



## Comparison of carbon screen-printed and disk electrodes in the detection of antioxidants using CoPc derivatives

Fungisai Matemadombo<sup>a,c</sup>, Constantin Apetrei<sup>b</sup>, Tebello Nyokong<sup>c</sup>,  
María Luz Rodríguez-Méndez<sup>a,\*</sup>, José Antonio de Saja<sup>d</sup>

<sup>a</sup> Dept. Inorganic Chemistry, Industrial Engineers School, University of Valladolid, Spain

<sup>b</sup> Department of Chemistry, Physics and Environment, Faculty of Sciences and Environment, "Dunărea de Jos" University of Galați, Romania

<sup>c</sup> Chemistry Department, Rhodes University, P.O. Box 94, Grahamstown 6140, South Africa

<sup>d</sup> Dept. Condensed Matter Physics, Faculty of Sciences, University of Valladolid, Spain

### ARTICLE INFO

#### Article history:

Received 2 December 2011

Received in revised form 7 February 2012

Accepted 8 February 2012

Available online 10 March 2012

#### Keywords:

Screen-printed electrode

Disk electrode

Antioxidant

Phthalocyanine

Kinetics

Principal component analysis

### ABSTRACT

Cobalt phthalocyanine (CoPc) and cobalt phthalocyanine carboxylic derivatives (CoTCPc and CoOCPc) have been used as electrocatalysts for the detection of the antioxidants vanillic acid, caffeic acid, pyrogallol, and ascorbic acid on screen-printed carbon and disk electrode surfaces. The cobalt phthalocyanines were used to detect vanillic acid (with limit of detection ranging from 1.15  $\mu\text{M}$  to 2.42  $\mu\text{M}$  at potentials of 0.55–0.88 V vs. Ag|AgCl), caffeic acid (with limit of detection ranging from 1.17  $\mu\text{M}$  to 2.20  $\mu\text{M}$  at potentials of 0.30–0.81 V vs. Ag|AgCl), pyrogallol (with limit of detection ranging from 1.16  $\mu\text{M}$  to 3.63  $\mu\text{M}$  at potentials of 0.52–0.63 V vs. Ag|AgCl), and ascorbic acid (with limit of detection ranging from 1.16  $\mu\text{M}$  to 1.58  $\mu\text{M}$  at potentials of 0.34–0.46 V vs. Ag|AgCl). The kinetic studies also demonstrate diffusion-controlled processes at the electrode surface. The SPCE electrodes have better detection properties towards vanillic acid, caffeic acid, pyrogallol while the disk electrodes had better ascorbic acid detection properties as proven by kinetic studies. Both types CoPc-influenced electrodes show 100% discrimination of the antioxidants.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

Antioxidants are a broad group of active biological substances which are widespread in foods [1]. Among antioxidants, polyphenols are of great interest due to their health benefits [2–4]. In addition, polyphenols influence the quality and the organoleptic characteristics of foods and affect their antioxidant capacity [5,6]. Several analytical methodologies have been proposed in order to quantify phenolic compounds in food, beverages and biological fluids. These techniques include chromatographic, electrophoretic and optic techniques [6,7]. Electrochemical techniques have often been considered superior, due to their higher sensitivity, negligible effect of the sample turbidity and inherent portability [6].

During the last years, a new technology for the analysis of foods has been developed, called electronic tongue that consists of an array of electrodes with cross selectivity coupled to a pattern recognition software [8,9]. The most used methods in

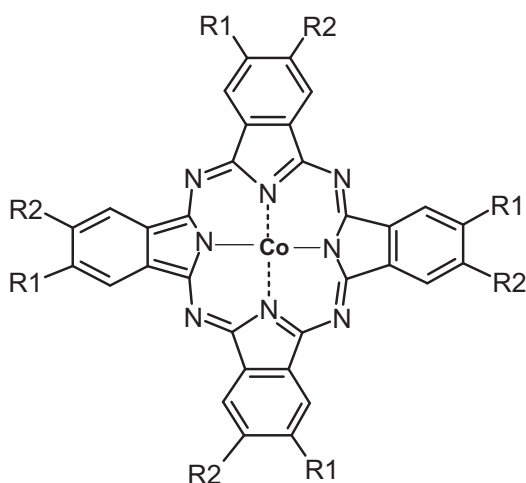
e-tongues employ electrochemical techniques, including potentiometry [10–12], amperometry [13], cyclic voltammetry [14–16] or impedance measurements [16–18]. Much attention has been paid to the analysis of foods and beverages, and in particular, to the analysis of antioxidants [19,20], antioxidants in oils [21] wines [22–24] and beers [25]. By using PCA, it is possible to discriminate between samples of different characteristics [26].

One of the main challenges in electronic tongues is to find the appropriate sensing materials for each particular application. Metallophthalocyanines (MPcs), a wide family of materials that belong to the family of tetrapyrrolic compounds, have demonstrated to be an interesting choice as sensitive materials because the changes produced by the presence of other molecules can be monitored using a variety of transduction methods [27–29]. In particular, these fully  $\pi$ -conjugated macrocyclic molecules have attracted considerable interest as chemical modifiers in electrochemical sensors due to their rich electrochemical and electrocatalytic activities [27–31]. In addition, the electrochemical signals produced by the presence of analytes can be monitored using a variety of electrochemical methods that include potentiometry, amperometry, voltammetry or impedimetry [32–35].

Metallophthalocyanine (MPc) electrochemistry in the solution phase is typified by multiple and often reversible redox processes localized on the metal center and the Pc ring [30,36], but ring

\* Corresponding author at: Dpto. de Química Inorgánica, E.T.S. de Ingenieros Industriales, Universidad de Valladolid, Po. del Cauce 59, 47011 Valladolid, Spain. Tel.: +34 983 423540; fax: +34 983 423310.

E-mail addresses: [mluz@dali.eis.uva.es](mailto:mluz@dali.eis.uva.es), [mluz@eis.uva.es](mailto:mluz@eis.uva.es) (M.L. Rodríguez-Méndez).



**1: CoPc: R1 = R2 = H**

**2: CoTCPc: R1 = H, R2 = COOH**

**3: CoOCPc: R1 = R2 = COOH**

**Fig. 1.** Molecular structures of cobalt phthalocyanine (CoPc, **1**), cobalt tetracarboxy phthalocyanine (CoTCPc, **2**) and cobalt octacarboxy phthalocyanine (CoOCPc, **3**).

substituents have been known to have a significant effect on the MPC electrochemical sensing ability [37]. These redox pathways may be further influenced by the solvent and the axial ligand [38] and are important in natural and industrial catalytic reactions of phthalocyanines.

First row transition metals have d-orbitals situated between the HOMO and LUMO gap of the Pc ligand and consequently show electrochemical reactivity: electrochemical processes occurring on the metal in the Pc are expected especially for Fe, Co, and Mn derivatives [39], and hence Co derivatives were used in this work. In addition, it is well known that the catalytic activity of metallophthalocyanines for the oxidation of several molecules can be “tuned” by manipulating the  $E^{\circ}$  formal potential, using proper groups on the macrocyclic ligand [40,41]. In spite of the potential advantages of cobalt phthalocyanine carboxyl derivatives, they have not been used as electroactive materials for construction of arrays of sensors. Therefore, the objective of this work is to compare two types of electrochemical experimental setups based on these Pcs and to evaluate their capability to discriminate several antioxidants. For this purpose, cobalt phthalocyanine (CoPc, **1**), cobalt tetracarboxyphthalocyanine (CoTCPc, **2**) and cobalt octacarboxyphthalocyanine (CoOCPc, **3**), Fig. 1, sensing units with distinct selectivity have been prepared using screen-printed carbon electrodes (SPCEs), and traditional disk electrodes for the detection and discrimination of four antioxidants including three phenols: vanillic acid (monophenol), caffeic acid (a diphenol) and pyrogallol (a triphenol) and ascorbic acid (a dihydroxyfuran) which is one of the main antioxidants found in foods as a preservative. The capability of discrimination of the array of sensors toward antioxidants has been analyzed by the principal component analysis (PCA).

## 2. Experimental

### 2.1. Materials

The cobalt complexes **1–3** were synthesized according to reported procedures [42–44]. Ethanol and dimethylformamide

(DMF) were purchased from Scharlau. L-Tartaric acid was purchased from Sigma. NaOH was purchased from Panreac. Pyrogallol and caffeic acid were purchased from Sigma–Aldrich. Vanillic acid was purchased from Fluka. L-(+)-Ascorbic acid was purchased from Riedel-de Haën. The antioxidants were dissolved in a model wine solution (hydroalcoholic solution) consisting of 12% (v/v) ethanol and 0.033 M L-tartaric acid adjusted to a pH of 3.6 using NaOH. This hydroalcoholic solution simulates the conditions at which the phenols are found in wines. Deionized water was obtained from a Millipore-Q-system.

### 2.2. UV–vis measurements

UV–visible spectra were recorded on a UV-1603 UV–visible spectrophotometer (Shimadzu). In UV–vis studies [antioxidant] = [MPC] = 1 mM.

### 2.3. Electrochemical procedure

#### 2.3.1. Screen-printed carbon electrodes

The electrochemical studies were carried out using DRP-110 screen-printed electrodes (SPCE) purchased from Dropsens (Spain). The electrodes contained three screen-printed electrodes: a working electrode made of carbon (4 mm diameter); a counter electrode also made of carbon and a silver reference electrode. The electrodes were connected to a potentiostat ( $\mu$ Stat 400 BioPotentiostat/Galvanostat) adapted to these electrodes fabricated by the same company using a DSC boxed connector.

A significant advantage of using a disposable SPCE is that no cleaning steps are needed being the SPCE replaced between measurements. Therefore, 1 mM of the corresponding CoPc derivative (10  $\mu$ L in DMF, final concentration = 0.5 mM) mixed with 1 mM antioxidant solution (10  $\mu$ L in hydroalcoholic solution, final concentration = 0.5 mM) was placed onto a new screen-printed carbon electrode surface and the resulting solution analyzed by cyclic voltammetry.

Cyclic voltammograms were registered from 0 to 1.2 V (except otherwise indicated) at a scan rate of 100  $\text{mV s}^{-1}$ .

#### 2.3.2. Disk electrodes

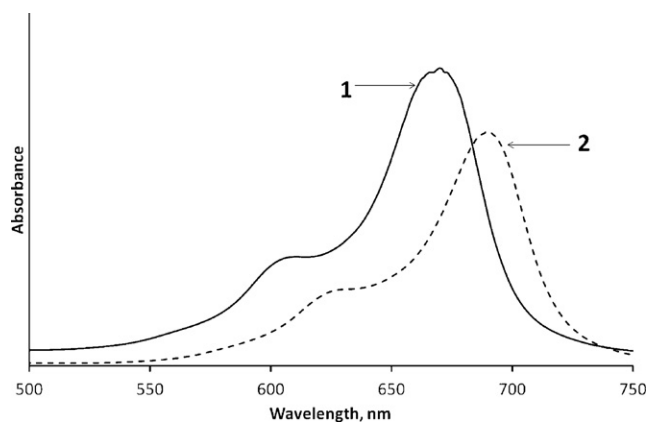
Cyclic voltammetry studies were recorded using a PARSTAT 2273 potentiostat (EG&G). A conventional three-electrode system consisting of a BASi glassy carbon electrode (3.00 mm diameter) as a working electrode, a platinum wire counter electrode and an Ag|AgCl/KCl (3 M) reference electrode were employed. The Ag|AgCl/KCl (3 M) reference electrode has an offset potential of 0.222 V vs. the normal hydrogen electrode.

For the disk electrode setup, 10  $\mu$ L of the corresponding CoPc derivative (1 mM in DMF) was placed onto a cleaned glassy carbon electrode surface for 30 min to dry.

Cyclic voltammograms were registered from 0 to 1.2 V (except otherwise indicated) at a scan rate of 100  $\text{mV s}^{-1}$ . The electrochemical responses to antioxidants were recorded in 1 mM antioxidant solutions. After use electrodes were cleaned by polishing using 0.05  $\mu\text{m}$  alumina followed by an ultrasonic bath cleaning in deionized water for a few minutes, in order to remove any residual alumina.

### 2.4. Data analysis

Cyclic voltammograms were disk analyzed by principal component analysis (PCA) which is a non-supervised technique used to explain the variance in a data matrix [26] (The Unscrambler v. 9.1, CAMO ASA, Norway and Matlab v5.3., The Mathworks Inc., Natick, MA, USA). So, using PCA, it is possible to find the structure and



**Fig. 2.** UV–visible spectra of CoTCPC before (1) and after (2) addition of vanillic acid. CoTCPC concentration  $\approx 1 \mu\text{M}$ .

correlation in a data set and to make a calibration data set, which can be used to predict test data.

All antioxidant samples were measured seven times with each sensor. The analysis was carried out using, as input data source, pre-processed voltammograms obtained by the adaptation of a data reduction technique based on predefined response ‘bell-shaped-windowing’ curves called ‘kernels’ [45]. Using this approach, 10 parameters per curve were obtained.

### 3. Results and discussion

#### 3.1. UV–visible spectra studies of antioxidants

As an example, Fig. 2 shows the UV–visible spectra of CoTCPC before (1) and after (2) addition of vanillic acid. The Q-band maximum shifts for all the MPCs (complexes 1–3) on addition of the various antioxidant solutions due to the electron donating nature of the latter [46]. Electron donating groups shift the Q band to the red. It is possible that the antioxidants coordinate to the central Co metal of the phthalocyanines. Electrochemical studies between the two types of species could then be more confidently done.

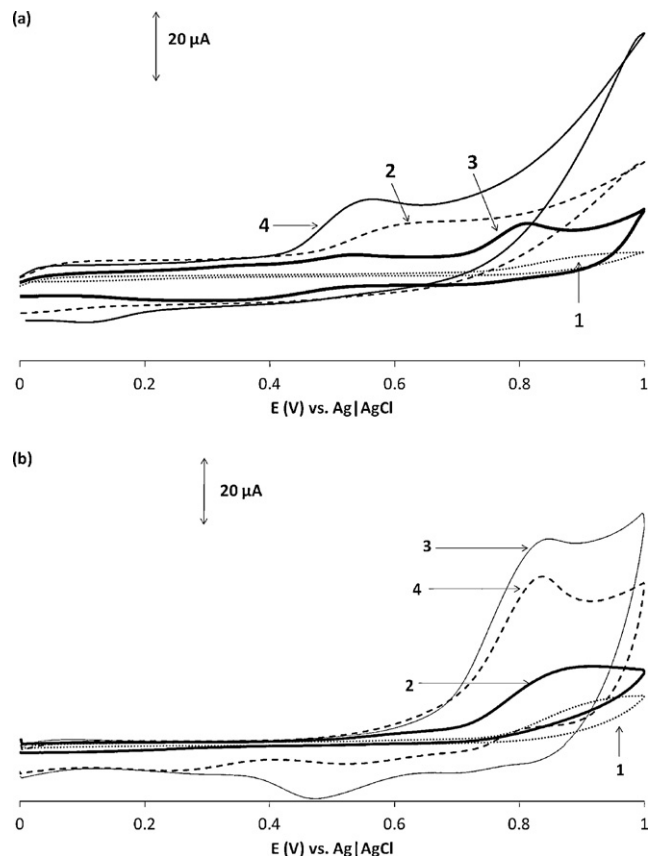
#### 3.2. Electrochemical studies of antioxidants

##### 3.2.1. Vanillic acid

Fig. 3a shows the cyclic voltammograms registered when using the unmodified SPCE and the three electrodes chemically modified with the three phthalocyanine compounds in contact with vanillic acid solutions. A broad and relatively insignificant vanillic acid oxidation peak was observed for the unmodified SPCE (Fig. 3a, plot 1). Better-defined vanillic acid oxidation peaks with higher peak current intensities and less positive peak potentials were observed when CoPc, CoTCPC, and CoOCPc were added in the vanillic acid solution at 0.60 V, 0.80 V and 0.55 V vs. Ag|AgCl respectively, Table 1. The increase in current and shifting of potentials to less positive values confirm electrocatalytic activity.

Fig. 3b shows the cyclic voltammograms registered using the bare and the modified disk electrodes recorded in 1 mM vanillic acid solution. A weak peak was observed for vanillic acid on unmodified disk electrode (Fig. 3b, plot 1). Vanillic acid oxidation peaks were observed between 0.81 V and 0.88 V vs. Ag|AgCl for the CoPc-modified electrodes, Table 1. Vanillic acid oxidation occurs on unmodified electrode at approximately 0.93 V vs. Ag|AgCl and the peak current is enhanced (and overpotential decreased) upon modification, Fig. 3b, confirming catalytic activity.

In comparing the cyclic voltammogram responses of the SPCEs (Fig. 3a) and disk electrodes (Fig. 3b), it can be seen that the



**Fig. 3.** Cyclic voltammograms of vanillic acid (1), CoPc+vanillic acid (2), CoTCPC+vanillic acid (3), and CoOCPc+vanillic acid (4) solutions recorded on a screen-printed carbon electrode (a) and a disk electrode (b). For the screen-printed carbon electrode recordings: [vanillic acid]=[MPC]=0.5 mM, while the disk electrodes were recorded in 1 mM vanillic acid solution. Scan rate = 100 mV s<sup>-1</sup>.

phthalocyanine complexes on the SPCEs detected vanillic acid at lower potentials, Table 1, and the phthalocyanine modified disk electrodes gave larger peak current response.

Linear relationships between the peak current and square root of scan rate for both SPCEs and disk electrodes of this work (figures not shown) in all analytes indicate a diffusion-controlled analyte electrocatalytic oxidation by the CoPc complexes.

The Tafel slope was determined using the standard equation for a totally irreversible process [47,48], Eq. (1):

$$E_p = \frac{2.3RT}{2(1-\alpha)nF} \log \nu + K \quad (1)$$

where  $\alpha$  is the transfer coefficient,  $\nu$  is the scan rate,  $n$  is the number of electrons involved in the rate determining step and  $K$  is the intercept. Plots of  $E_p$  vs.  $\log \nu$  for SPCE immersed in cobalt phthalocyanine derivatives–vanillic acid solutions gave linear relationships, Fig. 4a. Tafel slopes in the region of 186–241 mV decade<sup>-1</sup> were obtained for the SPCE-used cobalt phthalocyanine derivatives, Table 1. Tafel slopes larger than the normal 30–120 mV decade<sup>-1</sup> are known and have been related either to chemical reactions coupled to electrochemical steps or to substrate-catalyst interactions in a reaction intermediate [49,50]. It may therefore be suggested that vanillic acid and the catalyst (MPC) interaction may be the main cause of the large Tafel slopes.

Fig. 4b shows the plot of  $E_p$  vs.  $\log \nu$  for all the disk electrodes modified with complexes 1–3. Using Eq. (1), a high Tafel slope of  $\sim 170$  mV decade<sup>-1</sup> for the disk electrode modified with complex 1, Table 1, again indicates extensive vanillic acid and catalyst (complex 1 in this case) interaction. Disk electrodes

**Table 1**  
Electrochemical parameters for vanillic acid (pH 3.6) determination using the MPc complexes of this work.<sup>a</sup>

Complex	SPCE			Disk electrode		
	1	2	3	1	2	3
Detection potential (V)	0.60	0.80	0.55	0.88	0.81	0.83
Tafel slope (mV decade <sup>-1</sup> )	241.0	202.8	186.4	168.1	108.8	117.7
$\alpha$	0.76	0.71	0.68	0.83	0.73	0.75
$n_t$	1.98	2.06	1.96	1.97	1.99	2.15
LOD ( $\mu\text{M}$ )	1.57	1.61	1.15	2.42	1.18	1.95
Sensitivity ( $\text{AM}^{-1} \text{cm}^{-1}$ )	1.05	0.35	1.29	0.041	0.065	0.054
Stability as % decay <sup>b</sup>	5.6	4.3	2.3	3.3	8.2	8.6

<sup>a</sup> SPCE, screen-printed carbon electrode;  $n_t$ , total number of electrons involved; LOD, limit of detection.

<sup>b</sup> Over 30 continuous scans.

modified with complexes **2** and **3** displayed Tafel slopes closer to  $120 \text{ mV decade}^{-1}$ , Table 1, suggesting that the first one electron transfer is rate determining.

As all SPCEs recorded in the various CoPc–vanillic acid solutions gave higher Tafel slopes in comparison to their disk electrode counterparts, it can be observed that chemical reactions coupled to electrochemical steps or substrate-catalyst interactions are more efficient for the former electrode setup. This may be due to the fact that as the CoPc derivatives, being in solution are more able to interact with the antioxidant species, than adsorbed to the electrode surface.

Values of  $\alpha$  above 0.5, obtained for all electrodes studied in this work (SPCE and disk), indicate that there is a greater probability of forming products in the reaction-activated transition, Table 1. The  $\alpha$  values for the MPc complexes are tentative since the Tafel slopes are large and do not fall within the  $30\text{--}120 \text{ mV decade}^{-1}$  region.

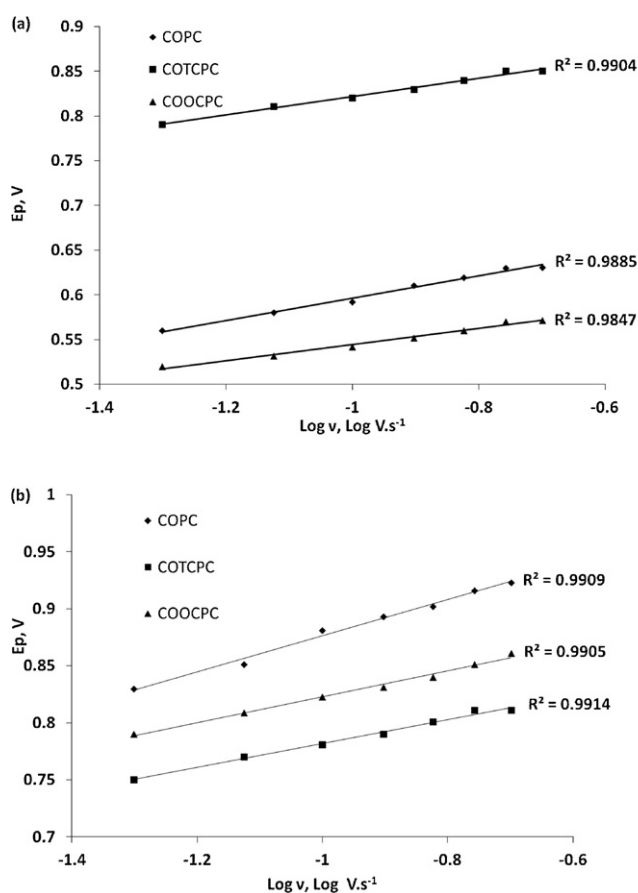
Nevertheless, the disk-modified electrodes gave slightly higher  $\alpha$  values suggesting that product formation is more efficient here in comparison to on the SPCEs.

The total number of electrons ( $n_t$ ) involved in the electrocatalytic oxidation of vanillic acid was calculated using Eq. (2):

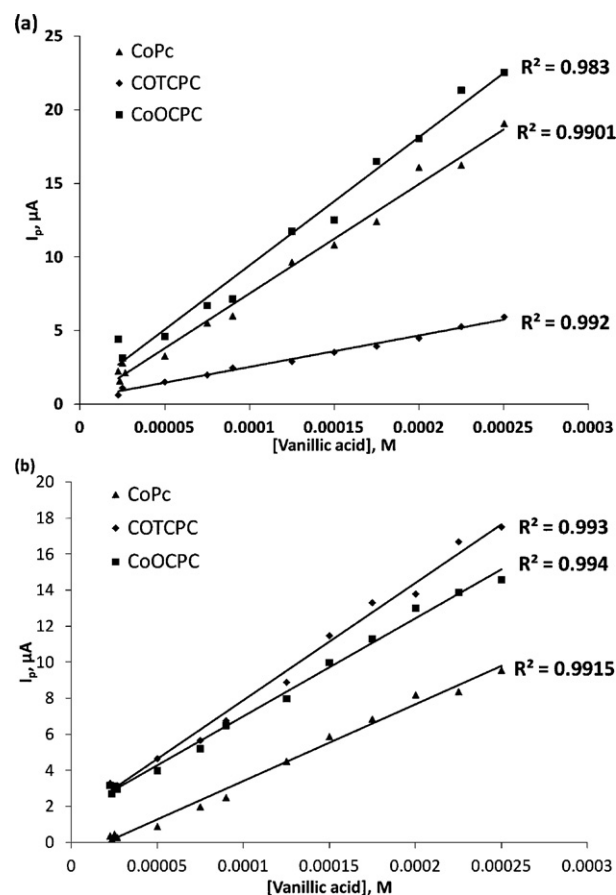
$$i_p = 2.99 \times 10^5 n_t [(1 - \alpha)n]^{1/2} A C_0 D^{1/2} \nu^{1/2} \quad (2)$$

where  $A$  is the area of the electrode ( $\text{cm}^2$ ),  $C_0$  is the concentration of the electroactive reactant ( $\text{mol cm}^{-3}$ ) and  $D$  is the diffusion coefficient of vanillic acid [51]. The total number of electrons transferred for both types of electrodes was two, Table 1, a value which correlates with the literature [52].

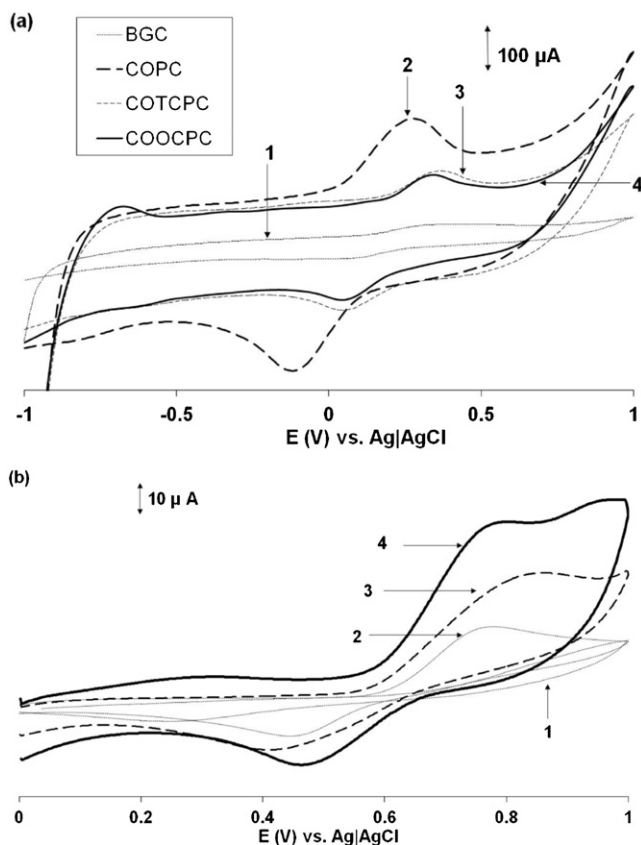
Fig. 5a and b shows the linear relationships between peak current and vanillic acid concentration ( $10^{-5}$  to  $10^{-4} \text{ M}$  range) for all SPCEs and disk electrodes, respectively, proving that they may reliably be used for the determination of vanillic acid in this



**Fig. 4.** Plot of  $E_p$  vs.  $\log \nu$  for all the MPc + vanillic acid solutions of this work on SPCEs (a) and disk electrodes (b).



**Fig. 5.** Plot of  $I_p$  vs. vanillic acid concentration for all the MPcs of this work on SPCEs (a) and disk electrodes (b).



**Fig. 6.** Cyclic voltammograms of caffeic acid (1 or BGC), CoPC+caffeic acid (2), CoTCPc+caffeic acid (3), and CoOCPC+caffeic acid (4) solutions recorded on a screen-printed carbon electrode (a) and a disk electrode (b). For the screen-printed carbon electrode recordings: [caffeic acid]=[MPc]=0.5 mM, while the disk electrodes were recorded in 1 mM caffeic acid solution. Scan rate = 100 mV s<sup>-1</sup>.

concentration range. The vanillic acid limits of detection ( $3\sigma$  criteria) for both types of electrodes are in the  $\mu\text{M}$  range, Table 1. The CoPC- and CoOCPC- + vanillic acid mix on the SPCE gave better limits of detection in comparison to their disk electrode counterparts, while the situation was reversed for CoTCPc.

The vanillic acid sensitivities of all CoPcs, when analyzed as a mix with vanillic acid on the SPCEs, lay in the  $0.35\text{--}1.29\text{ A M}^{-1}\text{ cm}^{-1}$  region with complex 3 displaying the highest value, Table 1. For the disk-modified electrodes, vanillic acid sensitivities of all CoPC-modified electrodes ranged between  $0.041$  and  $0.065\text{ A M}^{-1}\text{ cm}^{-1}$  with complex 2 displaying the highest value, Table 1. Therefore, the SPCE immersed in cobalt phthalocyanine derivative–vanillic acid solutions are much more sensitive in comparison to the disk electrode modified electrodes.

Both types of electrodes displayed good stability as there was only less than 10% decay in peak current output over 30 continuous scans recorded in 0.5 mM vanillic acid solution, Table 1. But, on average, the SPCE immersed in cobalt phthalocyanine derivative–vanillic acid solutions are more stable as there was a relatively lower decay.

### 3.2.2. Caffeic acid

Fig. 6a shows the cyclic voltammograms obtained using SPCEs covered with a solution of 0.5 mM caffeic acid–cobalt phthalocyanine derivative. A weak and poorly defined peak was observed for caffeic acid on SPCE (Fig. 6, plot 1), but the peak current is enhanced (and overpotential decreased) upon addition of cobalt phthalocyanine derivatives, Fig. 6a. Caffeic acid oxidation peaks were observed between 0.30 V and 0.40 V vs. Ag|AgCl for all CoPcs, Table 2.

Fig. 6b (plot 1) shows the cyclic voltammograms for the caffeic acid solution performed on the CoPC-modified disk electrode. No significant peaks were observed for the unmodified electrode. But caffeic acid oxidation peaks were observed between 0.76 V and 0.81 V vs. Ag|AgCl for the CoPC-modified disk electrodes, Table 2.

The SPCE electrodes were far superior to the disk electrodes in the detection of caffeic acid as proven by the reversibility of caffeic acid on SPCEs and not on the disk electrodes, Fig. 6, and by the fact that the SPCEs detected caffeic acid at much lower potentials compared to the disk electrodes, Table 2.

Using Eq. (1), high Tafel slopes for all the SPCEs caffeic acid–CoPcs derivatives, Table 2, again indicates extensive caffeic acid and catalyst (complexes 1–3) interaction. Tafel slopes in the region of  $244\text{--}276\text{ mV decade}^{-1}$  were obtained for all CoPC-modified disk electrodes, Table 2. It may be suggested that caffeic acid and the catalyst (MPc) interaction may be the main cause of the much larger Tafel slopes since similar interactions have been documented [53].

The values of  $\alpha$  calculated in this electrochemical study for both SPCE and disk electrodes, indicate that there is a greater probability of forming products in the reaction activated transition, Table 2. This is more so for the disk modified electrodes because the  $\alpha$  values were greater in comparison to SPCEs, Table 2. Using Eq. (2), a value, which agrees with the literature, of two electrons was calculated to be involved in the electro oxidation of caffeic acid [52] Table 2.

Linear relationships between peak current and caffeic acid concentration (figures not shown but similar to Fig. 5) were observed in both electrodes used (SPCE and disk), and can therefore dependably be used for the determination of caffeic acid in the  $10^{-5}$  to  $10^{-4}\text{ M}$  range. Caffeic acid detection limits for all CoPC electrocatalysts are in the  $\mu\text{M}$  region, Table 2. Complex 1 displayed the best LOD when as a vanillic acid solution mix on SPCE but gave the highest LOD when attached to the disk electrode, Table 2, suggesting that it would be more efficiently used on SPCEs.

On average, the SPCEs electrodes of this work gave higher sensitivities to caffeic acid in comparison to disk electrodes, Table 2. The stabilities of complex 1 on both SPCE and disk electrode were similar whereas complexes 2 and 3 were more stable on SPCEs than on disk electrodes as proven by the lower percent decay over 30 continuous cyclic voltammetry recordings, Table 2.

### 3.2.3. Pyrogallol

Cyclic voltammograms of 0.5 mM pyrogallol–CoPC complexes solutions using SPCE are shown in Fig. 7a. Electrocatalysis by the CoPC complexes of this work are observed due to the fact that in the presence of CoPC complexes SPCE (plots 2–4) detected pyrogallol at higher peak currents in comparison to individual antioxidant solution (plot 1), Fig. 7a (in the absence of CoPcs, the SPCE gave a very poor peak current response). In the presence of CoTCPc, the SPCE detected pyrogallol at the lowest oxidation potential of 0.54 V vs. Ag|AgCl while in the presence the other CoPcs detected pyrogallol between 0.50 and 0.65 V, Table 3.

Fig. 7b shows the cyclic voltammograms of all disk electrodes of this work recorded in 1 mM pyrogallol solution. Electrocatalysis by the CoPC complexes of this work are observed due to the fact that CoPC modified disk electrodes (plots 2–4) detected pyrogallol at higher peak currents in comparison to an unmodified disk electrode (plot 1), Fig. 7b. CoOTCPc-modified electrode detected pyrogallol at the lowest oxidation potential of 0.56 V vs. Ag|AgCl while the other modified disk electrodes of this work detected pyrogallol at  $\sim 0.6\text{ V}$ , Table 3.

From Table 3, it can be seen that the disk modified electrodes detected pyrogallol at higher detection potentials in comparison to their SPCE counterparts. But, from Fig. 7, the disk-modified electrodes were superior in terms of peak current response. This result is similar to that obtained for vanillic acid (Fig. 3).

**Table 2**  
Electrochemical parameters for caffeic acid (pH 3.6) determination using the MPC complexes of this work.<sup>a</sup>

Complex	SPCE			Disk electrode		
	1	2	3	1	2	3
Detection potential (V)	0.30	0.40	0.38	0.77	0.81	0.76
Tafel slope (mV decade <sup>-1</sup> )	171.2	215.8	217.8	276	246	244
$\alpha$	0.66	0.73	0.73	0.79	0.76	0.76
$n_t$	1.96	2.09	1.95	1.99	2.03	2.01
LOD ( $\mu\text{M}$ )	1.18	2.11	2.20	1.74	1.59	1.17
Sensitivity ( $\text{A M}^{-1} \text{cm}^{-1}$ )	0.04	0.14	0.21	0.038	0.031	0.033
Stability as % decay <sup>b</sup>	4.4	2.1	1.4	4.3	6.3	6.6

<sup>a</sup> SPCE, screen-printed carbon electrode;  $\alpha$ , transfer coefficient;  $n_t$ , total number of electrons involved; LOD, limit of detection.

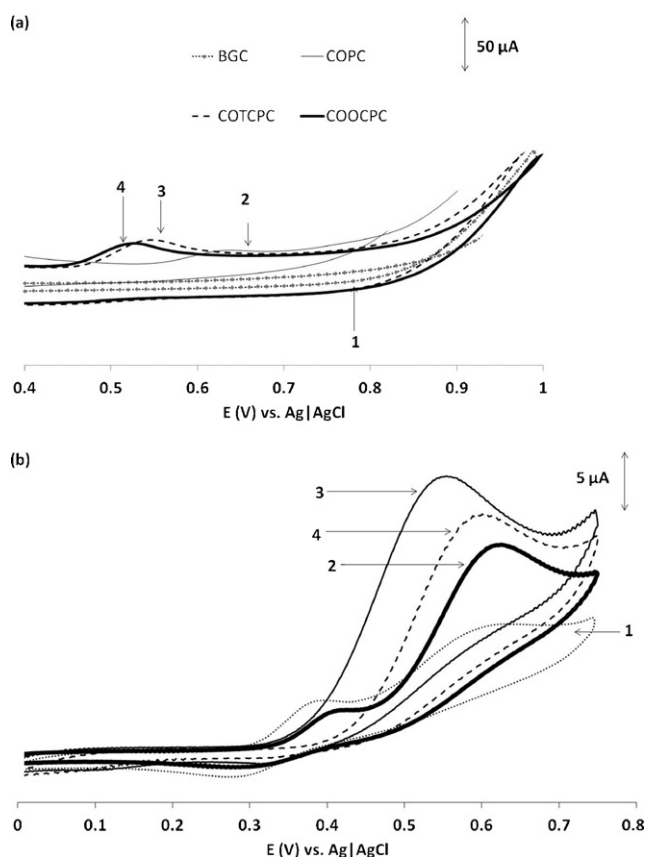
<sup>b</sup> Over 30 continuous scans.

**Table 3**  
Electrochemical parameters for pyrogallol solution (pH 3.6) determination using the MPC complexes of this work.<sup>a</sup>

Complex	SPCE			Disk electrode		
	1	2	3	1	2	3
Detection potential (V)	0.62	0.54	0.52	0.63	0.60	0.56
Tafel slope (mV decade <sup>-1</sup> )	211.4	192.4	171.2	214.4	189.0	219.0
$\alpha$	0.72	0.69	0.66	0.72	0.69	0.73
$n_t$	2.02	2.13	1.96	1.98	2.20	1.99
LOD ( $\mu\text{M}$ )	2.44	1.98	2.02	3.63	1.16	2.64
Sensitivity ( $\text{A M}^{-1} \text{cm}^{-1}$ )	0.0496	0.0446	0.0524	0.012	0.030	0.023
Stability as % decay <sup>b</sup>	9	4	2	5	3	2

<sup>a</sup> SPCE, screen-printed carbon electrode;  $\alpha$ , transfer coefficient;  $n_t$ , total number of electrons involved; LOD, limit of detection.

<sup>b</sup> Over 30 continuous scans.



**Fig. 7.** Cyclic voltammograms of pyrogallol (1), CoPc+pyrogallol (2), CoTCPc+pyrogallol (3), and CoOCPc+pyrogallol (4) solutions recorded on a screen-printed carbon electrode (a) and a disk electrode (b). For the screen-printed carbon electrode recordings: [pyrogallol]=[MPC]=0.5 mM, while the disk electrodes were recorded in 1 mM pyrogallol solution. Scan rate = 100 mV s<sup>-1</sup>.

The high Tafel slopes obtained for complexes 1–3 on both types of electrodes (more so for the disk modified electrodes), Table 3, indicate extensive pyrogallol and MPC interaction [48–50]. There is a greater, and similar because  $\alpha \approx 0.7$ , probability of forming products in the reaction activated transition state for all electrodes (SPCE and disk) as all  $\alpha$  values were greater than 0.5. Again, the  $\alpha$  values for the MPC complexes are tentative since the Tafel slopes are large and do not fall within the 30–120 mV decade<sup>-1</sup> region. Two electrons were calculated, using Eq. (2), to be involved in the electro oxidation of pyrogallol [52], Table 3.

The linear relationships obtained between plots of peak current vs. pyrogallol concentration prove that all electrodes of this work (SPCE and disk) can dependably determine pyrogallol in the 10<sup>-5</sup> to 10<sup>-4</sup> M range (figures not shown but similar to Fig. 5).

The CoTCPc is consistently better for detecting pyrogallol because it gave the best LOD on both SPCE (1.98  $\mu\text{M}$ ) and disk electrode (1.16  $\mu\text{M}$ ), Table 3. CoPc and CoTCPc displayed similar range LODs on their respective electrodes in the detection of pyrogallol, Table 3.

For the SPCEs, the SPCE with CoOCPc + pyrogallol mix displayed the highest pyrogallol sensitivity of 0.0524  $\text{A M}^{-1} \text{cm}^{-1}$ , Table 3. For the disk electrodes, CoTCPc-modified electrode displayed the highest pyrogallol sensitivity of 0.030  $\text{A M}^{-1} \text{cm}^{-1}$ , Table 3.

All the SPCEs and disk electrodes of this work displayed good pyrogallol detection stability proven by the less than 10% decays in peak current output over 30 continuous scans when recorded in 0.5 mM pyrogallol solution, Table 3. Nevertheless, the disk electrodes were slightly more stable in the detection of pyrogallol as proven by their lower percent decay, Table 3.

### 3.2.4. Ascorbic acid

Fig. 8a shows the cyclic voltammograms of SPCE recorded in 0.5 mM ascorbic acid–CoPc complexes solutions. In the absence of CoPc complexes, SPCE barely gave any cyclic voltammogram response indicating poor ascorbic acid detection. In the presence of CoPc complexes, SPCE detected ascorbic acid at approximately

**Table 4**  
Electrochemical parameters for ascorbic acid (pH 3.6) determination using the MPC complexes of this work.<sup>a</sup>

Complex	SPCE			Disk electrode		
	1	2	3	1	2	3
Detection potential (V)	0.42	0.34	0.36	0.68	0.40	0.51
Tafel slope (mV decade <sup>-1</sup> )	185.6	219.2	187.6	104.9	104.5	95.5
$\alpha$	0.68	0.73	0.69	0.72	0.72	0.69
$n_t$	2.03	1.98	1.96	1.99	2.05	2.19
LOD ( $\mu\text{M}$ )	1.58	1.47	1.37	1.33	1.16	1.28
Sensitivity ( $\text{A M}^{-1} \text{cm}^{-1}$ )	0.35	0.41	0.42	$1.03 \times 10^{-4}$	$8.99 \times 10^{-4}$	$8.92 \times 10^{-4}$
Stability as % decay <sup>b</sup>	2.83	2.64	3.84	6	4	4

<sup>a</sup> SPCE, screen-printed carbon electrode;  $n_t$ , total number of electrons involved; LOD, limit of detection.

<sup>b</sup> Over 30 continuous scans.

equal peak currents and at approximately the same potentials of 0.40 V vs. Ag|AgCl, Table 4.

Fig. 8b shows the cyclic voltammograms of all disk electrodes of this work recorded in 1 mM ascorbic acid solution. The unmodified disk electrode recorded ascorbic acid at a relatively low peak current response and displayed an unfavorably broad peak indicating poor ascorbic acid detection, Fig. 8b. CoTCPc-modified disk electrode detected ascorbic acid with the highest peak current and at the lowest potential of 0.40 V vs. Ag|AgCl, Table 4. Ascorbic acid oxidation peaks were observed at 0.51 and 0.68 V vs. Ag|AgCl for the CoOCPC- and CoPc-modified electrodes respectively, Table 4.

As for the other analytes of this work, the disk electrodes, in comparison to the SPCEs, generally gave higher peak currents with respect to ascorbic acid detection, but at higher potentials, Table 4.

For the SPCEs in the presence of all MPC complexes, the voltammetric responses displayed large Tafel slopes, Table 4, indicating extensive ascorbic acid and MPC interaction. All MPC complexes

on the disk modified electrodes displayed Tafel slopes closer to 120 mV decade<sup>-1</sup> (as opposed to 30 mV decade<sup>-1</sup>), Table 4, suggesting that the first one electron transfer is rate determining.

There is a greater, and similar, probability of forming products in the reaction activated transition state for all CoPc-complexes, for both SPCEs and disk electrodes, because all  $\alpha$  values are greater than 0.5, Table 4. Two electrons were calculated, again for both SPCEs and disk electrodes, to be involved in the electro oxidation of ascorbic acid [52], Table 4.

Linear relationships obtained between plots of peak current vs. ascorbic acid concentration prove that all electrodes of this work (SPCE and disk) can dependably determine pyrogallol in the 10<sup>-5</sup> to 10<sup>-4</sup> M range (figures not shown but similar to Fig. 5). Both electrode types displayed ascorbic acid detection limits in the  $\mu\text{M}$  region, Table 4. But the disk electrodes had slightly better ascorbic acid LOD values in comparison to the SPCEs proven by the larger cyclic voltammogram peak current responses to ascorbic acid, Fig. 8.

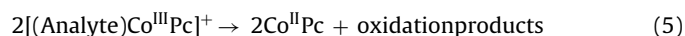
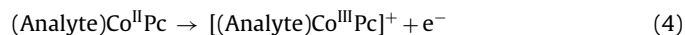
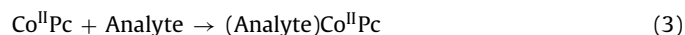
Ascorbic acid sensitivities of SPCE in the presence of all CoPc complexes were much larger than the disk modified electrodes as they were in the 10<sup>-1</sup> A M<sup>-1</sup> cm<sup>-1</sup> region while the latter electrodes displayed sensitivities in the 10<sup>-4</sup> A M<sup>-1</sup> cm<sup>-1</sup> region, Table 4.

Even though the SPCEs were slightly more stable than the disk modified electrodes (lower % decay in peak current), both electrode types were satisfactorily stable as proven by the less than 10% decay in peak current output over 30 continuous scans when recorded in 0.5 mM ascorbic acid solution, Table 4.

### 3.3. Mechanism of MPC-analyte interaction

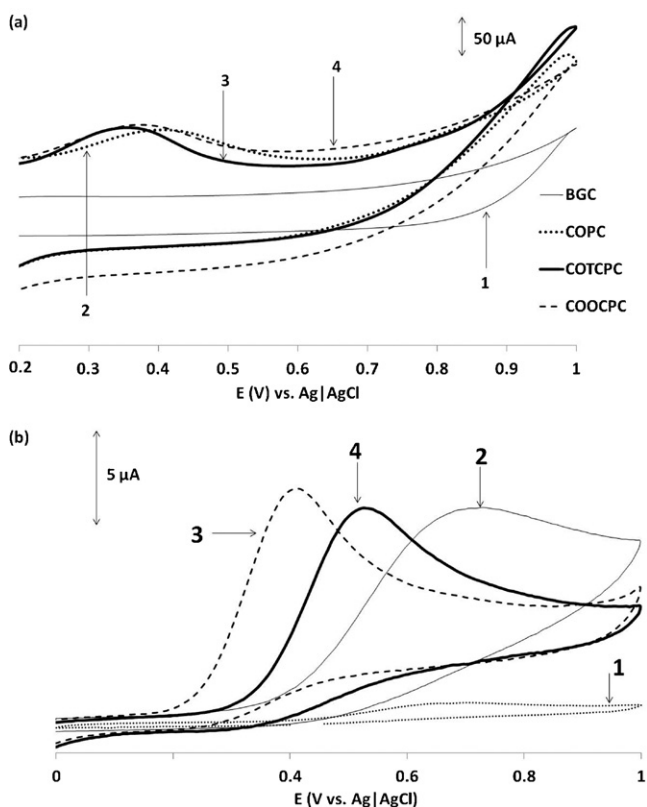
As both SPCE and disk electrodes used similar CoPc complexes, the mechanism of interaction between the CoPc complexes and the analytes (vanillic acid, caffeic acid, pyrogallol, and ascorbic acid) is summarized for both types of electrodes in this section.

The most likely mechanism for the oxidation of the analytes (Eqs. (3)–(5)) takes into account that the first one electron transfer is rate determining (from Tafel slopes) and that the total number of electrons transferred is two.

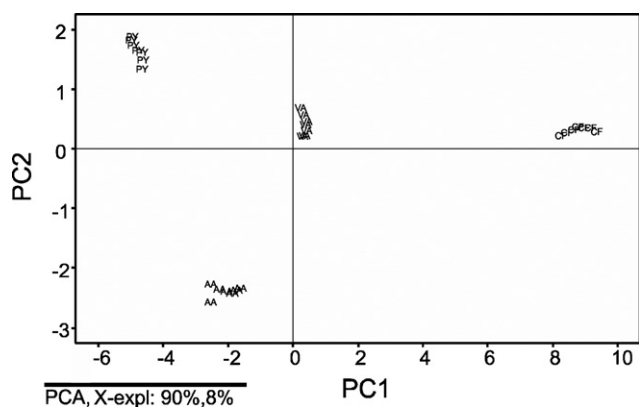


where Analyte represents vanillic acid, caffeic acid, pyrogallol, or ascorbic acid.

Eq. (3) is proposed on the basis of coordination of the analytes to CoPc, CoTCPc, and CoOCPC. Eq. (4) is also proposed because the catalytic oxidation of the analytes is within the range of Co<sup>III/II</sup> and is catalyzed by this couple. Two electrons are involved hence Eq. (5) is proposed.



**Fig. 8.** Cyclic voltammograms of ascorbic acid (1), CoPc+ascorbic acid (2), CoTCPc+ascorbic acid (3), and CoOCPC+ascorbic acid (4) solutions recorded on a screen-printed carbon electrode (a) and a disk electrode (b). For the screen-printed carbon electrode recordings: [ascorbic acid] = [MPC] = 0.5 mM, while the disk electrodes were recorded in 1 mM ascorbic acid solution. Scan rate = 100 mV s<sup>-1</sup>.



**Fig. 9.** PCA score plot of SPCEs in the presence of all CoPcs exposed to antioxidants. AA, ascorbic acid; VA, vanillic acid; CF, caffeic acid; PY, pyrogallol.

### 3.4. Data analysis

In this work, all the antioxidants were measured seven times with each sensor. A pre-processing method was used in order to extract the relevant information from the experimental data. The PCA was carried out using, as the input data source, pre-processed voltammograms obtained by the adaptation of a data reduction technique based on predefined response “bellshaped-windowing” curves called “kernels” [54,55]. Using this method, ten parameters per voltammogram were obtained and used as the input variable for statistical analysis.

#### 3.4.1. SPCE data analysis

Fig. 9 shows, for SPCEs in the presence of all CoPcs, the scores plot of the two first principal components calculated from the parameters extracted from the cyclic voltammograms. The first two principal components explain 98% of the information (PC1 = 90%; PC2 = 8%). As observed in Fig. 9, phenolic compounds appear in the same region of the diagram while ascorbic acid appears far away from the phenolic compounds. The second principal component is mostly responsible for the discrimination of the antioxidants according to their chemical structure (phenolic compounds and ascorbic acid).

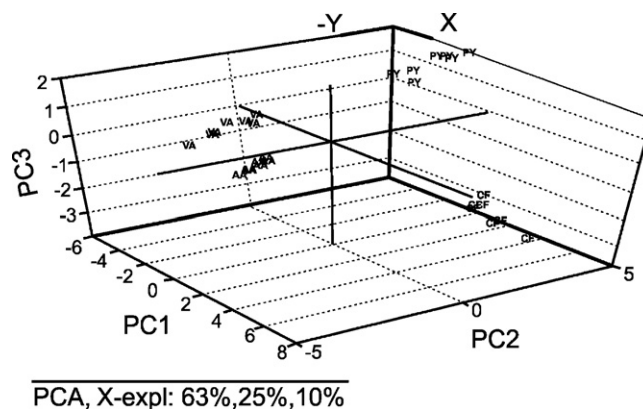
A closer look to the clusters corresponding to the phenolic compounds indicated that, the first principal component is mainly responsible for the discrimination of the phenols according to the number of –OH groups in the structure.

The PCA scores plot structure is in conformity with the electrochemical voltammograms registered for each antioxidant. The results indicate that it is clearly possible to discriminate antioxidants in function of chemical structure, Fig. 9.

#### 3.4.2. Disk electrode data analysis

PCA was again employed to evaluate the capability of the CoPc disk modified electrode sensors to discriminate among the antioxidants by using the obtained electrochemical signals as the input variable. Seven repetitions of each measurement were carried out. Fig. 10 shows the PCA scores plot of the principal components (PC1 vs. PC2 vs. PC3). The 1st, 2nd, and 3rd principal components account for 63%, 25%, and 10%, respectively, of the variation in the electrochemical signal. Overall, PC1, PC2 and PC3 explained 98% percent of the total variance between the samples.

The PCA scores plot structure is in agreement with the electrochemical voltammograms registered for each antioxidant. The results indicate that it is clearly possible to discriminate antioxidants as a function of the chemical structure.



**Fig. 10.** Score plot of PCAs of CoPc disk modified electrodes exposed to antioxidants. AA, ascorbic acid; VA, vanillic acid; CF, caffeic acid; PY, pyrogallol.

## 4. Conclusions

Cobalt phthalocyanines have been successfully used in the electrocatalysis of vanillic acid, caffeic acid, pyrogallol, and ascorbic acid solutions on screen-printed carbon (as a mixed CoPc-antioxidant solution) and disk electrode (as adsorbed CoPc species) onto surfaces.

The high Tafel slopes obtained for cobalt phthalocyanine complexes indicate extensive antioxidant and CoPc-complex interaction. The kinetic studies also show that there is a greater probability of forming products in the reaction activated transition state in the presence of CoPcs for both types of electrodes.

Both types of electrodes, in the presence of the CoPc complexes, can reliably be used for the determination of the antioxidant solutions in the  $10^{-5}$  to  $10^{-4}$  M range and both displayed antioxidant detection limits in the  $\mu$ M region.

The principal component method for the analysis of the electrochemical signals obtained showed that the cobalt phthalocyanines, when used as arrays of sensors for the antioxidant solutions in both the SPCE and the disk electrode format, showed a 100% discrimination of the solutions as a function of their chemical structure.

In comparing the SPCE and disk electrode types, the SPCEs were better than the disk electrodes at detecting vanillic acid because, even though they displayed a lower vanillic acid cyclic voltammogram peak current response, the signals were obtained at better potentials, the LOD values were lower and the sensitivities were higher.

SPCE is also perhaps the better electrode for caffeic acid detection in that better-defined and reversible caffeic acid cyclic voltammograms at lower detection potentials, and with better stability, were obtained than for disk electrodes.

It may again be concluded that the SPCEs of this work were better at detecting pyrogallol because pyrogallol cyclic voltammograms occurred at lower detection potentials (albeit not as well defined), the LOD values were generally better and the SPCEs displayed higher sensitivities.

But the disk electrodes were better at detecting ascorbic acid than the SPCEs because the disk electrodes ascorbic acid cyclic voltammograms were better defined with higher peak current responses (albeit at higher detection potentials) and they displayed lower LOD values.

Both SPCE and disk electrodes can equally, and reliably, be used to discriminate the antioxidants as a function of the chemical structure.

In terms of physical use, the SPCE is quicker (no adsorption time needed), more efficient as an experimental set-up (all electrodes are on one device) and the SPCEs can use very little sample making



sample use economical. But the GCE is more reusable than an SPCE meaning electrode use is more cost-effective.

## Acknowledgements

“Financial support by the Spanish Ministry of Science (grant AGL2009-12660/ALI) and FEDER is gratefully acknowledged. This work was also supported by the Department of Science and Technology (DST) and National Research Foundation (NRF) of South Africa through DST/NRF South African Research Chairs Initiative for Professor of Medicinal Chemistry and Nanotechnology and Rhodes University.

## References

- [1] M. Lucarini, G.F. Pedulli, Free radical intermediates in the inhibition of the autoxidation reaction, *Chem. Soc. Rev.* 39 (2010) 2106–2119.
- [2] A. Crozier, I.B. Jaganath, M.N. Clifford, Dietary phenolics: chemistry, bioavailability and effects on health, *Nat. Prod. Rep.* 26 (2009) 1001–1043.
- [3] L.D. Mello, D. Del Rio, L.G. Costa, M.E.J. Lean, A. Crozier, Polyphenols health. What compounds are involved? *Nutr. Metab. Cardiovasc. Dis.* 20 (2010) 1–6.
- [4] F. Saura-Calixto, M.E. Díaz-Rubio, Polyphenols associated with dietary fibre in wine—a wine polyphenols gap? *Food Res. Int.* 40 (2007) 613–619.
- [5] M. del Alamo, I. Nevares, Redox potential evolution during the red wine aging in alternatives systems, *Anal. Chim. Acta* 563 (2006) 255–263.
- [6] M.F. Barroso, N. de-los-Santos-Álvarez, C. Delerue-Matos, M.B. Oliveira, Towards a reliable technology for antioxidant capacity and oxidative damage evaluation: electrochemical (bio)sensors, *Biosens. Bioelectron.* 30 (2011) 1–12.
- [7] L.A. Kartsova, A.V. Alekseeva, Chromatographic and electrophoretic methods for determining polyphenol compounds, *J. Anal. Chem.* 63 (2008) 1024–1033.
- [8] M. del Valle, Electronic tongues employing electrochemical sensors, *Electroanalysis* 22 (2010) 1539–1555.
- [9] A. Riul Jr., C.A.R. Dantas, C.M. Miyazaki, O.N. Oliveira Jr., Recent advances in electronic tongues, *Analyst* 135 (2010) 2481–2495.
- [10] M. Jańczyk, A. Kutyla, K. Solohub, H. Wosicka, K. Cal, P. Ciosek, Potentiometric electronic tongues for foodstuff and biosample recognition—an overview, *Sensors* 11 (2011) 4688–4701.
- [11] Y.G. Vlasov, Y.E. Ermolenko, A.V. Legin, A.M. Rudnitskaya, V. Kolodnikov, Chemical sensors and their systems, *J. Anal. Chem.* 65 (2010) 890–898.
- [12] G. Verrelli, L. Lvova, R. Paolesse, C. Di Natale, A. D’Amico, Metalloporphyrin-based electronic tongue: an application for the analysis of Italian White Wines, *Sensors* 7 (2007) 2750–2762.
- [13] M. Scampicchio, S. Benedetti, B. Brunetti, S. Mannino, Electroanal amperometric electronic tongue for the evaluation of the tea astringency, *Electroanalysis* 18 (2006) 1643–1648.
- [14] M.L. Rodríguez-Méndez, V. Parra, C. Apetrei, S. Villanueva, M. Gay, N. Prieto, J. Martinez, J.A. de Saja, E-tongue based on voltammetric electrodes modified with electroactive materials. Applications, *Microchim. Acta* 163 (2008) 23–31.
- [15] F. Winquist, Voltammetric electronic tongues—basic principles and applications, *Microchim. Acta* 163 (2008) 3–10.
- [16] R.H. Labrador, R. Masot, M. Alcaniz, D. Baigts, J. Soto, R. Martinez-Manez, E. Garcia-Breijo, L. Gil, J.M. Barat, Prediction of NaCl nitrate and nitrite contents in minced meat by using a voltammetric electronic tongue and an impedimetric sensor, *Food Chem.* 122 (2010) 864–870.
- [17] D. Volpati, P. Alessio, A.A. Zanfolim, F.C. Storti, A.E. Job, M. Ferreira, A. Riul Jr., O.N. Oliveira Jr., C.J.L. Constantino, Exploiting distinct molecular architectures of ultrathin films made with iron phthalocyanine for sensing, *J. Phys. Chem. B* 112 (2008) 15275–15282.
- [18] G. Pioggia, F. Di Francesco, A. Marchetti, M. Ferro, A. Ahluwalia, A composite sensor array impedimetric electronic tongue—part I. Characterization, *Biosens. Bioelectron.* 22 (2007) 2618–2623.
- [19] A. Gutes, F. Cespedes, S. Alegret, M. del Valle, Determination of phenolic compounds by a polyphenol oxidase amperometric biosensor and artificial neural network analysis, *Biosens. Bioelectron.* 20 (2005) 1668–1673.
- [20] C. Apetrei, S. Casilli, M. de Luca, L. Valli, J. Jiang, M.L. Rodríguez-Méndez, J.A. de Saja, Spectroelectrochemical characterisation of Langmuir–Shaeffer films of heteroleptic phthalocyanine complexes. Potential applications, *Colloids Surf., A* 284–285 (2006) 574–582.
- [21] C. Apetrei, F. Gutierrez, M.L. Rodríguez-Méndez, J.A. de Saja, Novel method based on carbon paste electrodes for the evaluation of bitterness in extra virgin olive oils, *Sens. Actuators B* 121 (2007) 567–575.
- [22] M. Gay, C. Apetrei, I. Nevares, M. del Alamo, J. Zurro, N. Prieto, J.A. de Saja, M.L. Rodríguez-Méndez, Application of an electronic tongue to study the effect of the use of pieces of wood and micro-oxygenation in the aging of red wine, *Electrochim. Acta* 55 (2010) 6782–6788.
- [23] S. Buratti, D. Ballabio, S. Benedetti, M.S. Cosio, Prediction of Italian red wine sensory descriptors from electronic nose, electronic tongue and spectrophotometric measurements by means of genetic algorithm regression models, *Food Chem.* 100 (2007) 211–218.
- [24] X. Cetó, J.M. Gutiérrez, L. Moreno-Barón, L.S. Alegret, M. Del Valle, Voltammetric electronic tongue in the analysis of cava wines, *Electroanalysis* 23 (2011) 72–78.
- [25] M. Ghasemi-Vamankhasti, M.L. Rodríguez-Méndez, S.S. Mohtasebi, C. Apetrei, J. Lozano, S.H. Razavi, H. Ahmadi, J.A. de Saja, Monitoring the ageing of beers using a bioelectronic tongue, *Food Control* 25 (2012) 216–224.
- [26] I.T. Jolliffe, *Principal Component Analysis*, Series: Springer Series in Statistics, 2nd ed., Springer, New York, 2002.
- [27] H.S. Nalwa, *Supramolecular Photoactive and Electroactive Materials*, Academia Press, New York, 2001.
- [28] J.H. Zagal, F. Bedioui, J.P. Dodelet, *N4-Macrocyclic Metal Complexes*, Springer, 2006.
- [29] M.L. Rodríguez-Méndez, M. Gay, J.A. de Saja, New insights into sensors based on radical bisphthalocyanines, *J. Porphyrins Phthalocyanines* 13 (2009) 1159–1167.
- [30] A.B.P. Lever, The phthalocyanines—molecules of enduring value; a two-dimensional analysis of redox potentials, *J. Porphyrins Phthalocyanines* 3 (1999) 488–499.
- [31] L. Valli, Phthalocyanine-based Langmuir–Blodgett films as chemical sensors, *Adv. Colloid Interface Sci.* 116 (2005) 13–44.
- [32] D. Wilson, M.N. Abbas, A.L.A. Radwan, M. del Valle, Potentiometric electronic tongue to resolve mixtures of sulfide and perchlorate anions, *Sensors* 11 (2011) 3214–3226.
- [33] C.A. Olivati, A. Riul Jr., D.T. Balogh, O.N. Oliveira Jr., M. Ferreira, Detection of phenolic compounds using impedance spectroscopy, *Meas. Bioprocess Biosyst. Eng.* 32 (2009) 41–46.
- [34] P.B. Aoki, W. Caetano, D. Volpati, A. Riul Jr., C.J.L. Constantino, Sensor array made with nanostructured films to detect a phenothiazine compound, *J. Nanosci. Nanotechnol.* 8 (2008) 4341–4348.
- [35] M. Gay, C. Apetrei, I. Nevares, M. del Alamo, J. Zurro, J.A. de Saja, M.L. Rodríguez-Méndez, Application of an electronic tongue to study the effect of the use of pieces of wood and micro-oxygenation in the aging of red wine, *Electrochim. Acta* 55 (2010) 6782–6788.
- [36] M. L’Her, A. Pondaven, *Electrochemistry of Phthalocyanines*, in: K.M. Kadish, K. Smith, R. Guilard (Eds.), *The Porphyrin Handbook*, vol. 16, Academic Press, San Diego, 2002, pp. 117–163.
- [37] F. Matemadombo, N. Selthoth, T. Nyokong, Effects of the number of ring substituents of cobalt carboxyphthalocyanines on the electrocatalytic detection of nitrite cysteine and melatonin, *J. Porphyrins Phthalocyanines* 13 (2009) 986–997.
- [38] A.B.P. Lever, E.R. Milaeva, G. Speier, *The Redox Chemistry of Metallophthalocyanines in Solution*, in: C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines: Properties and Applications*, vol. 3, VCH Publishers, Inc., Weinheim, New York, 1993.
- [39] J.F. Myers, G.W.R. Canham, A.B.P. Lever, Higher oxidation level phthalocyanine complexes of chromium iron, cobalt and zinc-phthalocyanine radical species, *Inorg. Chem.* 14 (1975) 461–468.
- [40] J.H. Zagal, S. Griveau, J.F. Silva, T. Nyokong, F. Bedioui, Metallophthalocyanine-based molecular materials as catalysts for electrochemical reactions, *Coord. Chem. Rev.* 254 (2010) 2755–2791.
- [41] C. Apetrei, S. Casilli, M. De Luca, L. Valli, J. Jiang, M.L. Rodríguez-Méndez, J.A. de Saja, Spectroelectrochemical characterisation of Langmuir–Shaeffer films of heteroleptic phthalocyanine complexes. Potential applications, *Colloids Surf., A* 284–285 (2006) 574–582.
- [42] S.A. Mikhailenko, L.I. Solov’eva, E.A. Luk’yanets, Phthalocyanines and related compounds: XXXVII. Synthesis of covalent conjugates of carboxy-substituted phthalocyanines with alpha-amino acids, *Russ. J. Gen. Chem.* 74 (2004) 451–459.
- [43] K. Sakamoto, E. Ohno-Okumura, Synthesis of octasubstituted cobalt phthalocyanines and their redox properties, *J. Porphyrins Phthalocyanines* 3 (1997) 634–642.
- [44] N.P. Farrell, A.J. Murray, J.R. Thornback, D.H. Dolphin, B.R. James, Phthalocyanine complexes of ruthenium(II), *Inorg. Chim. Acta* 28 (1978) L144–L146.
- [45] M.L. Rodríguez-Méndez, C. Apetrei, J.A. de Saja, Evaluation of the polyphenolic content of extra virgin olive oils using an array of voltammetric sensors, *Electrochim. Acta* 53 (2008) 5867–5872.
- [46] M.J. Stillman, T. Nyokong, Absorption and magnetic circular dichroism spectral properties of phthalocyanines. Part 1: Complexes of the dianion (–2), in: C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines: Properties and Applications*, vol. 1, VCH Publishers, Inc., Weinheim, New York, 1989.
- [47] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, John Wiley and Sons, New York, 2001.
- [48] G. Mbambisa, P. Tau, E. Antunes, T. Nyokong, Synthesis and electrochemical properties of purple manganese(III) and red titanium(IV) phthalocyanine complexes octa-substituted at non-peripheral positions with pentylthio groups, *Polyhedron* 26 (2007) 5355–5364.
- [49] C.A. Caro, F. Bedioui, J.H. Zagal, Electrocatalytic oxidation of nitrite on a vitreous carbon electrode modified with cobalt phthalocyanine, *Electrochim. Acta* 47 (2002) 1489–1494.
- [50] J.-M. Zen, A. Senthil Kumar, M.-R. Chang, Electrocatalytic oxidation and trace detection of amitrole using a Nafion/lead–ruthenium oxide pyrochlore chemically modified electrode, *Electrochim. Acta* 45 (2000) 1691–1699.
- [51] C. Apetrei, I.M. Apetrei, J.A. de Saja, M.L. Rodríguez-Mendez, Carbon paste electrodes made from different carbonaceous materials: application in the study of antioxidants, *Sensors* 11 (2011) 1328–1344.
- [52] A. Simić, D. Manojlović, D. Šegan, M. Todorović, Electrochemical behavior and antioxidant and prooxidant activity of natural phenolics, *Molecules* 12 (2007) 2327–2340.

- [53] S. Maree, T. Nyokong, Electrocatalytic behavior of substituted cobalt phthalocyanines towards the oxidation of cysteine, *J. Electroanal. Chem.* 492 (2000) 120–127.
- [54] M.L. Rodríguez-Méndez, M. Gay, C. Apetrei, J.A. de Saja, Biogenic amines and fish freshness assessment using a multisensor system based on voltammetric electrodes. Comparison between CPE and screen-printed electrodes, *Electrochim. Acta* 54 (2009) 7033–7041.
- [55] C. Apetrei, I.M. Apetrei, I. Nevares, M. del Alamo, V. Parra, M.L. Rodríguez-Méndez, J.A. de Saja, Using an e-tongue based on voltammetric electrodes to discriminate among red wines aged in oak barrels or aged using alternative methods: correlation between electrochemical signals and analytical parameters, *Electrochim. Acta* 52 (2007) 2588–2594.

## Biographies

**Fungisai Matemadombo** received his BSc (Chemistry and Biochemistry) degree from Rhodes University (South Africa) in 2003. He received his PhD (Chemistry) degree, also from Rhodes University, in 2010 and then did a post-doctoral study at the University of Valladolid (Spain). Fungisai has studied at Ecole Nationale Supérieure de Chimie de Paris and Université Paris Descartes, France (during his PhD) and at Universiteit Gent, Belgium (during his MSc). His research interests include the development and analysis of innovative and technologically diverse molecules that can be used as efficient anti-cancer agents, sensors and catalysts. He has authored several publications in peer-reviewed journals.

**Constantin Apetrei** was born in Falticeni (Romania), in 1975. He received BSc in Chemistry in 1977 from the University of Iasi (Romania) and the PhD in 2007 from the University of Galati (Romania). He is presently professor at the University of Galati (Romania) in the Department of Chemistry. His current field of research interests is related to the development of electrochemical sensors for the analysis of foods and beverages. He is co-author of 15 papers.

**Tebello Nyokong** holds a DST/NRF professorship in chemistry at Rhodes University (South Africa). She joined Rhodes University in 1992 and has been undertaking research on electrode modification using phthalocyanines. The electrodes are modified by self-assembly and polymerization. Her recent interests include combining phthalocyanines with carbon nanotubes for improved electrocatalytic activity. The modified electrodes are used for analyses of biologically important molecules. She is on the editorial boards of *Global Journal of Physical Chemistry*, *International Journal of Electrochemical Science* and *Advanced Materials Letters*. All this work is reflected in over 330 publications including book chapters.

**María Luz Rodríguez-Méndez** received the PhD in Chemistry from the University of Valladolid (Spain) in 1990. Since 2010 she holds the Inorganic Chemistry Chair at the Industrial Engineers School of the University of Valladolid. She has been undertaking research in the preparation and the structural characterization of thin films of phthalocyanines and their potential applications. Her main current interest is in the development of sensors based on phthalocyanines. At the present moment, she is involved in a Project devoted to the development of an electronic nose, an electronic tongue and an electronic eye for the assessment of the organoleptic characteristics of wines and olive oils. She is author or co-author of over 120 publications and seven books.

**José Antonio de Saja** was born in Miranda de Ebro (Spain), in 1940. He is a Professor and Head of the Department of Condensed Matter Physics at the University of Valladolid. His present research interest is at the intersection of materials science, physics, physical chemistry and device engineering and focus on novel nanostructured materials (mainly from LB monolayers). At the present moment he is participating in a Project devoted to the development of an electronic nose, an electronic tongue and an electronic eye for the assessment of the organoleptic characteristics of wines and olive oils. He is author or co-author of over 300 publications and has edited eleven books.