Talanta 160 (2016) 138–143

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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

Miriam Aragó, Cristina Ariño *, Àngela Dago, José Manuel Díaz-Cruz, Miquel Esteban

Departament de Química Analítica, Facultat de Química, Universitat de Barcelona, Martí i Franquès, 1-11, 08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 15 April 2016
Received in revised form
30 June 2016
Accepted 3 July 2016
Available online 4 July 2016

Keywords:
Hydroquinone
Catechol
Resorcinol
Voltammetry
Screen-printed electrodes
Partial least squares calibration

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 μmol 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.

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

* Corresponding author.
E-mail address: cristina.arino@ub.edu (C. Ariño).

http://dx.doi.org/10.1016/j.talanta.2016.07.007
0039-9140/

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 mol L^{-1} NaH_2PO_4 and 0.1 mol L^{-1} Na_2HPO_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 μAutolab 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 mol L^{-1} 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 mol L^{-1} PBS solution at 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.

2.3. 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.

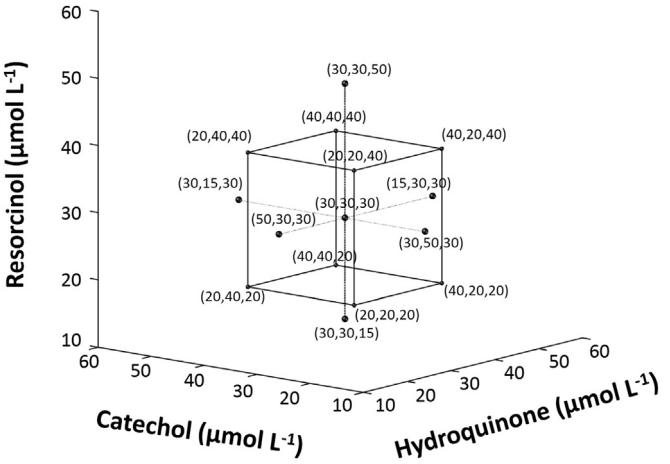

Fig. 1. Representation of the five-level experimental design followed in the present work. Numbers in parenthesis indicate the concentration levels of the three analytes (HQ, CC, RC in μmol L^{-1}). Axis: x (Hydroquinone), y (Catechol), z (Resorcinol).

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] R^2 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.

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 modeling error is obtained from the analysis of the predicted vs. actual concentration plots, being the