

## Simultaneous determination of guaicol and chloroguaiacol by SWV using boron-doped diamond electrode and PLS algorithms

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Contamination of water resources or waste sites with organic pollutants represents a serious environmental problem. The determination of phenol and its derivative compounds is of great importance, since these species are released into the environment by a large number of industries. In addition, some of these compounds, such as guaiaicol and chloroguaiacol, have been determined to be recalcitrant, toxic to aquatic species, genotoxic, lipophilic with propensity for bioaccumulation. There is considerable interest in their measurement in environmental matrices. Analytical methods for the detection and quantification of mixtures of phenols are usually based on analytical separation techniques, which allow the identification and quantification of individual constituents. Many methods have been developed for the determination of phenolic compounds, such as chromatographic, fluorimetric and spectrophotometric methods. However, these techniques do not easily allow continuous monitoring, they are expensive, time-consuming, need skilled operators. Thus, the development of new methods, that allows the simultaneous determination, without previous separations of these compounds is a relevant subject of research. However, very few reports have described the employment of electrochemical techniques for simultaneous phenols detection<sup>2</sup>.

The aim of this work was presenting a method to determine simultaneously guaiaicol and chloroguaiacol by Square Wave Voltammetry (SWV) using boron-doped diamond electrode (BDDE) and Partial Least Squares (PLS) regression. Among the electroanalytical techniques used nowadays, SWV has proved to be extremely sensitive for the detection of organic molecules. BDD electrodes have received much attention recently due to a very large electrochemical window resulting from the low reactivity of their surface. PLS was used owing to necessity of quantification of guaiaicol and chloroguaiacol that presented peaks highly overlapped.

Boron-doped 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 0.5 up to 1.2 V and the operational conditions optimized were 35 Hz, 0.002 V and 0.08 V to the frequency, step potential and amplitude respectively. The voltammograms obtained were submitted to baseline correction by moving average with peak width of 0.01. The concentration range to guaiaicol and chloroguaiacol was from  $2.0 \times 10^{-6}$  to  $3.0 \times 10^{-5}$  mol L<sup>-1</sup>. The measurements were carried out in 5 ml of buffer McIlvaine pH 3.25, 0.05 mol L<sup>-1</sup> containing the mentioned analytes. A cathodic treatment in -3 V during 3 s, under vigorous agitation, after at least 5 sequential analyses, was performed to keep the precision of measurements. Two different PLS algorithms were applied, the SIMPLS<sup>3</sup> and the *powered* PLS (PPLS)<sup>4</sup>. The variables were meancentered and selected. The number of samples in the calibration/prediction sets were of 20/10 and 19/10 for guaiaicol e chloroguaiacol respectively. The number of factors in the model was determined by cross validation applying the leave-one-out method, based on the calculation of root mean square errors of cross-validation (RMSECV). The parameters presented in the table indicate the model predictive ability for unknown samples using two different algorithms. The parameters considered for an external validation set were the root mean square errors (RMSEP), the correlation coefficient (r) and the relative error. Three principal conclusions can be obtained according to the results presented on the table below: (i) the guaiaicol prediction was significantly better comparing to the chloroguaiacol; (ii) the simultaneous determination of these compounds using BDDE is possible even in low concentrations despite the high voltammetric signal overlapping; (iii) the PPLS algorithm showed to be slightly better than SIMPLS to these data sets.

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	RMSECV		Factors		RMSEP		r		Relative error (%)					
	A	B	A	B	A	B	A	B	A			B		
									min	mean	max	min	mean	max
Gua	0.0085	0.0064	4	4	0.0035	0.0028	0.99	0.99	0.27	1.81	5.06	0.03	1.30	3.89
Cgua	0.0116	0.0115	6	5	0.0160	0.0070	0.97	0.99	3.63	14.40	33.37	1.70	11.20	24.20

A - SIMPLS, B - PPLS

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