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Olive oils qualitative evaluation using a potentiometric electronic tongue: a review of practical applications

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ABSTRACT

Olive oil is a food product highly prone to fraud, including mislabeling of olive oil commercial category, geographical or olive cultivar origin. Several analytical techniques have been reported to assess olive oil quality, authenticity as well as to detect possible adulterations, namely gas-, liquid- and mass-spectrometry chromatography, DNA and spectroscopy based methods. However, in general, these techniques require expensive pre-sample treatments, are time-consuming and need cost equipments and high skilled technicians. So, fast and more cost-effective methods are still needed and their development a challenge. Among these, electrochemical sensors have been proposed within this field of research, including both voltammetric and potentiometric electronic noses and electronic tongues, individually or as a fused methodology. In this study it is intended to review some of the most recent applications described in the literature including those of the research team regarding the application of a potentiometric electronic tongue, containing cross-sensitive lipidic membranes, to discriminate single-cultivar extra-virgin olive oils by cultivar or sensory intensity, showing its range of applicability and the possibility of using this artificial taste sensor as a complementary/alternative methodology for olive oil sensory analysis.

Keywords: Single Cultivar Extra Virgin Olive Oil; Sensory Analysis; Potentiometric Electronic Tongue; Chemometrics

INTRODUCTION

Olive oil is a food product of major economical relevance being its consumption related with health benefits. Several kinds of olive oils are commercially available, being their price quite dependent on olive oil quality grade, cultivar and geographical origin. Extra-virgin olive oils (EVOO) are more expensive but also highly appreciated by consumers, than virgin olive oils (VOO) or even lampante olive oils (LOO). More, recently, some higher expensive EVOO have appear in the market, linked to increasing search of new and different traditional or gourmet foods, namely EVOO and VOO certified as Protected Denomination of Origin (PDO), biological EVOO, single-cultivar EVOO or olive oils produced from centenary olive trees.

Olive oil is also one of the food products more prone to adulterations as well as to frauds including mislabeling.

Therefore, several analytical techniques have been described in the literature to detect and/or verify possible frauds involving the production and commercialization of olive oils, in order to guarantee consumer's confidence when purchasing this high-value product and to minimize the risk of unfair competition among olive oil producers.

Official methods and recommended practices have been established by the American Oil Chemists' Society to assess olive oil quality (Nunes, 2013). However, some of these methods are quite expensive, non-green techniques, and require fulfillment of straight standardized procedures to ensure accuracy. Other procedures have been proposed trying to overcome these drawbacks, namely gas-, liquid-chromatography and, more recently, mass-spectrometry based-methodologies (Bakhouche et al., 2013; Garcia et al., 2013; Garrido-Delgado et al., 2011; Karabagias et al., 2013; Lauri et al., 2013; Longobardi et al., 2012; López-Feria, Cárdenas, García-Mesa, & Valcárcel, 2008; Matos et al., 2007; Montealegre et al., 2010; Romero, & Brenes, 2012; Ruiz-Samblás et al., 2012). These methodologies are based on the identification and quantification of several chemical olive oil components that allow assessment of the quality, authenticity or adulteration of olive oils. Also, DNA-based methods have been proposed to authenticate the varietal origin of olive oils (Bazakos et al., 2012) and non-destructive spectroscopy-based methods have been used to evaluate olive oils quality, authenticity and possible adulterations (Dais, & Hatzakis, 2013; Nunes, 2013; Pizarro et al., 2013). Nevertheless, these approaches require highly-skilled technicians and usually are not suitable for *in situ* applications, being far beyond the economic possibilities of small producers or retailers.

Therefore, recently several more cost-effective, portable, fast and simpler based electrochemical methods have been developed and their potential within the olive oil field evaluated. Electrochemical sensors have been applied to evaluate olive oil quality and as a practical tool in authentication or adulteration studies. Among these, both voltammetric and potentiometric approaches, which include the use of electronic eyes, noses and tongues (E-eyes, E-noses and E-tongues, respectively), individually or combined, have been described in the literature for olive oil evaluation. In **Table 1**, a summary of the most recent published works dealing with the application of electrochemical devices for olive oil analysis is presented.

As can be inferred by the number of papers recently published concerning the application of electrochemical sensors for olive oil assessment and the reported success, these sensor approaches seem to be a practical complementary/alternative tool for routine assays. Moreover, these methodologies usually present several advantages compared with traditional analytical techniques, namely are cost-effective, fast, miniaturized, portable and green-technologies.

An overall state of the art will be presented at the *Symposium*, including a more detailed study regarding the recent works of the research team, complemented with new applications of the potentiometric E-tongue (**Figure 1**), for sensory evaluation of monovarietal EVOO.

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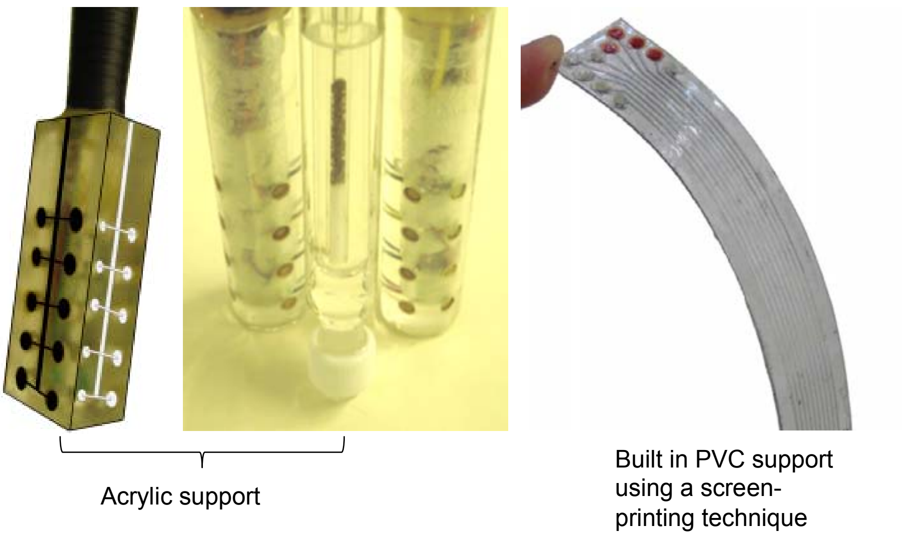

Figure 1. Potentiometric E-tongue

Table 1. Summary of electrochemical methodologies reported in the literature for olive oil evaluation

Type of device	Electrochemical principle/type of sensors	Field of application in olive oil analysis	References
E-nose (EN)	EN: Resistance measurement in metal-oxide sensors.	On-line detection of lampante olive oils.	García-González & Aparicio (2004)
E-tongue (ET)	ET: Voltammetry with oil-based carbon paste electrodes.	Olive oils and seeds oils discrimination; Olive oils quality discrimination.	Apetrei, Rodríguez-Méndez & de Saja (2005)
E-eye, E-tongue, E-nose	EN: Resistance measurement in metal-oxide sensors; ET: Voltammetry with oil-based carbon paste electrodes.	Olive oils discrimination according to different degree of bitterness.	Apetrei, Apetrei, Villanueva, de Saja, Gutierrez-Rosales & Rodriguez-Mendez (2010)
E-tongue	ET: Voltammetry with polypyrrole-modified sensors.	Total polyphenol quantification content in olive oils.	Apetrei & Apetrei (2013)
E-nose	EN: Amperometry using pure metals and doped SnO2 sol–gel thin films.	Single-cultivar EVOO discrimination.	Cimato et al. (2006)
E-nose and E-tongue	EN: Conductivity or change of potential measurement in metal-oxide sensors; ET: Amperometry with a glassy carbon electrode.	Geographical origin and authentication of EVOO.	Cosio, Ballabio, Benedetti & Gigliotti (2006)
E-nose E-tongue	EN: Conductivity or change of potential measurement in metal-oxide sensors; ET: Amperometry with a glassy carbon electrode.	Evaluation of different storage conditions of EVOO.	Cosio, Ballabio, Benedetti & Gigliotti (2007)
E-nose	EN: Conductivity measurement in Metal-oxide sensors.	Monitoring oxidative status evolution of virgin olive oils.	Lerma-García, Simó-Alfonso, Bendini & Cerretan (2009)
E-tongue	ET: Voltammetry with platinum microelectrode.	Olive oils quality and geographical origin discrimination.	Oliveri, Baldo, Daniele & Forina (2009)
E-nose	Quartz Crystal Microbalance sensors using chromatographic adsorbents as sensing thin films.	Olive oils discrimination.	Escuderos, Sánchez & Jiménez (2010)
E-nose	Quartz Crystal Microbalance sensors using chromatographic adsorbents as sensing thin films.	Differentiation of virgin and extra virgin from lampante olive oils.	Escuderos, Sánchez & Jiménez (2011)
E-nose	EN: Conductivity measurement in Metal-oxide sensors.	Olive oils geographical origin discrimination.	Haddi et al. (2011)
E-nose E-tongue	EN: Conductivity measurement in Metal-oxide sensors; ET: Voltammetry with metals, glassy carbon and a metal oxide.	Olive oils geographical origin discrimination.	Haddi et al. (2013)
E-tongue	ET: Potentiometric with lipidic polymeric membranes.	Single-cultivar EVOO discrimination.	Dias, Fernandes, Veloso, Machado, Pereira & Peres (2014)
E-tongue	ET: Potentiometric with lipidic polymeric membranes.		Peres, Veloso, Pereira & Dias (2014)