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Simultaneous determination of hydroquinone, catechol and resorcinol by voltammetry using graphene screen-printed electrodes and partial least squares calibration

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Abstract

Catechol (CC), resorcinol (RC) and hydroquinone (HQ) are dihydroxybenzene isomers that usually coexist in different samples and can be determined using voltammetric techniques taking profit of their fast response, high sensitivity and selectivity, cheap instrumentation, simple and timesaving operation modes. However, a strong overlapping of CC and HQ signals is observed hindering their accurate analysis. In the present work, the combination of differential pulse voltammetry with graphene screen-printed electrodes (allowing detection limits of 2.7, 1.7 and 2.4 $\mu\text{mol L}^{-1}$ for HQ, CC and RC respectively) and the data analysis by partial least squares calibration (giving root mean square errors of prediction, RMSEP values, of 2.6, 4.1 and 2.3 for HQ, CC and RC respectively) has been proposed as a powerful tool for the quantification of mixtures of these dihydroxybenzene isomers. The commercial availability of the screen-printed devices and the low cost and simplicity of the analysis suggest that the proposed method can be a valuable alternative to chromatographic and electrophoretic methods for the considered species. The method has been applied to the analysis of these isomers in spiked tap water.

Keywords: hydroquinone; catechol; resorcinol; voltammetry; screen-printed electrodes; partial least squares calibration.

1. Introduction

Simultaneous analysis of organic compounds with similar chemical properties is a subject of major interest in analytical chemistry. The usual way to deal with this problem is introducing in the analytical procedure a separation step, such as chromatography, previous to the detection. However the possibility to apply a partially selective analytical technique combined with a multivariate data treatment is a question that should be considered.

Catechol (CC), resorcinol (RC) and hydroquinone (HQ) are dihydroxybenzene isomers that are widely used as chemicals in different manufactured products (cosmetics, pesticides, dyes, medicines, etc.). These compounds have high toxicity and low degradability, and they are considered environmental pollutants [1,2]. By these reasons, the development of rapid and sensitive determination methods for their simultaneous analysis is required. Methods including a separation step like liquid chromatography, gas chromatography or capillary electrophoresis are very common. In these methodologies different detection procedures can be applied. Among them, absorption [3-6], fluorescence [7-9] or chemiluminescence [10] detection modes are the most usual. However amperometric detection [11,12] or mass spectrometry [9] are also considered. The possibility to analyze these dihydroxybenzene isomers without previous separation requires techniques or methodologies with high selectivity. One possibility could be the use of a sensor array as that proposed by Qiu et al. [13] in which the selectivity is implemented taking into account the different reactivity of the analytes with some imprinted polymers giving a chemiluminescence array sensor. Another possibility would be the use of a

highly selective technique; it is in this point where voltammetry can play a key role. The advantages of voltammetric techniques are their fast response, high sensitivity and selectivity, together with their cheap instrumentation and their simple and timesaving operation. Due to the electroactive character of dihydroxybenzene isomers the use of voltammetry could be a good option as some references in the literature try to demonstrate [14-20]. In these works the principal aim is to develop methodologies with high sensitivity, and this is solved introducing modifications in different types of carbon based electrodes [14-20]. However, in all the works a strong overlapping of CC and HQ signals is observed that prevents an accurate analysis of these compounds.

An alternative solution for that could be the combined use of voltammetry and a multivariate data treatment method to take profit of the advantages of electroanalytical techniques and the capacity of chemometrics to interpret overlapped signals for the analysis of these isomers.

To carry out voltammetric measurements, a graphene screen printed electrode (SPE) has been considered. The suitability of SPE, which has been demonstrated in the literature in multiple applications [21-24], is consequence of: i) the low-cost which permits the fabrication of numerous highly-reproducible single-use SPEs; ii) the high possibilities of modification; iii) the versatility of its miniaturized size; and iv) the possibility of connecting them to portable instrumentation. All these properties make possible highly specific on-site determinations. In the present work a SPE modified with graphene has been selected with the aim of improving the sensitivity of the device.

Thus, in this work, a methodology based on differential pulse voltammetric measurements in a screen printed carbon electrode modified with graphene and a partial least-squares (PLS) data treatment has been developed and applied to the analysis of CC, RS and HQ in tap spikedwater.

2. Materials and Methods

2.1. Chemicals and reagents

Hydroquinone and resorcinol were provided by Sigma-Aldrich (Barcelona, Spain) and catechol by Fluka (Barcelona, Spain). Phosphate buffer solution (PBS) pH 7.0 was prepared

by mixing the suitable amounts of $0.1 \text{ mol L}^{-1} \text{ NaH}_2\text{PO}_4$ and $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_4$, both provided by Sharlau (Barcelona, Spain). All chemicals used were of analytical reagent grade, and the solutions were prepared in ultrapure filtered water obtained from Milli-Q plus 185 system (Millipore, Milford, Massachusetts, USA).

Solutions of dihydroxybenzene isomers were prepared in free oxygen media and stored in the dark at 4°C to prevent oxidation.

2.2. Instrumentation

Differential pulse voltammetric experiments were performed using a μ Autolab System Type III (EcoChemie, Netherlands) attached to a Metrohm 663 VA Stand (Metrohm, Switzerland) and a personal computer with GPES 4.9 Software (EcoChemie, Netherlands). A combined redox electrode (Crison, Barcelona, Spain) was used as reference (Ag/AgCl ($3 \text{ mol L}^{-1} \text{ KCl}$)) and auxiliary (Pt plate) electrodes. The working electrode was a graphene screen-printed electrode (SPE) with 4 mm diameter provided by Dropsens (Oviedo, Spain) (ref. DRP-110GPH). The screen-printed electrode was connected to the Autolab System by means of a flexible cable (ref. CAC, DropSens). Differential pulse voltammograms that follow the oxidation process of the dihydroxybenzene isomers were recorded from -0.2 V to 0.9 V applying a step potential of 0.005 V , a pulse amplitude of 0.05 V and a pulse time of 0.05 s .

Ionic strength and pH were adjusted in all measurements (calibration, validation and sample solutions) with a $0.1 \text{ mol L}^{-1} \text{ PBS}$ solution at $\text{pH}=7$.

All measurements were carried out in a glass cell at room temperature (20°C) after oxygen removal.

A Crison MicropH 2000 pH-meter (Crison, Barcelona, Spain) was used to measure pH.

2.2. Data treatment

The PLS method requires the construction of a calibration model from two subsets of data obtained from measures of known mixtures of the analytes. One set, named calibration data set, is used for the calibration itself, and the other, named validation data set, is used for the external validation of the model. Once the model is constructed, it is applied to the unknown samples to determine their composition.

Voltammograms of the calibration solutions were arranged in a data matrix X and, previously to the data treatment, submitted to a baseline correction. The baseline correction method considered has been the weighted least square (WLS) baseline preprocessing method that uses an automatic approach to determine which points are most likely due to the baseline alone. This approach iteratively fits a baseline to each voltammogram and determines which variables are clearly above or below the baseline. The points below the baseline are considered more significant in the fitting process. In general this baseline subtraction is not numerically safe as derivatives, although the interpretation of the resulting loadings can be easier. To build the model three different PLS1 models were performed, one for each compound. In this model the experimental data matrix (containing the voltammograms of the 15 calibration solutions) and the target vector that includes the concentrations of one analyte ($n=15$ concentration values) were decomposed for a given number of principal components or latent variables (LV). The “leave-one-out” cross-validation method has been used to establish the optimal number of PLS latent variables.

An important point in the PLS method is the presence of outliers that may have a detrimental effect on the quality of the calibration model. By this reason their presence should be checked. Usually they are detected by a visual inspection of the predicted vs. measured concentration plot.

The evaluation of the modelling error is obtained from the analysis of the predicted vs. actual concentration plots, being the root mean square error of the calibration (RMSEC) the parameter which provides information about the fit of the model to calibration data. Other relevant parameters are: the root mean error of cross-calibration (RMSECV) that measure the ability of the model to predict concentrations; the root mean square error of prediction (RMSEP) which provides information about the fitting of the model to prediction data; the relative percentage error in concentration prediction (RE); and the correlation coefficient (R^2) between predicted and actual concentration values of validation samples.

Experimental data were transferred to MATLAB v.7.9.0 [25]. PLS analyses were performed with PLS Toolbox version 7.8.2 from Eigenvector Research, also implemented in MATLAB [26]. The baseline correction was applied using a program implemented in the PLS Toolbox.

2.3. Experimental design

The application of PLS requires a well-established experimental design. In the present study, a central composite design has been used, where a set of standards has been prepared according to a five-level design, as shown in Figure 1. This experimental design let us to obtain a calibration model with a reasonable number of experiments for the three compounds considered (catechol, resorcinol and hydroquinone). In this case 15 calibration solutions, also named training solutions, defined by the five-level model were considered. 6 validation or test solutions were also prepared and used for prediction. The test solutions concentrations were: 40 $\mu\text{mol L}^{-1}$ of HQ, 30 $\mu\text{mol L}^{-1}$ of CC and 30 $\mu\text{mol L}^{-1}$ of RC; 30 $\mu\text{mol L}^{-1}$ of HQ, 30 $\mu\text{mol L}^{-1}$ of CC and 40 $\mu\text{mol L}^{-1}$ of RC; 30 $\mu\text{mol L}^{-1}$ of HQ, 40 $\mu\text{mol L}^{-1}$ of CC and 30 $\mu\text{mol L}^{-1}$ of RC; 20 $\mu\text{mol L}^{-1}$ of HQ, 30 $\mu\text{mol L}^{-1}$ of CC and 15 $\mu\text{mol L}^{-1}$ of RC; 45 $\mu\text{mol L}^{-1}$ of HQ, 20 $\mu\text{mol L}^{-1}$ of CC and 30 $\mu\text{mol L}^{-1}$ of RC; and 15 $\mu\text{mol L}^{-1}$ of HQ, 45 $\mu\text{mol L}^{-1}$ of CC and 20 $\mu\text{mol L}^{-1}$ of RC. This step allows the validation of the model and assays its accuracy. All measurements were done randomly to improve the robustness of the experiment.

3. Results and discussion

Prior to the multivariate calibration study, univariate calibration experiments have been performed with the aim to establish the limiting concentrations for subsequent analysis; in this study concentrations of the different isomers from 1 to 50 $\mu\text{mol L}^{-1}$ have been considered and measurements have been done with a graphene SPE (DRP-110GPH) which in preliminary experiments showed a much better sensitivity than the usual carbon SPE (DRP-110 by Dropsens). Table 1 presents the calibration plots obtained for each compound and the detection and quantification limits (LOD and LOQ) evaluated as 3 and 10 times the standard deviation of the intercept over the slope of the calibration curve, respectively. These results show a good linearity of the signals and acceptable LOQ values in comparison with those of the literature

[14-20]. Additions of increasing concentrations of each one of the dihydroxybenzene isomers in solutions containing constant concentration of the other two compounds have also been done. Figure 2 shows the voltammograms obtained in these studies together with a set of voltammograms considering the simultaneous additions of CC, RC and HQ. These voltammograms show peaks at around 0.045 V, 0.150 V, and 0.550 V (vs. an Ag/AgCl reference electrode) that correspond to HQ, CC and RC respectively. A clear evolution of the signals with concentration is observed together with the evident overlapping of HQ and CC peaks (around 0.1 V between peaks) that justifies the need to apply some multivariate data treatment.

For the simultaneous analysis of HQ, CC and RC, the PLS method has been constructed and validated. In this process voltammograms of calibration (or training) and validation (or test) solutions obtained as it has been explained in the Experimental design section have been considered. As an example Figure 3a shows a set of experimental voltammograms of the training solutions which evidences the overlapping of the peaks of the analytes and the important contribution of the baseline. These voltammograms, previously to the data treatment, were submitted to a baseline correction (Figure 3b).

As it is explained before, in ~~in~~ this work, three different PLS1 models were separately built for each analyte; these models were constructed using the 15 training solutions, although in all cases one or two outliers were detected and subsequently eliminated analyzing the predicted vs. actual concentration plots. Once the outliers were removed, the number of LV was evaluated before building the PLS model being 4 for HQ, 3 for CC and 4 for RC, which are not very large given the complexity of the system. The results obtained for the prediction set of samples are shown in Figure 4 and Table 2, being the square correlation coefficients R^2 and the root mean square error values of the prediction (RMSEP) for the three analytes very satisfactory. As expected, RMSECV and RMSEP values are just slightly higher than the intrinsic error generated in the constructions of the model (RMSEC), thus showing a good prediction ability for the samples which have not been included in the model. From these results, it can be

concluded that although the model for CC (Figure 4b) is less predictive than those for HQ and RC, the PLS models obtained are suitable to solve the problem of overlapped peaks.

To validate the proposed methodology, the simultaneous analysis of HQ, CC and RC in tap water was performed. Because the water sample considered does not contain these compounds, the investigated sample was spiked with a known amount of the three analytes. Three samples of tap water spiked with $24.8 \mu\text{mol L}^{-1}$ of HQ, CC and RC (in 0.1 mol L^{-1} of PBS $\text{pH}=7$ media) were considered. The results obtained in the analysis of this tap water are shown in Table 3, indicating that recoveries are very satisfactory, and suggesting that the proposed chemometric method can be used in combination with differential pulse voltammetric measurements for the analysis of HQ, CC and RC in tap water.

4. Conclusions

The combination of differential pulse voltammetry with graphene screen-printed electrodes and the data analysis by partial least squares calibration is a powerful tool for the quantification of mixtures of dihydroxybenzene isomers. This fact is supported by the goodness of the results obtained in the partial least squares calibration process that gives RMSEP values of 2.6, 4.1 and 2.3 for HQ, CC and RC respectively, and by the acceptable recoveries obtained in the analysis of a tap spikedwater sample. The commercial availability of the screen-printed devices considered and the low cost and simplicity of the analysis suggest that the proposed method can be a valuable and cheaper alternative to chromatographic and electrophoretic methods for the considered species.

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References

- [1] Límites de exposición profesional para agentes químicos en España. 2014. Instituto Nacional de Seguridad e Higiene en el Trabajo (INSHT) (www.insht.es)
- [2] EEC Directive 80/77/CEE 15-7-1990. Official Journal of the European Communities (30/08/1990) European Community, Brussels, 1990.
- [3] C.H. Lin, J.Y. Sheu, H.L. Wu, Y.L. Huang, Determination of hydroquinone in cosmetic emulsion using microdialysis sampling coupled with high-performance liquid chromatography, *J. Pharm. Biomed. Anal.* 38 (2005) 414 - 419.
- [4] N. Guan, Z. Zeng, Y. Wang, E. Fu, J. Cheng, Open tubular capillary electrochromatography in fused-silica capillaries chemically bonded with macrocyclic dioxopolyamine, *Anal. Chim. Acta* 418 (2000) 145 – 151.
- [5] C. Desiderio, L. Ossicini, S. Fanali, Analysis of hydroquinone and some of its ethers by using capillary electrochromatography, *J. Chromatogr. A* 887 (2000) 489 – 496.
- [6] D. Allen, Z. El Rassi, Capillary electrochromatography with monolithic silica columns III. Preparation of hydrophilic silica monoliths having surface-bound cyano groups: chromatographic characterization and application to the separation of carbohydrates, nucleosides, nucleic acid bases and other neutral polar species, *J. Chromatogr. A* 1029 (2004) 239 – 247.
- [7] G. Marrubini, E. Calleri, T. Coccini, A.F. Castoldi, L. Manzo, Direct analysis of phenol, catechol and hydroquinone in human urine by coupled-column HPLC with fluorimetric Detection, *Chromatographia* 62 (2005) 25 - 31.
- [8] N. A. Penner, P. N. Nesterenko, Simultaneous determination of dihydroxybenzenes, aminophenols and phenylenediamines in hair dyes by high-performance liquid chromatography on hypercross-linked polystyrene, *Analyst* 125 (2000) 1249 – 1254.
- [9] S.C. Moldoveanu, M. Kiser, Gas chromatography/mass spectrometry versus liquid chromatography/fluorescence detection in the analysis of phenols in mainstream cigarette smoke, *J. Chromatogr. A* 1141 (2007) 90 – 97.

- [10] S.L. Fan, L.K. Zhang, J.M. Lin, Post-column detection of benzenediols and 1,2,4-benzenetriol based on acidic potassium permanganate chemiluminescence, *Talanta* 68 (2006) 646 – 652.
- [11] W.C. Yang, X.D. Yu, A.M. Yu, H.Y. Chen, Study of a novel cationic calix[4]arene used as selectivity modifier in capillary electrophoresis with electrochemical detection, *J. Chromatogr. A* 910 (2001) 311 – 318.
- [12] T. Xie, Q. Liu, Y. Shi, Q. Liu, Simultaneous determination of positional isomers of benzenediols by capillary zone electrophoresis with square wave amperometric detection, *J. Chromatogr. A* 1109 (2006) 317 – 321.
- [13] H. Qiu, C. Luo, M. Sun, F. Lu, L. Fan, X. Li, A chemiluminescence array sensor based on graphene-magnetite-molecularly imprinted polymers for determination of benzenediol isomers, *Anal. Chim. Acta* 744 (2012) 75 – 81.
- [14] Z. Wang, S. Li, Q. Lv, Simultaneous determination of dihydroxybenzene isomers at single-wall carbon nanotube electrode, *Sensors & Actuators B* 127 (2007) 420 - 425.
- [15] X. Zhang, S. Duan, X. Xu, Electrochemical behavior and simultaneous determination of dihydroxybenzene isomers at a functionalized SBA-15 mesoporous silica modified carbon paste electrode, *Electrochim. Acta* 56 (2011) 1981 - 1987.
- [16] H. Yin, Q. Zhang, Y. Zhou, Q. Ma, T. Liu, L. Zhu, S. Ai, Electrochemical behavior of catechol, resorcinol and hydroquinone at graphene-chitosan composite film modified glassy carbon electrode and their simultaneous determination in water samples, *Electrochim. Acta* 56 (2011) 2748 - 2753.
- [17] Y. Zhang, S. Xiao, J. Xie, Simultaneous electrochemical determination of catechol and hydroquinone based on graphene-TiO₂ nanocomposite modified glassy carbon electrode, *Sensors & Actuators B* 204 (2014) 102 - 108.
- [18] Y. Liu, W. Wang, H. Wei, Simultaneous determination of dihydroxybenzene isomers based on thionine functionalized multiwall carbon nanotubes modified electrode, *J. App. Electrochem.* 44 (2014) 667 - 674.

- [19] H. Zhang, X. Bo, L. Guo, Electrochemical preparation of porous graphene and its electrochemical application in the simultaneous determination of hydroquinone, catechol and resorcinol, *Sensors & Actuators B* 220 (2015) 919 - 926.
- [20] W. Zhang, J. Zheng, Z. Lin, Highly sensitive simultaneous electrochemical determination of hydroquinone, catechol and resorcinol based on carbon dot/reduced graphene oxide composite modified electrodes, *Anal. Methods* 7 (2015) 6089 - 6094.
- [21] J. Iniesta, L. García-Cruz, A. Gomis-Berenguer, C.O. Ania, Carbon materials based on screen-printing electrochemical platforms in biosensing Applications, *SPR Electrochemistry* 13 (2016) 133 - 169.
- [22] A. Hayat, J.L. Marty, Disposable screen printed electrochemical sensors: Tools for environmental monitoring, *Sensors* 14 (2014) 10432 - 10453.
- [23] Z. Taleat, A. Khoshroo, M. Mazloun-Ardakani, Screen-printed electrodes for biosensing: A review (2008-2013), *Microchim. Acta* 181 (2014) 865 - 891.
- [24] N. Thiyagarajan, J.L. Chang, K. Senthilkumar, J.M. Zen, Disposable electrochemical sensors: A mini review, *Electrochem. Comm.* 38 (2014) 86 - 90.
- [25] Matlab, version R2008b ed., Mathworks Inc.: Natick, MA, USA, 2008.
- [26] PLS-toolbox version 7.8.2 (Eigenvector Research Inc., Wenatchee, USA).

Table 1.- Calibration plots and limits of detection and quantification for hydroquinone (HQ), catechol (CC) and resorcinol (RC).

Compound	Calibration plot ^a	R ² ^b	X _{LOD} ^c (μmol L ⁻¹)	X _{LOQ} ^d (μmol L ⁻¹)
HQ	$y = 1.3221x + 0.2304$	0.9939	2.7	9.1
CC	$y = 1.5825x - 0.0398$	0.9961	1.7	5.6
RC	$y = 0.5706x - 0.2530$	0.9907	2.4	7.9

(a) x in μmol L⁻¹ and y is the peak area

(b) R² is the coefficient of correlation

(c) Detection limits evaluated as 3 times the standard deviation of the intercept over the slope of the calibration plot

(d) Quantification limits evaluated as 10 times the standard deviation of the intercept over the slope of the calibration plot

Table 2.- Figures of merit for PLS regression models of hydroquinone, catechol and resorcinol.

Compound	Nc ^a	RMSEP ^{b,d}	RMSECV ^{b,e}	RMSEC ^{b,f}	RE(%) ^g	R ² ^c
Hydroquinone	4	2.5888	3.5928	2.4905	8.15	0.925
Catechol	3	4.1173	3.5077	2.5916	9.79	0.912
Resorcinol	4	2.3318	3.1997	1.8690	8.13	0.954

(a) Nc is the number of components or latent variables used in the PLS model

(b) The values are given in $\mu\text{mol L}^{-1}$ units

(c) R² is the coefficient of correlation between predicted and actual concentration values of validation samples

(d) RMSEP is the root mean square error of prediction

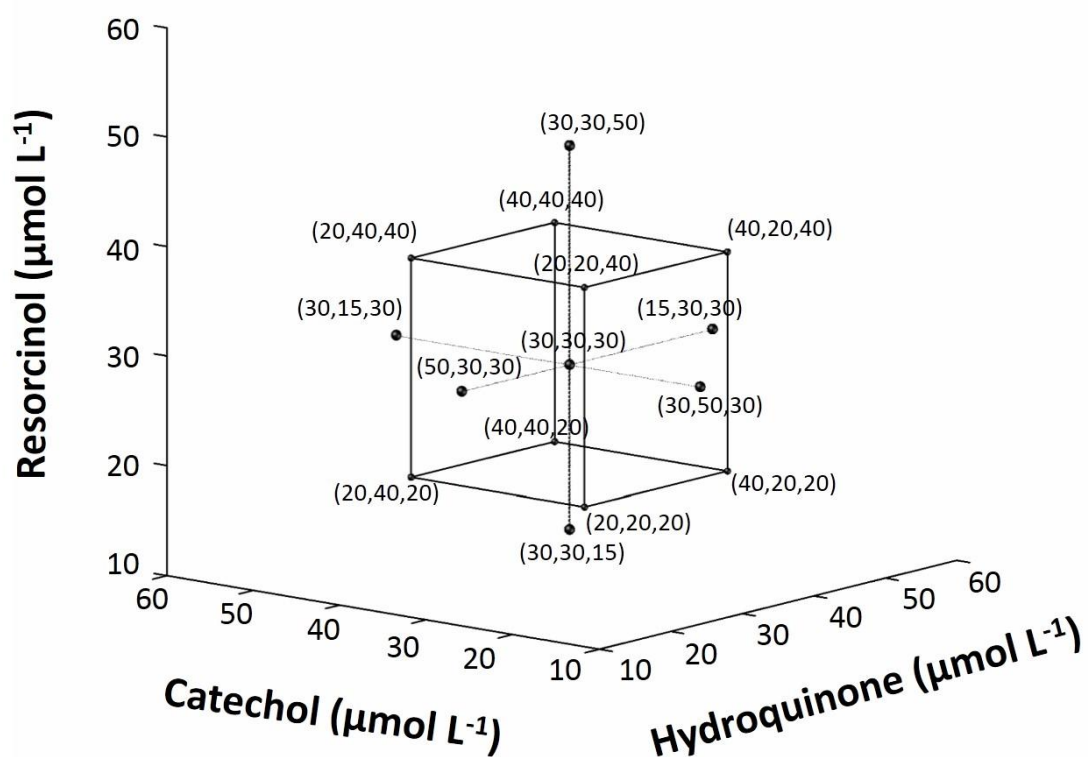
(e) RMSECV is the root mean square error of the cross validation

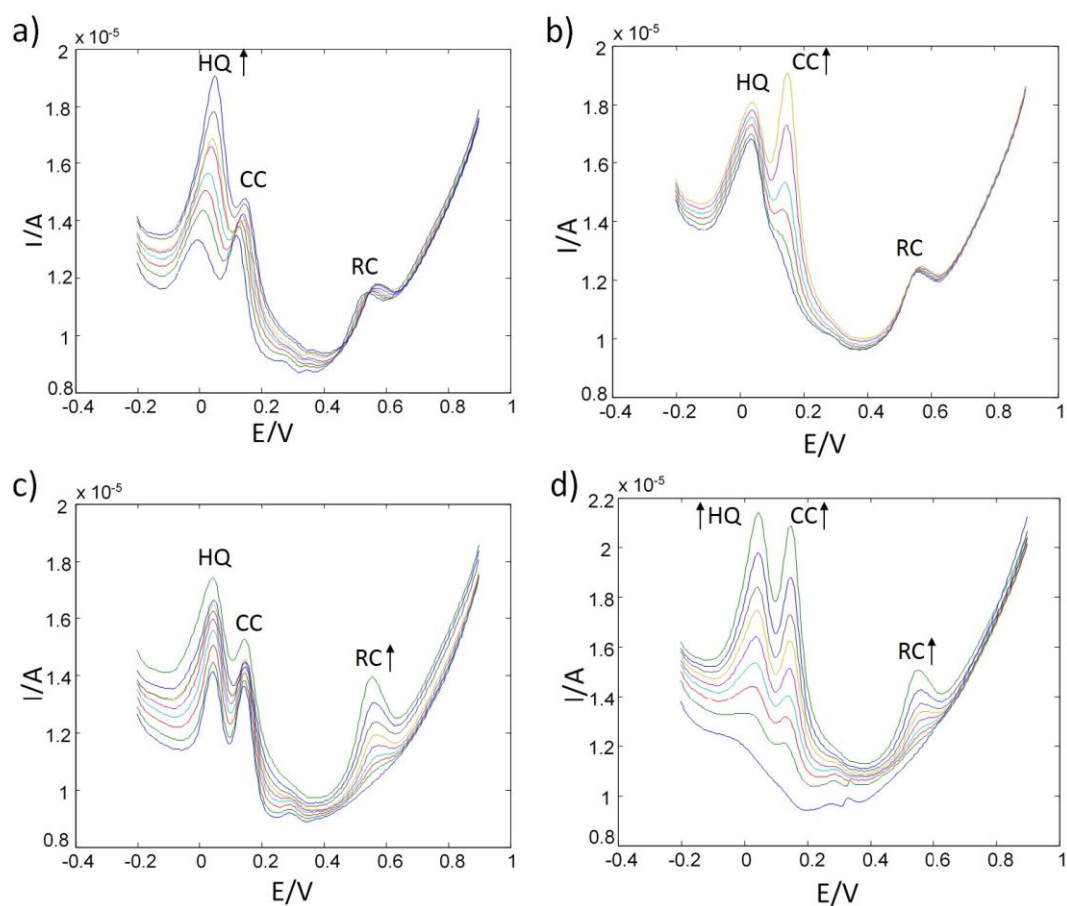
(f) RMSEC is the root mean square error of calibration

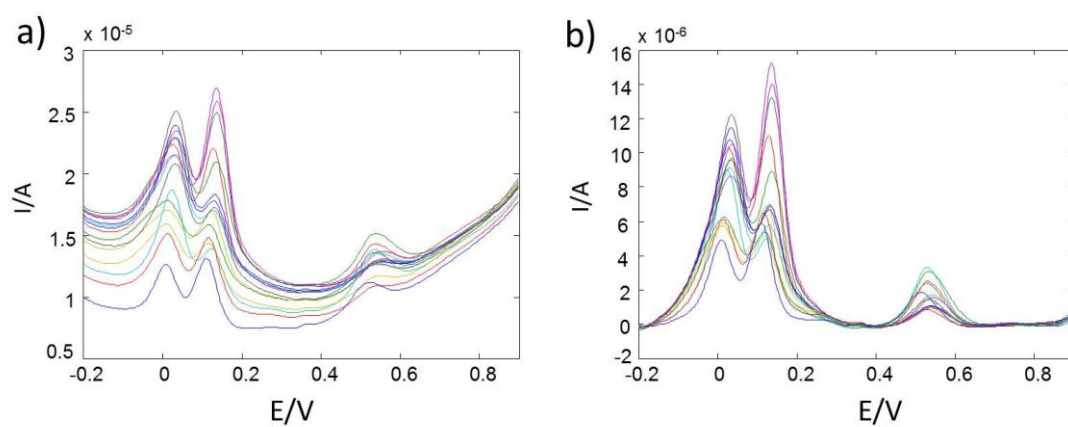
(g) RE(%) is the relative percentage error in concentration prediction

Table 3.- Results obtained of the analysis of dihydroxybenzene isomers (hydroquinone (HQ), catechol (CC) and resorcinol (RC)) in tap water samples. Three independent replicates were done with a spiked concentration of $24.8 \mu\text{mol L}^{-1}$ of each analyte.

	Measured					
	concentration ($\mu\text{mol L}^{-1}$)			Recovery (%)		
	HQ	CC	RC	HQ	CC	RC
S ₁	25.8	22.1	21.2	104	89	85
S ₂	27.5	27.4	24.9	111	111	100
S ₃	23.6	25.3	21.3	95	102	86







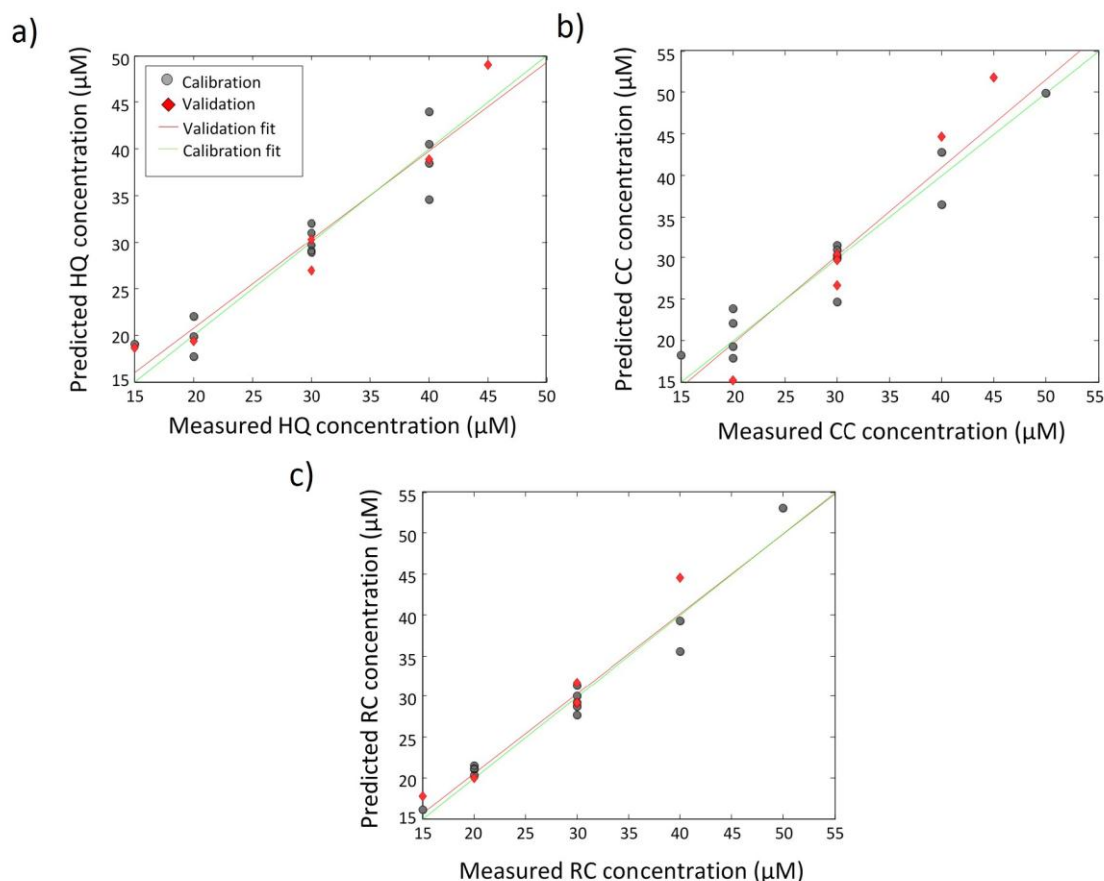


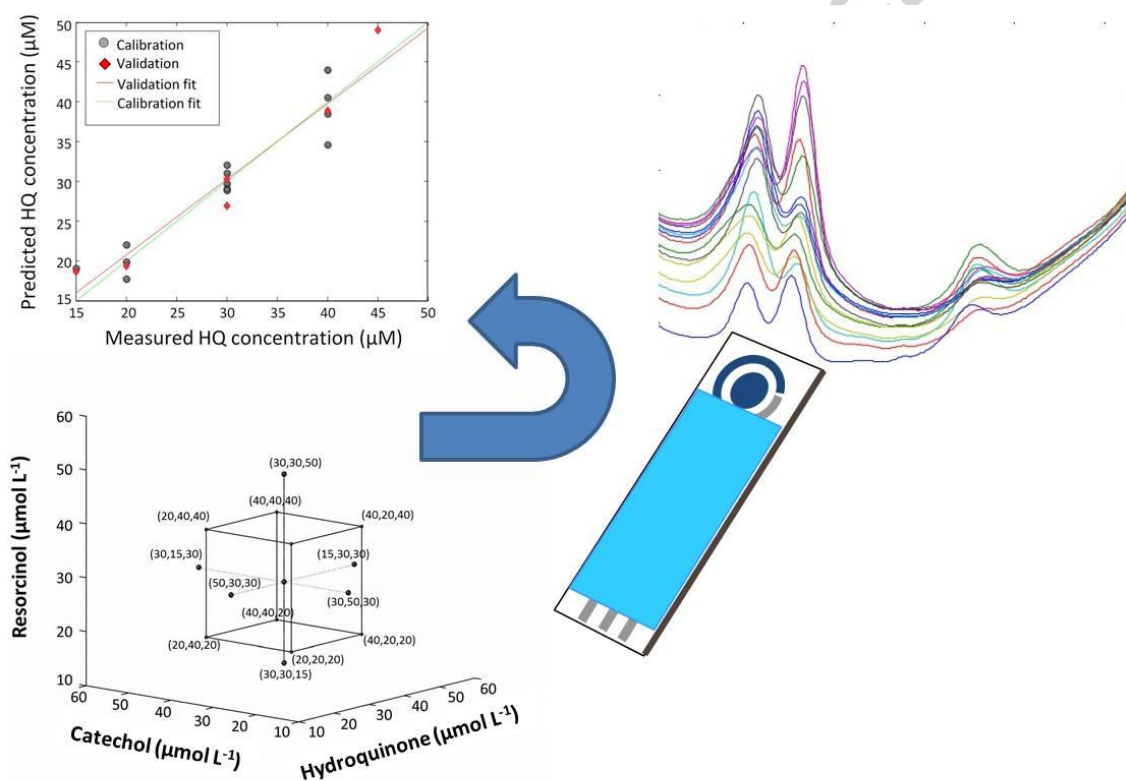
Figure 1.- Representation of the five-level experimental design followed in the present work. Numbers in parenthesis indicate the concentration levels of the three analytes (HQ, CC, RC in $\mu\text{mol L}^{-1}$). Axis: x (Hydroquinone), y (Catechol), z (Resorcinol).

Figure 2.- Differential pulse voltammograms obtained with a graphene-SPCE electrode (0.1 mol L^{-1} PBS pH 7.0). a) Different HQ concentrations (1, 5, 7.5, 10, 15, 20, 25 and 35 $\mu\text{mol L}^{-1}$) in the presence of 15 $\mu\text{mol L}^{-1}$ of CC and 22.8 $\mu\text{mol L}^{-1}$ of RC; b) different CC concentrations (1, 5, 10, 15, 26.5 and 38.1 $\mu\text{mol L}^{-1}$) in the presence of 16.5 $\mu\text{mol L}^{-1}$ of HQ and 22.8 $\mu\text{mol L}^{-1}$ of RC; c) different RC concentrations (1, 5, 7.5, 10, 15, 20, 25, 25 and 50 $\mu\text{mol L}^{-1}$) in presence of 16.5 $\mu\text{mol L}^{-1}$ of HQ and 15 $\mu\text{mol L}^{-1}$ of CC; d) different concentration of HQ, CC and RC (1, 5, 7.5, 10, 15, 20, 25, 35 and 50 $\mu\text{mol L}^{-1}$). Arrows indicate which analyte concentration varies.

Figure 3.- a) Experimental voltammograms of a set of calibration solutions. b) Voltammograms after correction of the baseline by weighted least squares (WLS).

Figure 4.- Predicted vs. measured concentrations of calibration and validation solutions for PLS models of a) hydroquinone (HQ), b) catechol (CC) and c) resorcinol (RC).

Graphical Abstract



highlights

Simultaneous determination of dihydroxybenzene isomers

Combined use of voltammetry with a graphene screen-printed electrodes and partial least squares data analysis

Resolution of overlapping signals of hydroquinone, catechol and resorcinol

Accepted manuscript