	+	+	10.80	13.00

^a Phosphate buffer for pH 7.0 and acetate buffer for pH 4.0.
(--)= no peak current observed.

Table 2 Doehlert matrix used in the optimization of factors PA and pH.

Runs	PA ^a (mV)	pH	Peak current (10 ⁻⁴ A)
1	0(70)	0(8)	4.00
1	0(70)	0(8)	4.00
1	0(70)	0(8)	3.98
1	0(70)	0(8)	3.95
2	0.866(90)	0.5(9)	7.90
3	0.866(90)	-0.5(7)	1.50
4	0(70)	-1(6)	2.00
5	-0.866(50)	-0.5(7)	9.00
6	-0.866(50)	0.5(9)	1.58
7	0(70)	1(10)	1.62

^a PA = pulse amplitude

Table 3 Doehlert matrix used in the optimization of factors BC and F.

Runs	BC ^a	F ^b (Hz)	Peak current (10 ⁻⁴ A)
1	0(0.25)	0(180)	7.2
1	0(0.25)	0(180)	7.4
1	0(0.25)	0(180)	7.5
1	0(0.25)	0(180)	7.6
2	0.866(0.40)	0.5(240)	6.8
3	0.866(0.40)	-0.5(120)	6.6
4	0(0.25)	-1(60)	4.0
5	-0.866(0.10)	-0.5(120)	6.9
6	-0.866(0.10)	0.5(240)	6.2
7	0(0.25)	1(300)	6.5

^a BC = buffer concentration (mol L⁻¹); ^b F = frequency (Hz)

variate optimization had been used.

The factors, DP and DT were not significant within the experimental domain, so the values were set at 0.0 V and 60 sec, respectively. The adsorption time dependence on analytical signal was more significant at lower time (5 sec) (data not shown), thus confirming the preconcentration effect of MP onto MWCNT surface. Therefore, we maintained the DP as 0.0 V due to lower probability of interference from concomitants present in real samples and the DT as 60 sec due to a higher reproducibility of analysis.

Considering the importance of factors, pH, PA, BC and F and their interactions, within the experimental domain, the final optimization process was performed by using a Doehlert matrix and response surface methodology. For this task, two Doehlert matrixes were built taking into account the significance of interactions *pHxF* and *BCxF*. The results obtained are shown in **Tables 2** and **3**. From these results quadratic models were employed for building a response surface (**Figs. 5** and **6**), which makes it possible to find the maximum values for the studied factors. As can be seen, the response surface led us to select the following experimental conditions: 7.95, 70 mV, 205 Hz and 0.3 mol L⁻¹ for sample pH, PA, F and BC, respectively.

Interference studies

To evaluate the interferences of possible co-existent species on environmental samples some inorganic ions (NO₃⁻, SO₄²⁻, PO₄³⁻ and Mn²⁺) and organic molecules (chlorpyrifos, dichlorvos and malathion) were tested at the same concentration of the assay of MP (2.23 µmol L⁻¹). No interference was detected when the inorganic ions were added to the system. However, the addition of the organic molecules, especially OPs, can increase the analytical signal in a directly proportional rate. These results demonstrated that the MWCNT electrode can not differentiate the type of OP, at least in this specific potential (-0.78 V). Thus, this method can be used on the assay of total OP without suffering any interference from the inorganic ions tested, in accordance with the proposed by Brazilian environmental regulatory agency (CONAMA, National Environment Council) for freshwater, class 4 (Brasil 2005).

Analytical features

The analytical method provided an analytical curve ranging from 0.56 up to 18.00 µmol L⁻¹ of MP with a good linear correlation coefficient ($r > 0.995$), whose equation for analytical curve was: peak current (µA) = 75.27 [methyl parathion (µmol L⁻¹)] - 21.97 (**Fig. 7**). Limits of detection (LD = 0.15 µmol L⁻¹) and quantification (LQ = 0.49 µmol L⁻¹) were calculated following IUPAC recommendation (Mocak *et al.* 1997).

Precision values, in terms of repeatability expressed as relative standard deviation (RSD) were 4.3 and 3.4% for MP solutions at 0.56 and 10.0 µmol L⁻¹ concentrations, respectively. Analytical frequency was 49 h⁻¹ considering the time of 60 sec and 10 sec in the adsorption and equilibrium time, respectively.

Comparative study of MWCNT electrode with graphite paste and glassy carbon electrodes

In order to emphasize the benefits of MWCNT as a nano-structured material in SWAdCSV measurements, experiments under optimized conditions, using different electrodes, i.e., GCE and graphite paste, were conducted. The results are shown in **Table 4**. As can be seen, the use of MWCNT electrode in comparison to graphite paste and glassy carbon electrodes increased the signal 3.4- and 7.1-fold, respectively, thus emphasizing the great advantages of MWCNT in detriment of other carbon electrodes. Moreover, an improvement on the repeatability of measurements made using MWCNT electrode can be observed by the low RSD value.

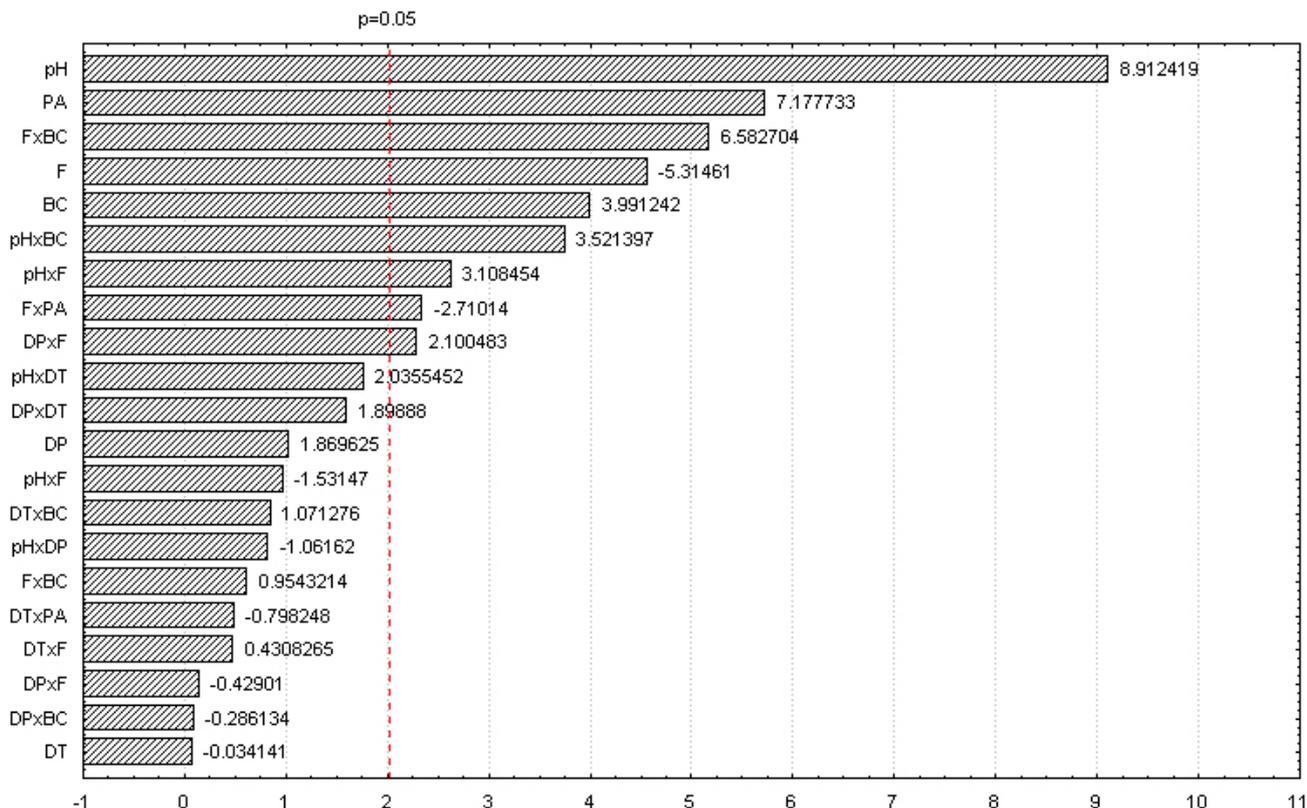


Fig. 4 Pareto chart built from data obtained by the 2^{6-1} fractional factorial design. (1) pH; (2) PD; (3) TD; (4) F; (5) PA; (6) BC.

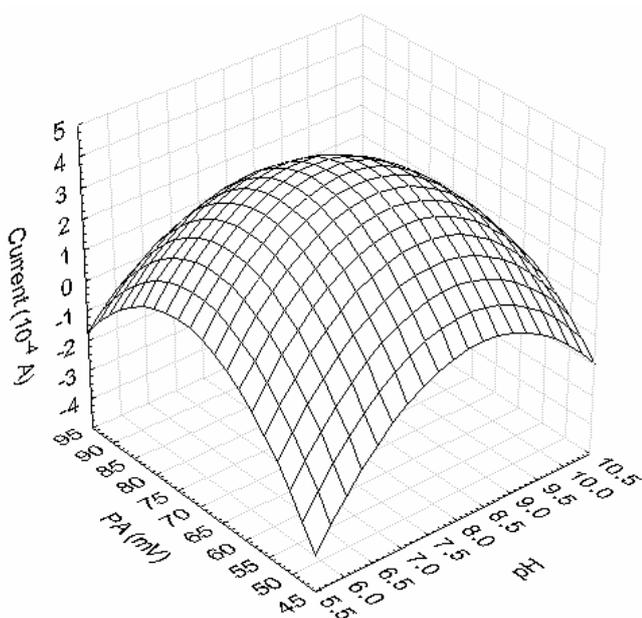


Fig. 5 Surface response obtained from Doehlert matrix for pHxPA.

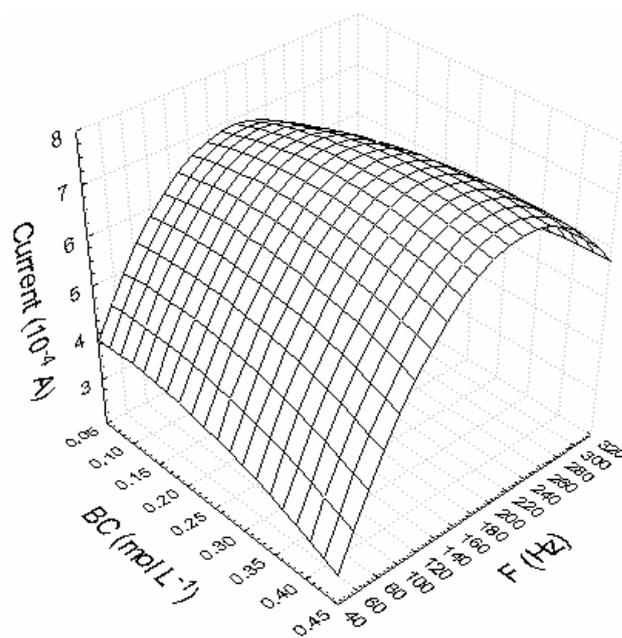


Fig. 6 Surface response obtained from Doehlert matrix for FxBC.

Analysis of water samples

The water samples used in this study were collected at the Furnas dam (1) and at the São Tomé river (2), both near Alfenas city, Minas Gerais, Brazil, and stored in glass bottles under refrigeration (2-8°C). The analyses of the samples were carried out without any pre-treatment, only by acclimatization to room temperature.

The application of the developed method was made on environmental water samples collected from the river and the dam, in which was not detected MP by the proposed method. Standard addition calibration was used for this task. Thus, the analyses were carried out on spiked samples and the recovery was calculated (Table 5). The data obtained for samples spiked with MP showed good recoveries, de-

monstrating the applicability of the method for this type of sample and its suitability to the CONAMA's resolution (National Environment Council) (Brazil 2005).

CONCLUSION

MWCNT provided to the homemade electrode a considerable capacity to amplify the current signal of the MP irreversible reduction at -0.78 V when compared with GCE and carbon paste electrode. A 7.1 fold increase on the capacity of the MWCNT electrode was found when comparing it to GCE, basically due to their electrochemical properties including nanostructured dimension, a very well organized graphene sheet with an electrical charge symmetrically distributed, associated to the porous surface formed by its

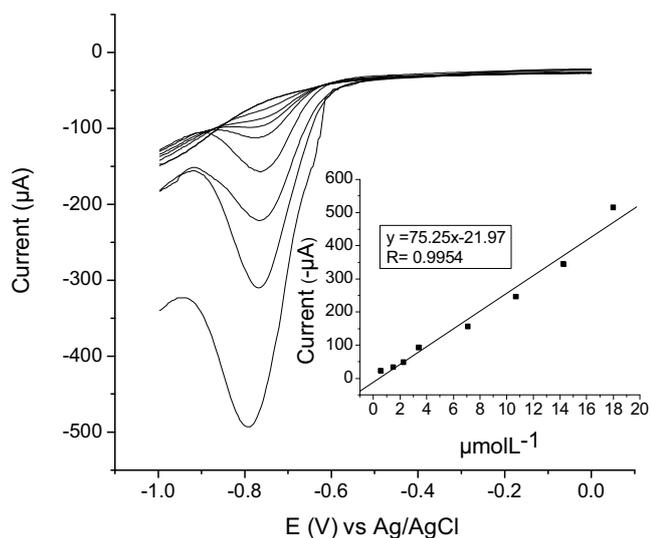


Fig. 7 Square-Wave voltammograms of MP ($0.56 - 18.0 \mu\text{mol L}^{-1}$). Inset shows the calibration curve for MWCNT electrode at the optimized conditions.

Table 4 Comparative study of performance of glassy carbon electrode, carbon paste electrode and MWCNT electrode under optimized conditions and MP solution at $2.23 \mu\text{mol L}^{-1}$.

Electrode	μA^a	Surface area (mm^2)	Current density (J) ($\mu\text{A}/\text{mm}^2$)	RSD (%)
Glassy carbon electrode	3.7	7.07	0.5233	3.0
Graphite electrode paste	13.8	12.57	1.0979	1.4
Multiwalled carbon nanotube paste electrode	46.5	12.57	3.6993	0.9

^a Current, $n=3$.

Table 5 Recovery studies on real water samples, spiked at $2.23 \mu\text{mol L}^{-1}$ of MP.

Sample	Added ($\mu\text{mol L}^{-1}$)	Recovered ^a	% Recovered	RSD (%)
Furnas Dam	2.23	2.21	99.1	2.7
São Tomé river	2.23	2.17	97.2	1.9

^a $\mu\text{mol L}^{-1}$, $n=3$.

dispersion in mineral oil. These features confer to the MWCNT electrode properties of microelectrode, thus improving the signal to noise relationship in a significant way and consequently decreasing the limits of detection and quantification of the method.

Among the results obtained it could be concluded that the developed method is simple and easy, considering its application on aqueous samples. The technique of SWAdCSV has an advantage over other used techniques due to its swiftness and effectiveness owing to the possibility to preconcentrate the sample on the electrode surface. The few quantity of pollutant solvents required and the low cost of the reagents and materials suggest that it can be largely spread. The effectiveness of the factorial design and Doehlert matrix assured the possibility to test more factors than usual when a univariate design is used and consequently determine more accurately the value for each evaluated parameter.

Finally, it must be emphasized the feasibility for building a home made electrode with simple and cheap components without loss the accuracy, repeatability and robustness.

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