



# Electrochemical quartz crystal microbalance analysis of the oxidation reaction of phenols found in wines at lutetium bisphthalocyanine electrodes

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## ABSTRACT

An electrochemical quartz crystal microbalance (EQCM) was used to investigate the processes associated with the mass changes accompanying the phenol oxidation catalysed by a lutetium bisphthalocyanine (LuPc<sub>2</sub>) film-modified Pt/quartz electrode.

The study focused on the analysis of the oxidation of phenols usually found in wines, including vanillic, ferulic, caffeic and gallic acids dissolved in a hydroalcoholic solution simulating the matrix of a red wine.

It has been shown that LuPc<sub>2</sub> modified EQCM sensors immersed in hydroalcoholic solution exhibit significant mass changes upon electrochemical cycling produced by the ingress/egress of ions necessary to maintain the electroneutrality of the film.

Cyclic voltammograms of LuPc<sub>2</sub>/QCM electrodes immersed in phenols also undergo mass changes associated with the ingress/egress of ions. In addition, progressive mass changes occur upon successive scans. The oxidation/reduction of monophenols produces a progressive increase in the mass, whereas ortho-diphenols show the opposite behaviour. These phenomena have been interpreted in terms of the adsorption of the phenols to the LuPc<sub>2</sub> layer and their capability to electropolymerise at the electrode surface.

The combination of cyclic voltammetry with electrochemical quartz microbalance (EQCM) has demonstrated its capability to elucidate the complex processes occurring at the surface of voltammetric sensors chemically modified with bisphthalocyanines.

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## 1. Introduction

Polyphenols are a class of antioxidants that are present in a variety of foods and beverages such as wines [1] and their dietary intake has been associated with beneficial health effects [2,3]. In addition, this family of compounds has a strong influence in the organoleptic characteristics of wines [4].

Phenolic compounds have been analysed using a variety of methods that include chromatographic, electrophoretic and optic techniques [5]. Electrochemical methods have also been extensively applied [6].

Phthalocyanines have had noticeable success in the field of electrochemical sensors because these metal complexes act as mediators for electrochemical reactions and exhibit electrocatalytic activity for a variety of reactions [7–9]. Due to these properties, phthalocyanines have been successfully used as

sensitive materials in voltammetric electrodes for the qualitative detection of polyphenolic compounds [10–12]. Moreover, voltammetric sensors based on phthalocyanines have been used as the sensing elements of electronic tongues, which consist of an array of sensors with cross-selectivity, and use mathematical procedures for signal processing based on pattern recognition and/or multivariate data analysis [13–16].

The electrochemical signals obtained from phthalocyanine-based voltammetric electrodes show a high degree of complexity due to the variety of redox processes which occur at the electrode surface. Such processes are caused by the oxidation–reduction of both the electrode material and the phenolic compounds. In addition, the interactions between the electrode modifier and the polyphenols (i.e. electrocatalytic effect) and the diffusion of ions inside the film to counterbalance the charge changes can influence the electrochemical response [12,17,18].

The importance of these voltammetric sensors makes it necessary to acquire knowledge of the processes occurring at the electrode/solution interface. In particular, it is important to investigate the movement of ions and solvent accompanying the electron transfer process. There is also a need to analyse the possible polymerisation processes occurring at the electrode surface that can

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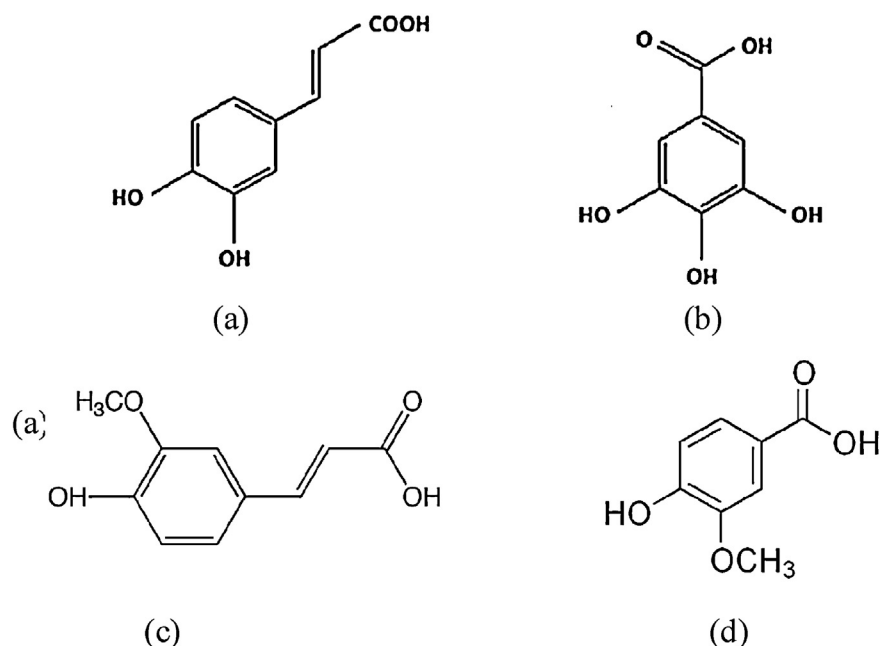


Fig. 1. Phenols included in the study: (a) caffeic acid; (b) gallic acid; (c) ferulic acid and (d) vanillic acid.

modify the activity of the sensitive layer while decreasing the lifetime of the electrodes [19].

Three decades after the introduction of the in situ application of the piezoelectric quartz crystal for researching electrochemical systems by Nomura and Iijima [20], the use of the electrochemical quartz crystal microbalance (EQCM) has become a well-established technique for the investigation of mass changes associated with electrochemical surface processes, such as electrosorption, electropolymerisation or ion insertion [21].

EQCM has been used to investigate the formation of polymeric products formed by the electro-oxidation of phenolic compounds on the surface of Au and Pt electrodes [19].

A few studies published in the field of phthalocyanines refer to QCM covered with MPcs, but these studies are limited to mass changes [22–25]. Only recently the EQCM has been applied to study the role of the movement of ions and the mass transport in the electrochemistry metallophthalocyanines (MPc) (Pc ring in oxidation state  $-2$ ) [26].

We now present an electrochemical quartz crystal microbalance study of thin films of a sandwich type phthalocyanine, the lutetium bisphthalocyanine ( $\text{LuPc}_2$ ) (a free radical derivative with ring in oxidation state  $-1.5$ ). This derivative is of particular interest due to its rich electrochemistry and electrocatalytic properties, which are attributed to its free radical character [10,11]. In this work,  $\text{LuPc}_2$  thin films have been used to measure tiny mass changes (order of nanograms) that occur when the sensor is immersed in hydroalcoholic solutions of antioxidants, of interest in the wine industry. Four antioxidants (caffeic acid, gallic acid, ferulic acid and vanillic acid) present in wines have been studied, and their adsorption and polymerisation processes were discussed in terms of the mass changes during the electrochemical experiment and their chemical structures.

## 2. Materials and methods

### 2.1. Reactants, QCM and electrochemistry

All reactants were purchased from Sigma–Aldrich and were used without further purification. Fig. 1 depicts the phenolic compounds used in the study.

Lutetium bisphthalocyanine ( $\text{LuPc}_2$ ) was synthesised following a previously reported method [27]. The antioxidants (caffeic acid, gallic acid, vanillic acid and ferulic acid) were dissolved ( $0.5 \text{ mol L}^{-1}$ ) in a hydroalcoholic medium similar to that found in wines. This model solution of wine was prepared from a 12% (v/v) ethanol solution, to which 0.033 M tartaric acid was added. Then NaOH was added to give a final pH of 3.6.

QCM measurements were carried out with a quartz crystal microbalance QCM 200 model, purchased from Stanford Research Systems. The mass-sensitive oscillators were 1-in. diameter, 5-MHz AT-cut planoconvex quartz crystals coated with Pt (Pt/QCM).

$\text{LuPc}_2$  films were deposited onto the quartz crystal oscillators ( $\text{LuPc}_2/\text{Pt/QCM}$ ) by means of the spin-coating technique; spin coater Mikasa 1H-D7 from a  $\text{LuPc}_2$  chloroform solution  $10^{-2} \text{ mol L}^{-1}$  by applying 700 rpm. The mass of the  $\text{LuPc}_2$  deposited onto the electrodes was  $69.09 \pm 1.37 \mu\text{g}$  ( $50.43 \mu\text{g cm}^{-2}$ ).

The oscillators were used simultaneously as the working electrode of the electrochemical measurements. Cyclic voltammograms were carried out using a Parstat 2273 potentiostat (EG&G) using a conventional three electrode cell, where a Pt sheet was used as the counter electrode and an Ag/AgCl electrode as the reference electrode. Cyclic voltammograms and massograms were registered from 0.0 V (coinciding with the open cell voltage) to +1.3 V. The reverse bias voltage was applied from +1.3 V to  $-0.7 \text{ V}$ ; the cycle was then closed by biasing the voltage from  $-0.7 \text{ V}$  to 0.0 V (vs. Ag/AgCl) at a scan rate of  $0.1 \text{ V s}^{-1}$ .

### 2.2. Calibration of the QCM

The calibration of the quartz crystal microbalance was carried out by galvanostatic deposition of copper onto the platinum surface. A  $0.5 \text{ mol L}^{-1}$  solution of  $\text{CuSO}_4$  in  $0.1 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  (pH = 1.37) was subjected to a reducing potential, and copper was deposited with a fixed cathodic current of 2 mA for 70 s. Excellent linearity was observed in  $\Delta f$  vs.  $Q$  plots (the calibration curve was  $y = 9.00 \times 10^{-5}x + 0.02$ ,  $R^2 = 0.999$ ; deposition:  $38 \text{ mg cm}^{-2}$  of copper).

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