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Optimization of voltammetric conditions for the determination of guaicol and chloroguaiacol using boron-doped diamond electrode and RSM aproach

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The determination of phenol and its derivatives in the environment is one of the widespread analytical procedures due to their large use in industry and due to their wide toxicity to humans and most aquatic organisms. Phenols can also impart unpleasant taste and odor to drinking water and food products, even at low concentrations. According to published works, phenols toxicity and organoleptic properties are manifested in the ppb range. Thus, there is a need for sensitive, reproducible, stable, easy-to-use, and low-cost analytical methods for monitoring phenols and chlorinated phenols in water supplies[1]. Among the most sensitive analytical methods to detect and quantify of phenols, the electroanalytical methods have attracted very little attention in the literature despite the fact these methods potentially incur low costs and employ fast analysis. The reason for this limited use is probably due to the fact that sensitive and stable electrochemical detection of these pollutants is usually not possible with most electrode materials because the electrode passivation. Nevertheless, in recent years, boron-doped diamond (BDD) has demonstrated to be an attractive material for electroanalytical applications, in view of its unique properties such as robustness, chemical inertness, resistance to electrode fouling, wide potential window and low background currents[2]. Among the electroanalytical techniques generally used, square wave voltammetry (SWV) has proved to be extremely sensitive for the detection of phenolic compounds. However, the utilization of SWV on BDD electrodes is not straightforward and a careful choice and optimization of the experimental parameters is required to obtain a higher sentivity.

The aim of this work was the optimization of the voltammetric conditions using Response Surface Methodology (RSM)[3] approach for determination of guaicol and chloroguaiacol simultaneously using BDD electrodes and SWV.

Guaiacol and chloroguaiacol have been determined to be recalcitrant, toxic to aquatic species, genotoxic, lipophilic with propensity for bioaccumulation.

BDD electrode was grown and characterized by our research group. SWV experiments were performed using an Autolab potentiostat (PGSTAT20). Pt wire was used as counter electrode and a saturated calomel electrode (SCE) as reference. The potential was scanned in the range from 0.5 up to 1.2 V. Central Composite Design (CCD)[3] was used in a previous study. The parameters employed in this stage were: frequency (*Freq*), amplitude (*Ampl*) and pH. Their levels are shown in Table 1. Step potential was 2 mV. The concentration for both guaicol or chloroguaiacol was fixed in 1.0×10^{-4} mol L^{-1}. The measurements were performed in 5 ml of buffer Mcllvaine 0.05 mol L^{-1}. A cathodic treatment in -3 V during 3 s, under vigorous agitation, after at least 5 sequential analyses, was carried out to keep the precision of measurements. The analyzed response (*r*) was obtained in accordance with equation: $r = \left(i_p \cdot w^{-1} \cdot v^{-1/2} \right) \cdot 10^6$, where, i_p is the peak current in ampere (A), *w* is the width at half peak height and *v* is scan rate (Vs^{-1}). pH and *Ampl* were significant for both compounds and the values of its coefficients were respectively: -2.31 and 1.84 for guaicol and -3.17 and 1.05 for chloroguaiacol. This result indicated a displacement in the studied region. Thus a Doehlert design with two variables (pH and *Ampl*) was chosen to investigate the new region. The studied levels for pH were 2.50, 2.87, 3.25, 3.62, 4.00 and for Ampl were 0.07, 0.085, 0.1 V. The level for *Freq* was fixed in 35 Hz and the study was carried out only with guaicol, since both compounds replied linearly for the experiments using CCD.

The model: $r = 21.25 - 1.13$ pH $+ 0.84$ *Ampl* -1.30 pH^2 $- 1.27$ *Ampl*^{2} $- 1.4$ pHx*Ampl* obtained for Doehlert design was significant for regression and not significant for lack-of-fit whith a significance level, α, of 0.05. The analysis of surface response showed clearly that the best levels for variables studied were: pH 3.25, *Ampl* 0.08 V and *Freq* 35 Hz. These conditions provide a detection limit of 7.3×10^{-7} mol L^{-1} for chloroguaiacol and 3.2×10^{-7} mol L^{-1} for guaicol. The reached ppb level was only possible due to multivariate data analysis.

Table 1. Parameters and levels used in the CCD

	-1.682	-1	0	1	1.682
Ampl. (V)	0.04	0.05	0.07	0.09	0.10
Freq. (Hz)	10	20	35	50	60
pH	4.73	5.00	5.40	5.80	6.07

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