

Sonovoltammetric Determination of 4-Nitrophenol on Diamond Electrodes

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A determinação sonovoltamétrica do 4-nitrofenol foi estudada sobre um eletrodo de diamante dopado com boro. Foram observadas melhorias significativas na sensibilidade analítica devido à limpeza da superfície eletródica e ao aumento no transporte de espécies ao eletrodo proporcionados pelo ultra-som. Desta maneira, para os processos de oxidação e redução, os limites de detecção diminuíram de 11.7 para 3.87 e de 6.38 para 2.57 $\mu\text{g L}^{-1}$, respectivamente.

The sonovoltammetric determination of 4-nitrophenol was studied on a boron-doped diamond electrode. Significant improvements in the analytical sensibility were observed due to electrode surface cleaning and the enhancement in the transport of species to the electrode surface provided by ultrasound. Thus, for the oxidation and reduction process, the limit of detection diminished from 11.7 to 3.87 and from 6.38 to 2.57 $\mu\text{g L}^{-1}$, respectively.

Keywords: 4-nitrophenol, sonoelectroanalysis, diamond electrode

Introduction

Phenolic compounds, common organic pollutants in industrial and agricultural wastewaters,¹ have toxic effects on humans, animals and plants, even at very low concentrations. In particular, 4-nitrophenol (4-NP) is highly hazardous and cited in the list of pollutants of the USA, Environmental Protection Agency (EPA).² According to this agency, the permitted level of 4-NP in waters in general is 30 $\mu\text{g L}^{-1}$.

The importance of 4-NP determination is related to the degradation pathway of several organophosphorous pesticides such as fenitrothion and parathion that are decomposed in soils and waters producing 4-NP as an intermediate or a final product of the reaction.^{3,4}

Levels of 4-NP are usually quantified using chromatographic techniques, such as gas chromatography,⁵ high performance liquid chromatography,⁶ liquid chromatography associated with mass spectroscopy⁷ and capillary electrophoresis.⁸ On the other hand, electroanalytical methods have been proposed for 4-NP determination at the hanging mercury drop electrode,^{9,10} at modified glassy carbon electrodes¹¹⁻¹³ and at a boron-doped diamond (BDD) microelectrode.¹⁴

Organic molecules, such as pesticides and their degradation products, have usually strong interactions with

the surface of solid electrodes (adsorption process) thus hindering their use in analytical determinations. Moreover, numerous problems associated with the direct determination of these compounds in real and complex samples are encountered. For example, the presence of fats, proteins and carbohydrates in food matrices, lead to electrode fouling due to adsorption of these species and it can also reduce the sensibility of the detection methods. In this sense, power ultrasound has been employed to overcome such electrode fouling problem (passivation) due to the ultrasound ability for cleaning the surface electrode,¹⁵ allowing sensitive electroanalysis of some analytes to be carried out in a range of hostile media including eggs,¹⁶ blood,¹⁷ wine,¹⁸ among others.^{19,20} The introduction of ultrasound into voltammetric cells has a marked effect upon the mass transport and surface activation characteristics of an electrochemical system. Mass transport is greatly increased *via* acoustic streaming and micro jetting, resulting from cavitation collapse close to the electrode surface.²¹

Depending on the mechanical hardness of the electrode material, considerable damages to the electrode surface occurs in a relatively short time in the presence of power ultrasound.²² In this context, BDD electrodes showed no signs of mechanical damage under these insonated conditions²³ and may be regarded as the ideal electrode material for reliable procedures and long-term reproducibility.

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The beneficial properties of BDD when compared to other types of electrodes for electroanalysis are: *i*) a very low background current due to a low density of surface states, *ii*) a wide potential window due to the chemical inertness of the diamond surface and *iii*) mechanical robustness for practical applications, (e.g. in sonoelectroanalysis).²⁴

It should be also emphasized that a cathodic pre-treatment is a simple and very efficient way for generating highly active electrochemical BDD surfaces, resulting in very low quantification limits and high data reproducibility.²⁵ Meanwhile, a recent work²⁶ describes the loss of such activity with time of exposure of the BDD surface to the atmosphere, which is recovered by further cathodic polarizations. These results stress the need for performing the cathodic pre-treatment just before the electrochemical experiments are conducted, in order to ensure reliable and reproducible results.²⁶

Previous works from our laboratory have shown the direct electroanalytical determination of 4-NP in pure water²⁷ and contaminated waters,²⁸ of pentachlorophenol in pure and contaminated waters²⁹ as well as in a polluted soil,³⁰ 4-chlorophenol in pure water³¹ and carbaryl in contaminated waters³² using in all cases the square wave voltammetry (SWV) technique on BDD electrodes. However, the determination of 4-NP is severely affected by the strong adsorption of the oxidation products requiring frequent cleaning of the electrode surface.²⁷

Thus, the aim of this communication is to report the great improvements in the analytical determination of 4-NP by SWV on a BDD electrode when associated to ultrasound radiation, to confirm both the increase of mass transport and the cleaning of the electrode surface effects of this complementary technique.

Experimental

The boron-doped diamond films used (Adamant Technologies SA, La Chaux-de-Fonds, Switzerland) have a boron content of the order of 8000 ppm. The electrochemical experiments were carried out in a three electrode arrangement using a one-compartment Pyrex[®] glass cell (50 mL)³³ provided with an ultrasound tip entrance and degassing facilities for bubbling N₂. The working electrode had an exposed area of 0.25 cm². The reference system was the Ag/AgCl (3.0 mol L⁻¹ KCl) electrode and the counter one was a 1 cm² Pt foil. The ultrasound horn tip was placed in front of the working electrode face. Prior to the experiments for each analytic curve, in the absence and presence of ultrasound, the BDD electrode received a pre-treatment at +3.0 and -3.0 V during 5 and 30 s respectively in a H₂SO₄ (0.5 mol L⁻¹) solution.

Electrochemical measurements were performed using a PGSTAT 30 Autolab computer controlled potentiostat and the need for bipotentiostatic control³⁴ of the titanium horn tip was eliminated by insulating the transducer from the probe with a Teflon[®] disk.³³ Ultrasound was delivered into the cell *via* a VCX 130 model ultrasonic horn (Sonics & Materials, USA), capable of emitting 20 KHz ultrasound. The intensity of ultrasound power was controlled by varying the amplitude between 20 and 40%. An amplitude value of 20% was used during the SWV measurements in order to minimize localized heating of the solution and prolong the electrode life. In this manner, the maximum transmitted acoustic power was 14 watts and the acoustic energy transferred was 155 and 178 J for the oxidation and reduction processes of 4-nitrophenol on the diamond electrode, respectively. These energy values correspond to one SWV measurement for analyte oxidation (20 s) and reduction (23 s). Due to the small time of sonication of the solution, it was possible to perform voltammetric measurements at essentially constant temperature.

A 1.5×10^{-3} mol L⁻¹ stock solution of the pesticide (4-NP, Aldrich 99%) was prepared using water from the Milli-Q (Millipore) purification system. The buffer used as supporting electrolyte was Britton-Robinson (BR)³⁵ 0.1 mol L⁻¹ with the pH adjusted to 6.0 by the addition of proper amounts of a NaOH 1.0 mol L⁻¹ solution. All reagents were analytical grade. Analytical curves were obtained by spiking the supporting electrolyte with known amounts of 4-NP.

Results and Discussion

Pedrosa *et al.*²⁷ reported the anodic and the cathodic voltammetric behavior of 4-NP on a BDD electrode in aqueous solutions using SWV. This compound presents only one irreversible peak for both oxidation at 1.0 V *vs.* Ag/AgCl and reduction at -0.8 V *vs.* Ag/AgCl. The limits of detection (LOD) obtained were 8.4 µg L⁻¹ for the oxidation process and 12.1 µg L⁻¹ for reduction process, respectively. To improve the detection limits as well as to minimize the fouling of the electrode surface by strong adsorption of the electroactive species, the power of ultrasound combined with SWV measurements was applied to that system.

The first step in the development of a sono-electroanalytical methodology is the optimization of the experimental parameters, namely, the tip-electrode separation (*d*), the tip vibration intensity inside solution (amplitude, *A*) and the sonication time of the solution

before measurements. This should be complemented by optimization of the voltammetric parameters but, in the present case, those parameters were already optimized in the mentioned previous work.²⁷

Thus, using the optimized conditions of SWV reported by Pedrosa *et al.*²⁷ for the analytical determination of 4-NP on a BDD electrode (oxidation: SWV frequency (f) = 100 s⁻¹, SWV amplitude (a) = 50 mV, potential step (ΔE_s) = 2 mV and reduction: f = 100 s⁻¹, a = 60 mV, ΔE_s = 2 mV), a set of voltammograms related to 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 both electrochemical processes (oxidation and reduction) on a diamond electrode, the optimized conditions of ultrasound application were: d : 5 mm, A : 20% with the radiation applied just during the voltammetric scan.

As a consequence of the ultrasound radiation, a considerable increase of the transport of electroactive species towards the electrode surface was observed and the SWV response of the system was practically 4 times higher than those under silent conditions, as shown in Figure 1. Moreover, this figure also illustrates through curves 1-5 and 6-10 the other important aspect of ultrasound utilization in electrochemistry, that is, the cleaning effect of the electrode surface by cavitation collapse. As the 4-NP molecules undergo a considerable adsorption on the BDD surface, a diminution of the sensibility of the detection method is commonly noted. Thus, successive scan experiments in the same solution, in the absence and the presence of ultrasound, without intermediary cleaning of electrode surface were carried out. The successive voltammetric measurements in the absence of radiation showed a continuous diminution response due the adsorption of 4-NP oxidation products. Meanwhile, the curves obtained in the presence of ultrasound showed only very small experimental changes for successive responses. This demonstrates that the power of ultrasound in the optimized conditions is sufficient for cleaning the diamond electrode surface.

After optimization of the experimental ultrasound parameters, square wave voltammograms were obtained for the oxidation of 4-NP at different concentrations in BR buffer 0.1 mol L⁻¹ in the absence and presence of power ultrasound (Figure 2). The inset in Figure 2B, corresponds to the analytical curves, that is, the linear dependence of current intensity with 4-NP concentration for the interval under investigation (from 2.99 to 48.7 × 10⁻⁶ mol L⁻¹). The higher slopes observed for the analytical curves in the presence of ultrasound will certainly result in smaller values for the LOD (see below).

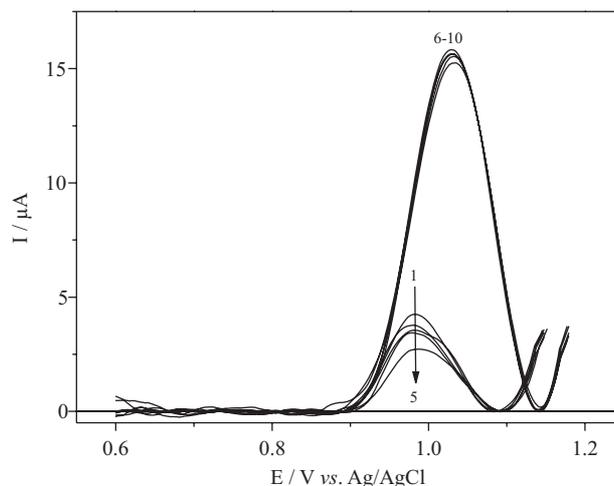


Figure 1. Successive responses for the SWV oxidation of 4-NP 19.7 × 10⁻⁶ mol L⁻¹ on a BDD electrode in the absence (1-5) and presence of radiation (6-10). Conditions: BR buffer 0.1 mol L⁻¹ (pH = 6.0) with f = 100 s⁻¹, a = 50 mV, ΔE_s = 2 mV. Ultrasound: d : 5 mm and A : 20%.

The determination of the limits of detection and quantification (LOD and LOQ, respectively) was performed according to the IUPAC procedure, using the standard deviation of the mean value of currents measured at the 4-NP oxidation potential for eight voltammograms of the blank and the slopes of the straight lines in the analytical curves.³⁶

The value of LOD determined for the oxidation process in presence of ultrasound was 2.79 × 10⁻⁸ mol L⁻¹ (3.87 μg L⁻¹), a value significantly smaller than that for the same process in absence of ultrasound, 8.44 × 10⁻⁸ mol L⁻¹ (11.7 μg L⁻¹). The linear regression parameters and the values of the detection and quantification limits for the oxidation process are included in Table 1.

For comparison, square wave voltammograms were also recorded for the reduction of 4-NP at the same concentration range in BR buffer 0.1 mol L⁻¹ in the absence and presence of ultrasound and are presented in Figure 3. The inset in

Table 1. Parameters from the analytical curves (oxidation and reduction) for 4-NP obtained by SWV on BDD electrode in the absence and presence of ultrasound

Parameters	Oxidation		Reduction	
	SWV	Sono-SWV	SWV	Sono-SWV
Slope / (A L mol ⁻¹)	0.2702	0.8507	0.8636	2.446
Correlation coefficient	0.9993	0.9992	0.9982	0.9995
S _B / (μA)	7.6 × 10 ⁻³	7.9 × 10 ⁻³	13.2 × 10 ⁻³	15.1 × 10 ⁻³
LOD / (μg L ⁻¹)	11.7	3.87	6.38	2.57
LOQ / (μg L ⁻¹)	39.1	12.9	21.3	8.58

* S_B is the standard deviation of the mean value for eight voltammograms of the blank, LOD: Limit of Detection, LOQ: Limit of Quantification.

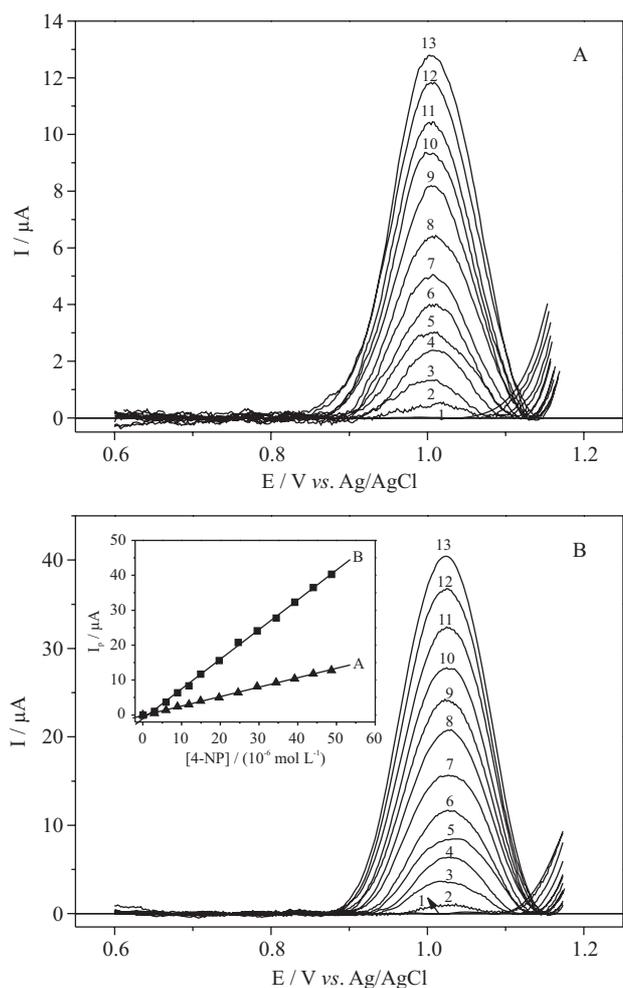


Figure 2. SWV responses (oxidation) obtained on a BDD electrode using different 4-NP concentrations in the absence (A) and presence of ultrasound (B): 0 (1), 2.99 (2), 5.98 (3), 8.95 (4), 11.9 (5), 14.9 (6), 19.7 (7), 24.6 (8), 29.5 (9), 34.4 (10), 39.2 (11), 44.0 (12), 48.7×10^{-6} mol L⁻¹ (13) in BR buffer 0.1 mol L⁻¹ (pH = 6.0) with $f = 100$ s⁻¹, $a = 50$ mV, $\Delta E_s = 2$ mV. Ultrasound conditions: d : 5 mm and A : 20%. Inset: Analytical curves for the oxidation process in the absence (A) and presence of ultrasound (B).

Figure 3B, corresponds to the analytical curves in the silent and insonated conditions. As in the previous study, the analytical curve in the presence of ultrasound showed a higher slope (sensitivity) in comparison to the analytical curve under the silent conditions. The determination of the LOD and LOQ followed the same procedure described before for the oxidation process. The calculated value for LOD in insonated conditions was 1.85×10^{-8} mol L⁻¹ ($2.57 \mu\text{g L}^{-1}$), smaller than LOD for silent conditions, 4.58×10^{-8} mol L⁻¹ ($6.38 \mu\text{g L}^{-1}$). All parameters measured for both the oxidation and the reduction processes in the absence and presence of ultrasound are collected in Table 1. It is clear from the table that the LOD and LOQ values for the reduction process are smaller than those obtained for oxidation. Nevertheless, all LOD and LOQ obtained values (silent and insonated conditions) are

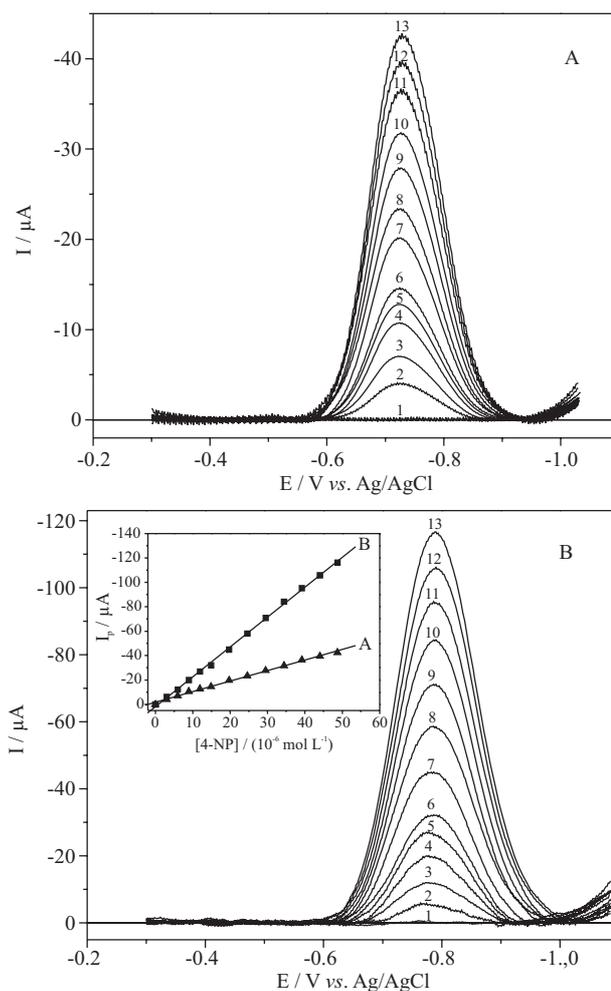


Figure 3. SWV responses (reduction) obtained on a BDD electrode using different 4-NP concentrations in the absence (A) and presence of ultrasound (B): 0 (1), 2.99 (2), 5.98 (3), 8.95 (4), 11.9 (5), 14.9 (6), 19.7 (7), 24.6 (8), 29.5 (9), 34.4 (10), 39.2 (11), 44.0 (12), 48.7×10^{-6} mol L⁻¹ (13) in BR buffer 0.1 mol L⁻¹ (pH = 6.0) with $f = 100$ s⁻¹, $a = 60$ mV, $\Delta E_s = 2$ mV. Ultrasound conditions: d : 5 mm and A : 20%. Inset: Analytical curves for the reduction process in the absence (A) and presence of ultrasound (B).

quite adequate for the application of this methodology in natural waters as well as in food samples.

In future works, the sonoelectroanalytical methodologies for 4-NP detection will be applied to complex matrices, as natural waters and foods. The ultrasound has the ability of cleaning the electrode surface from interfering species presents in those samples that could interact with the diamond surface diminishing the sensibility of the detection methods.

Conclusions

The results of this investigation have shown that the power of ultrasound associated to SWV using BDD electrodes can be a powerful alternative for organic

compounds detection that presents significative interactions with electrode surfaces (adsorption process). This is due to the increase of mass transport and cleaning of electrode surface effects that facilitate the construction of the analytical curves, since the intermediary cleaning of the electrode is not necessary.

Significant enhancements of the sensibilities of the detection methods in the presence of ultrasound are also observed in comparison to the silent conditions. Additionally, in the case of the 4-NP reduction process, the sensibility of the method is much higher than that observed for the oxidation process.

Acknowledgments

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