



## Selective determination of caffeic acid in wines with electrochemical sensor based on molecularly imprinted siloxanes



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### ABSTRACT

Caffeic acid (CA) is one of the phenolic compounds widely found in wines and it is associated to the quality of this beverage and also to various beneficial effects on health. Thus, a novel electrochemical sensor based on molecularly imprinted siloxanes (MIS) film was developed for the highly selective determination of CA. The MIS film was prepared by sol–gel process, using the acid catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS), phenyltriethoxysilane (PTEOS) and 3-aminopropyltrimethoxysilane (3-APTMS) in presence of CA as template molecule. The MIS film was immobilized onto Au electrode surface pre-modified with 3-mercaptopropyltrimethoxysilane (3-MPTS) and then characterized by Differential Pulse Voltammetry (DPV), Field Emission Scanning Electron Micrographs (FESEM) and Cross Polarization-Magic Angle Spinning Nuclear Magnetic Resonance of <sup>29</sup>Si (<sup>29</sup>Si CP-MAS NMR). Under the optimized conditions, the sensor showed a linear current response to the target CA concentration in the range from 0.500 to 60.0 μmol/L, with a detection limit of 0.15 μmol/L. The film exhibited high selectivity toward the template CA, as well as good stability and repeatability for CA determinations as well as for sensor preparation. Furthermore, the proposed sensor was applied to determine CA in wines samples and the results were in agreement with those obtained by a chromatographic method. The acceptable values of recovery implied its feasibility for practical application.

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### 1. Introduction

Wine contains numerous natural phenolic antioxidants (flavonoids, phenolic acids, hydroxycinnamic acids, etc.) which give rise to their preventive effect in view of different chronic diseases caused by free oxygen radicals, such as cancer, heart and coronary diseases [1]. The amount of hydroxycinnamic acids found in the wines also can affect the color, astringency, bitterness, oxidation level and clarity of the beverage [2].

Caffeic acid (CA), 3,4-dihydroxycinnamic acid is the major representative of hydroxycinnamic acids in wines [3]. In addition, many biological activities have been recently reported for CA, including antioxidant [4], antibacterial [5], anti-inflammatory [6], anti-tumor effects [7], etc. Thus, the determination of CA in wines, using reliable methods, for quality control and assessment of wines because of their effects on health and the taste of these products is considered at the moment a priority. At present, there are several analytical

methods for determination of CA in wines, including liquid chromatography [8,9] and capillary electrophoresis [3]. Recently were proposed just a few studies in which electrochemical techniques are used for a quantitative analysis of CA in this kind of beverage [10,11], although these methods have showed advantages as the minimal preparation of the sample, selectivity, sensitivity, reproducibility and rapid time of response.

Electrochemical sensors based on polymers [12–15], inclusive molecularly imprinted polymer (MIP) attracts increasing attention on account of the advantages including low cost, high specificity, stability and robustness [16,17]. Molecular imprinting can be envisaged as the selective manipulation of the size, shape and chemical functionality of a polymer matrix by a template molecule. The imprinting process is a well-established technique for the preparation of molecularly imprinted polymers (MIP) with a tailor-made affinity and specificity for the template molecule [18]. In this process, a template is added in monomers solution and the polymer chains self-organize around the template molecules, which can be detached by heating or washing methods without disturbing the geometry of the polymer. The removal of the template from the polymer matrix leaves sites complementary in template in size, shape and interaction that are capable of reversible recognition [19].

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The arrangement of the monomer units around the template can be achieved by weak intermolecular interactions such as electrostatic interactions, van der Waals forces and by hydrogen bonding, or via either covalent interaction. The highly selective recognition characteristics of the molecularly imprinted polymers are comparable to those of the natural biological species such as receptors and antibodies. MIP has been widely used in several applications involving biomimetic catalysis [16] and sensors [17], chromatography [20], solid phase extraction [21].

The vast majority of molecularly imprinted media are based on the use of organic acrylate or acrylic type polymers. One of the disadvantages of this polymerization reaction is the fact that it has to be necessarily induced by heating or UV radiation, in absence of oxygen [22,23]. Furthermore, a severe limitation of this type of imprinting is that the full potential of the MIP as a specific binding element is not exploited, since the diffusion into a particle is slow [24]. Thus, methods for the preparation of imprinting films have been developed as an attractive alternative to conventional MIP, including sol–gel process. Sol–gel materials are inorganic (siloxane) based polymers formed by an acid or base catalyzed hydrolysis and condensation of a series of silane monomers [25]. Once the hydrolysis reaction initiates, the condensation propagates, leading to the formation of sol–gel networks and some other by-products like water or alcohols, which can be easily removed by the drying processes. The two reactions go on side-by-side, and in this way the viscosity of the system gradually increases. At this point, the gels interconnect with each other and develop a network with excellent physical rigidity, chemical inertness and thermal stability properties [26]. The pH of the reaction media will determine whether the dominant process is hydrolysis or condensation. At low pH, i.e. acid catalyzed sol–gels, condensation occurs at an enhanced pace in comparison to hydrolysis. The result of this being that polymer growth is favored over cross-linking [27].

Compared with acrylic polymer-based films, sol–gel-based MIP, denominated molecularly imprinted siloxanes (MIS) [28], can easily control the thickness, porosity and surface area, while the selectivity and diffusion were comparable or even better, making sol–gel method suitable for the construction of electrochemical sensors [29]. It is important to emphasize that the MIS film synthesis is performed at ambient temperature, without induction by UV radiation and in presence of the oxygen, which enables to incorporate thermosensitive template molecules and simplifies the polymerization process.

In this sense, the aim of this work was to construct an electrochemical sensor based on MIS film for the selective and sensitive determination of CA in red and white wines samples. This MIS film was linked to gold electrode surface and the proposed sensor had good analytical performances for CA determination, including sensitivity, high selectivity, precision, accuracy, robustness and stability.

## 2. Experimental

### 2.1. Materials

3-Mercaptopropyltrimethoxysilane (3-MPTS), phenyltriethoxysilane (PTEOS), 2-ethoxyethanol and cinnamic (CiA), ferulic (FA), *p*-coumaric (CoA), vanilic (VA), gallic (GA), 1-hydroxy-2-naphthoic (HA) acids were purchased from Sigma–Aldrich®. Tetraethoxysilane (TEOS), 3-aminopropyltrimethoxysilane (3-APTMS) and caffeic acid were acquired from ACROS Organics. Hydrochloric acid was obtained from Merck. All chemicals were of analytical grade and were used as received. All solutions were prepared with ultrapure deionized water twice purified using a Milli-Q Academic A10 Water Purification System (Millipore,

resistivity > 18.2 MΩ at 25 °C). The pH values of the solutions were determined with a Fisher Scientific Accumet® Research pH meter model AR 15.

### 2.2. Instrumentation

All the electrochemical measurements were carried out using a potentiostat PGSTAT-10 Model from Autolab® Eco Chemie (Utrecht, The Netherlands) connected to a PC (Software GPES 4.9). A three-electrode system consisting of a saturated Ag/AgCl reference electrode, platinum wire as auxiliary electrode and modified gold electrode (AuE) as working electrode (3 mm diameter) was used for electrochemical measurements, at room temperature. The MIS film thickness was estimated by Nova 200 Nanolab DualBeam™ SEM/FIB (United States). The Field Emission Scanning Electron Micrographs (FESEM) was used to characterize the siloxane films morphologically, using a JEOL JSM-6340 F instrument. <sup>29</sup>Si CP-MAS NMR spectra were obtained at room temperature on a Bruker 400 MHz spectrometer.

### 2.3. Molecularly imprinted sensor preparation and procedures

#### 2.3.1. AuE pretreatment

Prior to coating, AuE was mechanically polished with 1.0, 0.5, 0.3 μm alumina slurry to a mirror finish, rinsed and ultrasonicated in deionized water and ethanol for 5 min. In the sequence, AuE was treated with a 3:1 (v/v) solution of concentrated sulfuric acid and 30% hydrogen peroxide for 5 min and rinsed with deionized water for 5 min. The electrode was connected to the potentiostat and dipped in aqueous H<sub>2</sub>SO<sub>4</sub> (0.5 mol/L) solution. The potential was cycled for 25 times between 0.0 and 1.6 V at a scanning rate of 100 mV/s. Finally, the AuE was rinsed with ethanol and quickly began the preparation of the molecularly imprinted siloxane.

#### 2.3.2. Preparation of proposed sensor

Firstly, in order to promote the adhesion of MIS film on the Au surface, the AuE was immersed in a 20 mmol/L 3-MPTS in dry ethanol for 2 h in the room environment. The electrode was then rinsed with copious amounts of ethanol and deionized water. Hydrolysis of the 3-MPTS layer was followed by dipping in aqueous HCl (0.1 mol/L) solution for 1 h. The AuE was removed from the HCl solution and dried at 50 °C for 30 min. The 3-MPTS layer was formed on the AuE surface (3-MPTS/AuE).

An organic–inorganic hybrid sol–gel was prepared by mixing 65 μL (0.27 mmol) of PTEOS, 65 μL (0.37 mmol) of 3-APTMS, 400 μL (1.8 mmol) of TEOS, 3.0 mL of 2-ethoxyethanol, 100 μL of 0.1 mol/L HCl as catalyst and 90 μL of deionized water. The chemicals were stirred by 50 min to obtain a homogeneous sol at room temperature. Then, 2 mL of the sol was mixed with 700 μL of 2-ethoxyethanol solution of 0.03 mol/L CA for additional 1 h. This solution was used for MIS film, while the original solution was used non-molecularly imprinted siloxane (NIS) film. The 3-MPTS/AuE was immersed in sol–gel and rotated at 1500 rpm for 15 min in order to form the film. Finally, the sensor was dried at 50 °C for 8 h to complete the condensation process as well as to remove any residual solvent. The CA molecules were removed by repetitive immersing MIS/AuE into 0.1 mol/L PBS (pH 8.0), following by drying at 50 °C for 8 h, being the MIS/AuE obtained.

#### 2.3.3. Rebinding experiments

MIS/AuE was dipped for 25 min in rebinding solution with CA and molecules with similar structures in citrate buffer solution, followed by electrochemical characterization by Differential Pulse Voltammetry (DPV) in sulfuric acid solution. The incubation time

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