

## Analytical Methods

## Sonovoltammetric determination of toxic compounds in vegetables and fruits using diamond electrodes

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## ABSTRACT

The direct determination of methylparathion in potato and corn extracts and its degradation product 4-nitrophenol in lemon and orange juices by ultrasound-assisted square wave voltammetry using diamond electrodes is reported here. The sonovoltammetric results for both analytes in pure water and in complex food samples showed greater sensitivity and precision and much lower limits of detection and quantification than the silent measurements. The limits of detection for methylparathion in water and corn extract were 4.86 and 10.1  $\mu\text{g L}^{-1}$ , respectively, values 55% and 72% lower than those obtained by silent voltammetry. The recovery values were also very satisfactory and varied between 83.5% and 96.2% for all systems. These improvements for the sonovoltammetric methods are due to electrode surface cleaning and mass transport enhancement towards the electrode surface and proved to be a powerful tool for the detection of toxic residues in complex samples without any pre-treatment or clean-up of the matrices.

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## 1. Introduction

Nowadays the immediate response to the necessity for an increasing production of food is a more intensive use of agrochemicals, including chemical fertilizers and pesticides (Carvalho, 2006). Thus, the environmental pollution caused by pesticides and their degradation products is a major ecological and health problem at the moment since residues from those compounds can be present in natural waters, vegetables and fruits. The determination of these residues in those complex samples is a rather difficult task due to the presence of a great amount of interfering substances. The chromatographic methods are the traditional form of detection for these toxic residues, but they usually include complicated pre-treatments or the clean-up of the samples (Hu et al., 2008; Maldaner, Santana, & Jardim, 2008; Ravelo-Perez, Hernandez-Borges, Borges-Miquel, & Rodriguez-Delgado, 2008; Zhang et al., 2008). Thus, these analyses are expensive, lengthy and employ a large volume of organic solvents that need to be treated afterwards.

On the other hand, a variety of electroanalytical methods have been developed for the detection of pesticide residues in food matrices at mercury and glassy carbon electrodes after an appropriate pre-treatment of the samples (Arribas, Bermejo, Chicharro, & Zapardiel, 2007; Ni, Qiu, & Kokot, 2004a, 2004b; Thirveni, Kumar, Sujatha, & Sreedhar, 2007a, 2007b). Other studies have reported the use of

the same two electrode materials (Brimecombe & Limson, 2007; Inam, Sarigul, Gulerman, & Uncu, 2006) or gold ultramicroelectrodes (de Souza & Machado, 2005; de Souza, Machado, & Pires, 2006) for the direct analysis of pesticides in food samples.

The direct electroanalytical determination of pesticides in complex matrices is hindered by the strong adsorption on the electrode surface of the interfering species contained in these samples. This causes irreproducibility in the voltammetric responses and contributes to the lowering of the analytical sensitivity. These adsorption phenomena make it difficult to use solid electrodes for the direct detection of target compounds in these samples. Meanwhile, power ultrasound has been employed in a number of electrochemical analyses to overcome electrode fouling problems (Banks & Compton, 2003, 2004; Garbellini, Salazar-Banda, & Avaca, 2008). The introduction of ultrasound into electrochemical systems is characterised by a significantly increased mass transport regime. This considerably enhances the sensitivity of the measurements in comparison to those obtained under silent conditions and also provides an activation of the electrode surface. As a consequence, the association of electrochemical methods and power ultrasound permits low limits of detection to be attained.

An important group of pesticides currently used in insect-pest control are the organophosphates such as, for example, methylparathion. These compounds are potent irreversible inhibitors of acetylcholinesterase, the enzymes responsible for nervous impulses transmission (Pedrosa, Caetano, Machado, Freire, & Bertotti, 2007). Another environmental problem is the degradation products of these pesticides, like the 4-nitrophenol molecule. The

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Environmental Protection Agency (EPA, 2008) cited this last compound as highly hazardous in the list of pollutants.

According to the Foreign Agricultural Service, the United States Department of Agriculture (USDA, 2008) and the National Agency for Sanitary Vigilance in Brazil (ANVISA, 2008), the pesticide methylparathion is extensively used in some Brazilian agriculture crops such as potato, corn and citrus fruits. Moreover, residues of 4-nitrophenol may be present in these cultures. The maximum residue limits (MRLs) for methylparathion are: 50, 500 and 1000  $\mu\text{g kg}^{-1}$  for the potato, corn and citrus crops, respectively. These agencies do not establish MRLs for 4-nitrophenol, because this compound is not used directly in agricultural crops. However, it is possible to do an analogy with the MRLs values cited for methylparathion. On the other hand, 4-NP can be present in the environment from other sources such as the manufacturing and chemical industry practices. Thus, the EPA establish MRL value of 4-NP for waters in general as 30  $\mu\text{g L}^{-1}$  (Pedrosa, Codognoto, Machado, & Avaca, 2004).

In a previous work, the sonovoltammetric determination of 4-nitrophenol in pure water samples using the boron-doped diamond (BDD) electrode was reported (Garbellini, Salazar-Banda, & Avaca, 2007). Significant enhancement of the sensitivities of the detection methods were observed in the presence of ultrasound in comparison to the silent conditions, particularly for the reduction process. An extension of those studies involving real and complex matrices is highly desirable. Thus, the aim of this work is to investigate the direct determination of methylparathion in potato and corn extracts and of 4-nitrophenol in lemon and orange juices by square wave voltammetry (SWV) on diamond electrodes in the absence and presence of ultrasound radiation.

## 2. Materials and methods

### 2.1. Apparatus

The electrochemical studies were carried out using a three electrode arrangement fitted into a one-compartment Pyrex<sup>®</sup> glass cell (50 mL) that has an entrance for the ultrasound tip and degassing facilities for bubbling  $\text{N}_2$  (Garbellini et al., 2008). The boron-doped diamond films used in this work (Adamant Technologies SA, La Chaux-de-Fonds, Switzerland) have a boron content of the order of 8000 ppm. The working electrode (BDD) had an exposed area of 0.25  $\text{cm}^2$ . The reference system was an Ag/AgCl (3.0 mol  $^{-1}$  KCl) electrode and the counter one was a 1  $\text{cm}^2$  Pt foil. The ultrasound horn tip was placed in front of the working electrode face.

The electrochemical technique used throughout this work was SWV using the following optimised parameters for methylparathion:  $f = 150 \text{ s}^{-1}$ ,  $a = 40 \text{ mV}$ ,  $\Delta E_s = 2 \text{ mV}$  while for 4-nitrophenol the parameters were:  $f = 100 \text{ s}^{-1}$ ,  $a = 60 \text{ mV}$ ,  $\Delta E_s = 2 \text{ mV}$ . The measurements were carried out using a PGSTAT 30 Autolab (Eco Chimie B.V., Netherlands) computer-controlled potentiostat. The need for bipotentiostatic control of the titanium horn tip (Marken & Comp-ton, 1996) was overcome by insulating the transducer from the probe with a Teflon disk (Garbellini et al., 2008). The ultrasound radiation was delivered into the cell via a VCX 130 model ultrasonic horn (Sonics & Materials, USA).

### 2.2. Reagents

Stock solutions  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  of the pesticide methylparathion (Supelco, 99.9%) in pure ethanol and of 4-nitrophenol (Aldrich, 99.0%) in Milli-Q water were prepared. For the detection of the two analytes under investigation a Britton–Robinson (BR) 0.1 mol  $\text{L}^{-1}$  buffer solution prepared with analytical grade reagents

and optimised at pH 7.0 for methylparathion and at pH 6.0 for 4-nitrophenol was always used as supporting electrolyte.

### 2.3. Sonovoltammetric procedure

The intensity of applied ultrasound power was controlled by the tip vibration amplitude (A) when placed inside the solution. An ultrasound intensity of 20% corresponding to a maximum power of 14 W was applied throughout this study during the voltammetric measurements in order to minimise localised heating of the solution and prolong the electrode life. A tip-electrode separation of 5 mm ( $d$ ) was used in all cases while the frequency had a constant value of 20 kHz.

### 2.4. Sample preparation

The fruit juices were obtained using five oranges or lemons having unitary weights of 150 and 80 g, respectively. The potato and corn extracts were obtained by mixing 100 g of each vegetable with 100 mL of Milli-Q water, homogenization in a liquefier and filtration to obtain an aqueous solution of these samples.

### 2.5. Analytical procedure

To ensure reliable and reproducible electroanalytical results both in the absence and presence of ultrasound the BDD electrode received a pre-treatment in a  $\text{H}_2\text{SO}_4$  (0.5 mol  $\text{L}^{-1}$ ) solution consisting of polarizations at +3.0 and -3.0 V during 5 and 30 s, respectively (Salazar-Banda et al., 2006). That pre-treatment was performed before the experiments for each calibration curve.

The calibration curves were obtained by spiking the supporting electrolyte with known amounts of the investigated compounds. For the determination of the limits of detection and quantification (LOD and LOQ, respectively), the standard deviation of the mean value of currents measured at the methylparathion and 4-nitrophenol peaks potentials for eight voltammograms of the blank ( $S_B$ ) was used together with the slope of the straight lines in the calibration curves ( $b$ ) and the equations below (Mocak, Bond, Mitchell, & Scollary, 1997):

$$LOD = 3S_B/b \quad (1)$$

$$LOQ = 10S_B/b \quad (2)$$

The recovery experiments were carried out by adding a known amount of one of each analyte to the solutions containing only the supporting electrolyte and at solutions containing the electrolyte and a fixed aliquot of the samples, followed by standard additions from the stocks solutions and plotting the resulting calibration curves. All measurements were performed in triplicate. The recovery efficiencies ( $R\%$ ) for the processes in the absence and presence of ultrasound were calculated using Eq. (3) where the value of analyte concentration found refers to the concentration obtained by extrapolation of the calibration curves in the corresponding system.

$$R\% = [\text{analyte}]_{\text{found}} / [\text{analyte}]_{\text{added}} \times 100 \quad (3)$$

Initial analyses of the extracts and juices were carried out by SWV in solutions containing the supporting electrolyte and increasing amounts of the samples. Those results showed the absence of contaminants in both types of food. The calibration curve for methylparathion was recorded in solutions having 5% of the total volume of the cell filled with the corresponding extract, while for 4-nitrophenol it was possible to use 15% of the juices without insolubility problems.

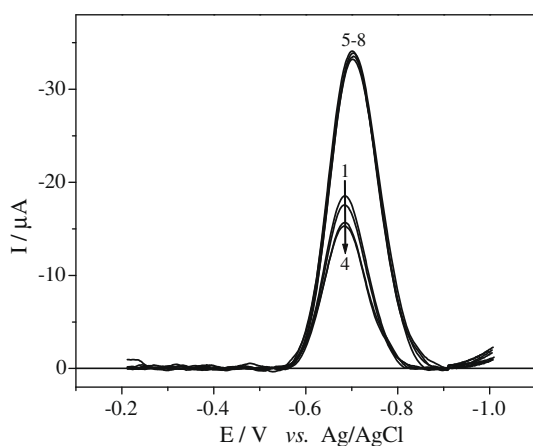
### 3. Results and discussion

#### 3.1. Sonovoltammetric determination of methylparathion in ultrapure water

In an earlier study (Pedrosa, Miwa, Machado, & Avaca, 2006), the detection of methylparathion by electrochemical reduction on the BDD surface at a potential of  $-0.7\text{ V}$  vs Ag/AgCl was hindered by the strong adsorption of electroactive species thus contributing to the electrode fouling. In the present study, the square wave voltammetry using the parameters already optimised (Pedrosa et al., 2006) was combined with the ultrasound radiation to minimise the inactivation of the diamond surface and to improve the sensitivity of the responses. The sonoelectroanalytical methodology was optimised varying some of its experimental parameters, namely, the tip-electrode separation, the tip vibration intensity in the solution and the sonication time of the solution before measurements, as previously done for the sonoelectrochemical detection of 4-nitrophenol in pure water (Garbellini et al., 2007).

A set of voltammograms recorded at various  $d$  values (25–5 mm),  $A$  values (20–40%) and sonication times before measurements (5–30 s) were recorded (figures not shown). These voltammograms obtained for the different ultrasound conditions were compared to each other and also with the measurements performed under silent conditions. For the electrochemical process on a diamond electrode, the optimised conditions of ultrasound application were:  $d$ : 5 mm,  $A$ : 20% with the radiation only applied during the voltammetric scan.

As a consequence of the ultrasound radiation, a considerable increase in the transport of electroactive species towards the electrode surface was observed as an increase in the current signal and the overall SWV response of the system was practically two times larger than those under silent conditions, as shown in Fig. 1. Moreover, this figure also illustrates through curves 1–4 and 5–8, the cleaning effect of the electrode surface by the cavitation collapse of microbubbles. As the methylparathion molecule undergoes strong adsorption on the BDD surface, a reduction of the sensitivity of the detection method is observed. Thus, successive scan experiments without an intermediary cleaning of electrode surface were carried out. The successive measurements in the absence of ultrasound radiation showed a continuous decrease of the response due to the adsorption of the analyte and/or its reduction products (curves 1–4). On the other hand, the curves obtained in the presence of ultrasound (curves 5–8) showed only very

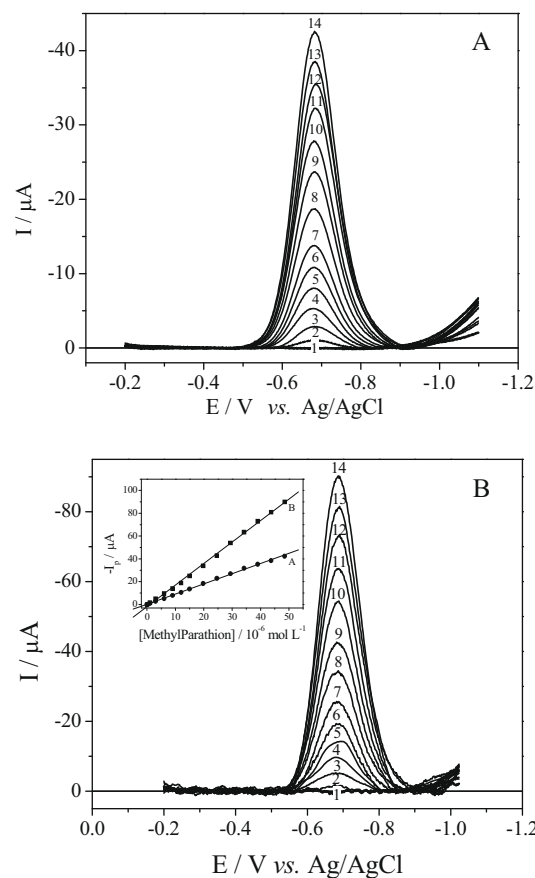


**Fig. 1.** Successive SWV responses for the reduction of methylparathion  $2.0 \times 10^{-5}\text{ mol L}^{-1}$  in a BR buffer  $0.1\text{ mol L}^{-1}$  (pH 7.0) on a BDD electrode in the absence (1–4) and presence of ultrasound radiation (5–8).

small changes for successive responses (with a relative standard deviation (rsd) of 1.16%). These experiments demonstrate the ability of ultrasound for cleaning the diamond electrode surface during electrochemical experiments.

After optimisation of the ultrasound parameters, square wave voltammograms were obtained for the reduction of methylparathion at different concentrations in a BR buffer  $0.1\text{ mol L}^{-1}$  in the absence (Fig. 2A) and in the presence of ultrasound (Fig. 2B). The inset in Fig. 2B, contains the two calibration curves for the interval under investigation (from  $1.00$  to  $48.5 \times 10^{-6}\text{ mol L}^{-1}$ ). The higher slope observed for the calibration curves in the presence of ultrasound (2.1 times in relation to silent conditions) will certainly result in smaller values for the LOD (see below). The precision of the sensitivity values given by the rsd was 3.9 times better for the insonated method (0.36%) than that obtained by silent voltammetry (1.41%).

The determination of the LOD and LOQ was performed according to the procedure described in the experimental section. The value of LOD determined for the process in presence of ultrasound was  $4.86\text{ }\mu\text{g L}^{-1}$ , a value smaller than the obtained for the same process in absence of ultrasound ( $10.8\text{ }\mu\text{g L}^{-1}$ ). Recovery experiments carried out using  $9.0$  and  $30.0 \times 10^{-6}\text{ mol L}^{-1}$  of analyte presented adequate results (between 97.1 and 98.9%). The linear regression parameters, the values of the LOD, LOQ and the recovery tests for the process are summarised in Table 1. It should be observed that LOD and LOQ values are inside of the MRLs for this pesticide in potato and corn samples ( $50$  and  $500\text{ }\mu\text{g kg}^{-1}$ , respectively). Therefore, the developed methodology can be applied in these samples (below).



**Fig. 2.** SWV responses for different methylparathion concentrations in the absence (A) and presence (B) of ultrasound:  $0$  (1),  $1.0$  (2) to  $48.5 \times 10^{-6}\text{ mol L}^{-1}$  (14) in BR buffer  $0.1\text{ mol L}^{-1}$  (pH 7.0). Inset in B: calibration curves for both cases.

**Table 1**  
Parameters from the calibration curves ( $n = 3$ ), LOD, LOQ and recovery percentages ( $n = 3$ ) for methylparathion obtained by SWV on a BDD electrode in the absence and presence of ultrasound for solutions containing only the supporting electrolyte and for solutions with the electrolyte and a fixed quantity of the vegetables extract samples.

Parameters	Supporting electrolyte		Potato sample		Corn sample	
	SWV	Sono-SWV	SWV	Sono-SWV	SWV	Sono-SWV
$b$ ( $A L mol^{-1}$ )	0.8919	1.885	0.5255	0.7363	0.3079	1.053
rsd <sup>a</sup> (%)	1.41	0.36	2.22	0.92	3.02	0.60
$r$	0.9992	0.9991	0.9998	0.9990	0.9960	0.9975
$S_B^b$ ( $\mu A$ )	$12.2 \times 10^{-3}$	$11.6 \times 10^{-3}$	$13.8 \times 10^{-3}$	$13.1 \times 10^{-3}$	$14.3 \times 10^{-3}$	$13.5 \times 10^{-3}$
LOD <sup>c</sup> ( $\mu g L^{-1}$ )	10.8	4.86	20.7	14.0	36.6	10.1
LOQ <sup>d</sup> ( $\mu g L^{-1}$ )	35.6	16.0	68.4	46.3	121	33.4
Rec 1 <sup>e</sup> (%)	$97.1 \pm 1.55$	$98.9 \pm 1.23$	$92.6 \pm 3.05$	$94.4 \pm 2.65$	$83.5 \pm 2.44$	$87.8 \pm 2.06$
Rec 2 <sup>e</sup> (%)	$98.0 \pm 1.86$	$97.5 \pm 2.66$	$94.1 \pm 2.83$	$96.2 \pm 3.72$	$86.4 \pm 3.20$	$93.7 \pm 2.90$

<sup>a</sup> Relative standard deviation of the sensitivity values.

<sup>b</sup>  $S_B$  is the standard deviation of the mean value for eight voltammograms of the blank.

<sup>c</sup> LOD: limit of detection.

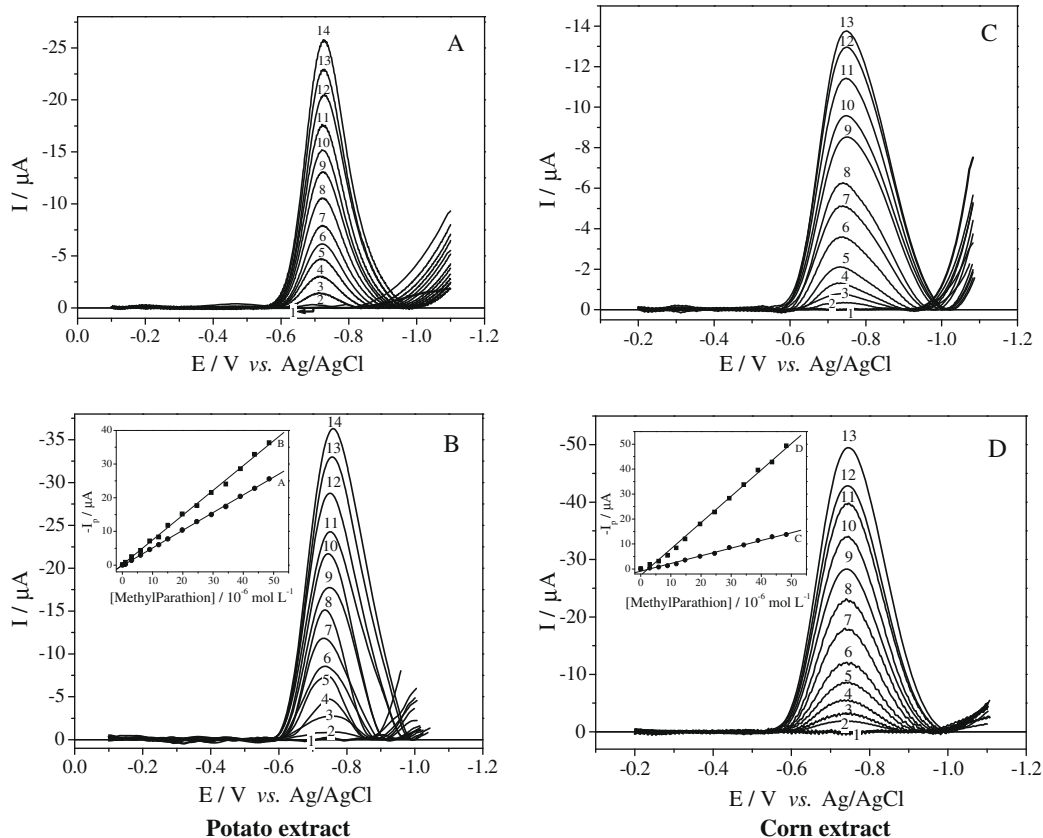
<sup>d</sup> LOQ: limit of quantification.

<sup>e</sup> Rec. 1 and 2: concentrations analyzed:  $9.0$  and  $30.0 \times 10^{-6} mol L^{-1}$ , respectively.

### 3.2. Determination of methylparathion in potato and corn samples

Initially, voltammograms in solutions containing the supporting electrolyte and various aliquots of the food samples were recorded. No reduction peaks were observed in either of the samples, demonstrating the absence of detectable residues of methylparathion in these matrices. Calibration curves in both the absence and presence of ultrasound in solutions containing the electrolyte and a fixed aliquot of potato (Fig. 3A and B) and corn (Fig. 3C and D) extracts were recorded aiming to evaluate the effect of possible interferences in the detection of the pesticide in these samples.

An increase in the sensitivity as well as an improvement in the precision of the sonovoltammetric methods were observed for both cases in relation to the silent conditions, as revealed by the  $b$  and  $rsd$  values in Table 1. This effect was more significant in the corn extract analysis (3.4 and 5.0 times, respectively) than in the potato analysis (1.4 and 2.4 times, respectively). For the first sample, it is possible that ultrasound promotes a more effective cleaning of the electrode surface in this complex media that contains a great number of interference substances. These sensitivity improvements resulted in a decrease of both the LOD and LOQ values, as shown in Table 1.



**Fig. 3.** SWV responses in solutions containing the supporting electrolyte and a fixed aliquot of the potato and corn samples spiked with different amounts of methylparathion in the absence (A and C) and presence of ultrasound (B and D). Concentrations in the solution with potato extract: 0 (1), 1.0 (2) to  $48.5 \times 10^{-6} mol L^{-1}$  (14) and with corn extract: 0 (1), 3.0 (2) to  $48.5 \times 10^{-6} mol L^{-1}$  (13). Insets in B and D: calibration curves for each case.

The LOD and LOQ values obtained in the determination of methylparathion in potato and corn samples are within the MRL values for this pesticide in such cultures. Recovery experiments in the absence and presence of ultrasound were carried out for each sample in concentrations of  $9.0$  and  $30.0 \times 10^{-6} \text{ mol L}^{-1}$  of the pesticide and the results are also collected in Table 1. They clearly demonstrate that the use of both the diamond electrode alone and that electrode in association with power ultrasound, allows attainment of good percentages of recovery in complex matrices. In addition, the sonovoltammetric measurements resulted in a higher recovery percentage for all measurements carried out with the food samples. High recovery percentages obtained in the sonovoltammetric experiments are mainly due to the cleaning of the electrode surface promoted by ultrasound.

### 3.3. Sonovoltammetric determination of 4-nitrophenol in citrus juices

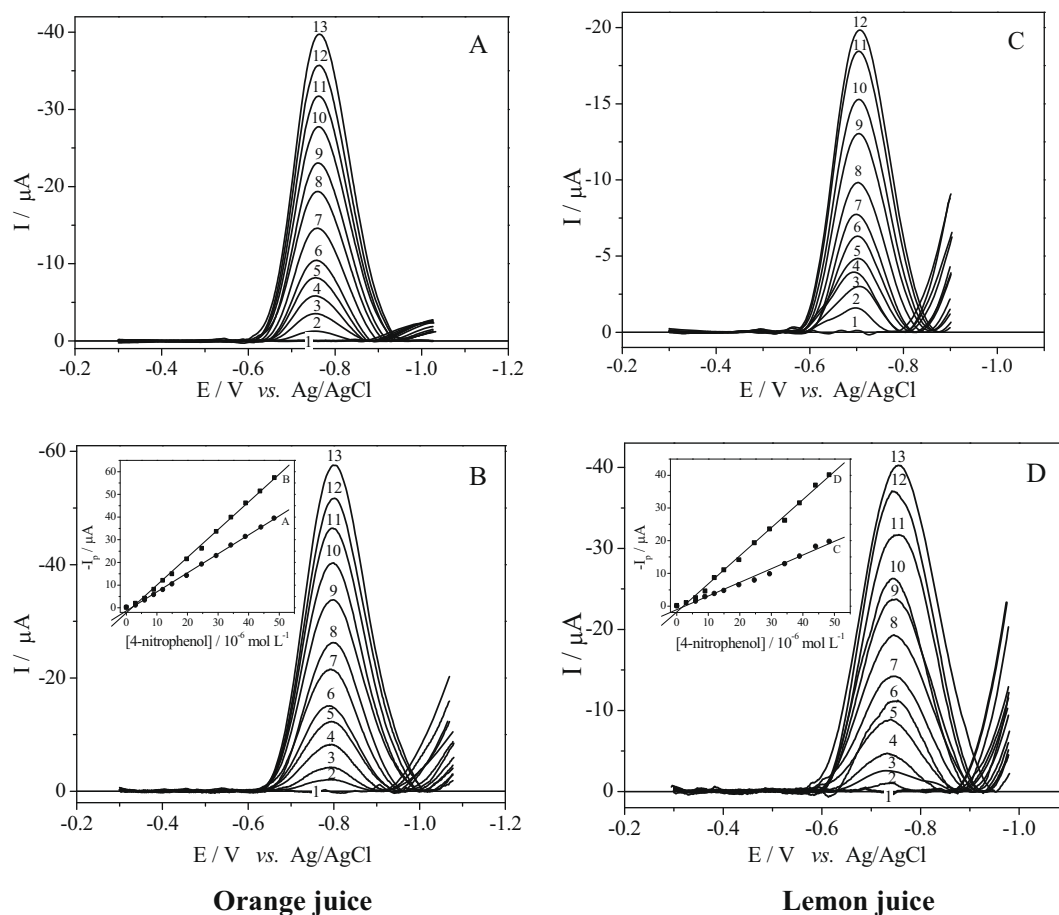
The LOD values previously obtained for the sonovoltammetric determination of 4-nitrophenol in pure water solutions (namely,  $3.87$  and  $2.57 \mu\text{g L}^{-1}$  for the oxidation and reduction process, respectively) (Garbellini et al., 2007) are quite adequate for the detection of the analyte in citrus juice samples, since the MRLs of methylparathion and, as a consequence, for the 4-nitrophenol molecule in these crops is  $1000 \mu\text{g kg}^{-1}$ . Therefore, the sonoelectroanalytical methodology for the direct detection of 4-nitrophenol in citrus juices will be described here.

The determination of 4-nitrophenol in juice samples by an oxidation process on the BDD electrode was hindered by the interfer-

ence of species contained in the matrices (particularly ascorbic acid). As a result, the use of ultrasound for this voltammetric study resulted in a lower sensitivity due to the increase in the transport of interfering species toward the electrode surface thus contributing for the electrode fouling.

Therefore, the electroreduction process of 4-nitrophenol was studied recording voltammograms in solutions containing the supporting electrolyte and various aliquots of the fruit samples. No voltammetric peak for either of the two samples was observed, demonstrating the absence of detectable residues of 4-nitrophenol in these citrus juices. Additionally, similar studies to those described for the analyses of methylparathion in vegetable samples were performed for 4-nitrophenol in citrus fruit juices to evaluate the effect of interferences on the response of this analyte. Fig. 4 presents the calibration curves obtained for 4-nitrophenol in the absence and presence of ultrasound in solutions containing the supporting electrolyte and a fixed quantity of orange (curves A and C) and lemon juice (curves B and D).

The increase in the sensitivity of the sonovoltammetric method for the determination of 4-nitrophenol in lemon juice in comparison to silent conditions (2.0 times) was slightly higher than the corresponding value obtained for orange juice (1.4 times). In addition, the precision (rsd) of the sensitivity values for the sonovoltammetric detection of the target compound in lemon and orange juices were, respectively 1.6 and 1.2 times better than the ones obtained under silent conditions. The increase in sensitivity for the sonovoltammetric methods in both citrus juices samples resulted in improvements of the LOD and LOQ values. These data are



**Fig. 4.** SWV responses in solutions containing the supporting electrolyte and a fixed aliquot of orange and lemon juices spiked with different amounts of 4-nitrophenol in the absence (A and C) and presence of ultrasound (B and D). Concentrations in the solution with the orange juice: 0 (1),  $3.0$  (2) to  $48.5 \times 10^{-6} \text{ mol L}^{-1}$  (13) and with lemon juice: 0 (1),  $6.0$  (2) to  $48.5 \times 10^{-6} \text{ mol L}^{-1}$  (12) for C and  $3.0$  (2) to  $48.3 \times 10^{-6} \text{ mol L}^{-1}$  (13) for D. Insets in B and D: calibration curves for each case.



**Table 2**  
Parameters from the calibration curves ( $n = 3$ ), LOD, LOQ and recovery percentages ( $n = 3$ ) for 4-nitrophenol obtained by SWV on a BDD electrode in the absence and presence of ultrasound for solutions containing only the supporting electrolyte and for solutions with the electrolyte and a fixed quantity of citrus fruit juices.

Parameters	Supporting electrolyte		Orange juice		Lemon juice	
	SWV	Sono-SWV	SWV	Sono-SWV	SWV	Sono-SWV
$b$ (A L mol <sup>-1</sup> )	0.8636	2.446	0.8386	1.222	0.4179	0.8579
rsd <sup>a</sup> (%)	1.84	1.36	1.92	1.62	2.60	1.66
$r$	0.9982	0.9995	0.9989	0.9987	0.9928	0.9969
$S_B^b$ (μA)	$13.2 \times 10^{-3}$	$15.1 \times 10^{-3}$	$14.6 \times 10^{-3}$	$16.2 \times 10^{-3}$	$13.8 \times 10^{-3}$	$17.1 \times 10^{-3}$
LOD <sup>c</sup> (μg L <sup>-1</sup> )	6.38	2.57	7.26	5.53	13.8	8.32
LOQ <sup>d</sup> (μg L <sup>-1</sup> )	21.3	8.58	24.2	18.4	46.0	27.7
Rec 1 <sup>e</sup> (%)	97.6 ± 1.76	96.6 ± 1.05	90.9 ± 2.37	93.0 ± 3.02	85.1 ± 3.63	86.2 ± 2.35
Rec 2 <sup>e</sup> (%)	98.2 ± 2.21	97.9 ± 1.18	92.7 ± 3.16	93.8 ± 2.81	84.3 ± 2.95	88.1 ± 2.07

<sup>a</sup> Relative standard deviation of the sensitivity values.

<sup>b</sup>  $S_B$  is the standard deviation of the mean value for eight voltammograms of the blank.

<sup>c</sup> LOD: limit of detection.

<sup>d</sup> LOQ: limit of quantification.

<sup>e</sup> Rec. 1 and 2: concentrations analyzed: 9.0 and  $30.0 \times 10^{-6}$  mol L<sup>-1</sup>, respectively.

presented in Table 2 and they are adequate for the assumed MRL values of 4-nitrophenol in these cultures.

Recovery studies in the absence and presence of ultrasound were performed for each sample at 4-nitrophenol concentrations of 9.0 and  $30.0 \times 10^{-6}$  mol L<sup>-1</sup> and the results are also included in Table 2. The percentage values demonstrate that the SWV and Sono-SWV on diamond surfaces are powerful analytical tools for the determination of 4-nitrophenol in citrus juice samples.

An interesting effect observed in the voltammetric curves (Figs. 3 and 4) is that the reduction of MP and/or 4-NP in solutions containing both the electrolyte and a fixed aliquot of food samples occurs at more negative potentials values (shifts of ~10–70 mV) when compared to the same processes occurring at solutions with only the electrolyte. This effect can be due to a previous adsorption of the some of the many components of the complex samples at the electrode surface thus making more difficult the electrochemical reduction of the analytes.

Finally, it is important to notice that all the insonated studies were performed without the intermediary cleaning of the electrode surface thus facilitating the experimental work and diminishing the time of routine analyses for food quality control and/or pollution control in food. Additionally, it is worthwhile mentioning that the electroanalytical determination of methylparathion and/or 4-nitrophenol in food is usually performed after pre-treatment of the samples (Del Carlo, Mascini, Pepe, Diletti, & Compagnone, 2004; Fan, Xiao, Liu, Zhao, & Zeng, 2008; Li, Wang, Wang, & Hu, 2006; Ni, Qiu, & Kokot, 2004b).

#### 4. Conclusions

The direct determination of organophosphate pesticides and their degradation products in complex food samples by ultrasound-assisted SWV experiments using diamond electrodes was successfully carried out in this investigation. The studies involved potato and corn extracts as well as orange and lemon juices. In all these food samples, no initial detectable residues of methylparathion or 4-nitrophenol were found. The comparison of the calibration curves recorded for the analytes under investigation in the absence and presence of ultrasound in solutions containing the supporting electrolyte and a fixed quantity of each food sample showed significant improvements in the sensitivity and precision for the sonovoltammetric methods for both compounds. These improvements are due to cleaning of the electrode surface and also to the increase in the mass transport of species to the electrode surface. Consequently, a considerable decrease of the limits of detection and quantification to values well below the maximum allowed concentration for both substances was observed in all cases.

Another advantage of the voltammetric measurements in the presence of ultrasound is that the intermediary cleaning of the electrode surface is not necessary thus resulting in a more rapid and reproducible analysis. In conclusion, the sonovoltammetric methodologies developed and presented here could be a convenient and efficient tool for the analysis of organophosphate agrochemicals and their residues in food. This should help the control of pollution in food and consequently contribute to the protection of human health.

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