Bioelectronic tongue based on voltammetric sensors and biosensors the analysis of antioxidants and phenolic composition of grapes

M.L. Rodríguez-Méndez[1*], C. Medina-Plaza[1], C. Apetrei[1], J.A. Fernandez-Escudero[2], E. Barajas[3], J.A. De Saja[4]

[1]Dept. Química Física y Química Inorgánica, E. T. S. Ingenieros Industriales, University of Valladolid (Spain)

[*]e-mail: mluz@eis.uva.es

[2]Estación Enológica de Castilla y León, Rueda, Valladolid (Spain)

[3]Instituto Tecnológico Agrario. Junta de Castilla y León Valladolid (Spain)

[4]Dept. Física de la Materia Condensada, Faculty of Sciences, U. of Valladolid (Spain)

In the last years new methods for the analysis of complex mixtures of liquids -the so-called electronic tongues- have been developed. They consist in arrays of liquid sensors coupled to pattern recognition software [1]. Such methods analyze the sample as a whole without need of separating it in simple components.

It has been demonstrated that the arrays formed by voltammetric electrodes modified with phthalocyanines (MPc) are able to discriminate complex liquids. Arrays of sensors based on MPcs have been successfully used to discriminate wines of different qualities, grape variety or wines prepared using different techniques or aged in different types of oak barrels [2]. The capability of discrimination is due to the sensibility of phthalocyanine sensors towards redox (i.e. polyphenols) and acids present in wines. Their electrocatalytic properties play also an important role in the discrimination capabilities of the array.

It is well known that the organoleptic characteristic of wines depend on the variety of grapes, and on the degree of maturity of the berries. Berry flavor and aroma compounds are synthesized within the berry during maturation. It is therefore important to define the quality of grapes and the optimal grape maturity for wine production and to develop clear chemical or biochemical traits that can be used to define the quality and peak of ripeness.

Sugar is a component often used to assess ripeness. Sugar content increases during ripening and is therefore a function of berry age. Assessments of acidity are also used to define the optimal time of harvest. This can be evaluated as either pH or titratable acidity or both. Increases in total phenolic content have been associated with maturity. In a principal component analysis of various ripening indices, phenolic content emerged as a key defining factor of grape maturity.

The objective of this work is to develop a bioelectronic tongue dedicated to the assessment of the maturity of grapes with particular attention to the phenolic maturity. For this purpose, an array of sensors formed by phthalocyanine sensors combined with biosensors (containing enzymes and phthalocyanines as electron mediators), has been developed specifically for this particular application.

The array is formed by two sets of electrodes. The first set consists in voltammetric sensors based on electrodes modified with metallic phthalocyanines (CuPc, ZnPc, FeP, CoPc and $LuPc_2$). A second set of biosensors based on enzymes (i.e. tyrosinase) immobilized on solid electrodes containing MPcs as electron mediators have also been prepared. Sensors have been tested towards model solutions of antioxidants usually present in berries. The electrochemical response of both families of electrodes is characterized by complex curves that contain information about the pH and the content of sugars and antioxidants (Figure 1). The sensibility, detection limit and stability of the sensors has been evaluated. These experiments have been used to select the most appropriate sensors to construct the array. The final array of sensors has been used to analyze red grapes of five different varieties (tempranillo, garnacha, prieto picudo, juan garcía and mencía) (From de D.O. Ribera de Duero. Spain) harvested at their optimal ripeness (as established by chemical parameters: acidity, sugar content, etc.) purposely selected and harvested for this study.

The preparation of the sample is a key step in the analysis of grapes. Several methods have neen reported in the literature. However, these methods have been developed to perform chromatographic or spectroscopic analysis [4]. In this work, a preparation method has been developed to adapt the samples to the voltammetric measurements.

The electrochemical response of both families of electrodes is related to the ions and to the electroactive molecules present in the solution, being particularly sensitive to pH and antioxidants. The use of sensitive materials with different chemical properties allows obtaining complementary information that enhances the capability of discrimination of the system.

The sensor array coupled with pattern recognition techniques is able to distinguish the grape varieties on account of their chemical nature.

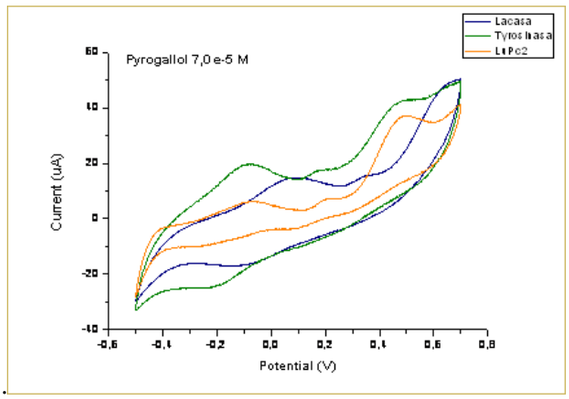

Figure 1. Response of thee electrodes towards pyrogallol (7.10^{-5} M in buffer phosphate pH-7)

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