Detection of virgin olive oil adulteration using a voltammetric e-tongue

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A R T I C L E   I N F O

A B S T R A C T

The detection of adulteration in extra virgin olive oils is of great interest in food industry. This article presents the first use of a voltammetric e-tongue for the detection of the adulteration of virgin olive oil. Adulterations of an extra virgin olive oil with different percentages of sunflower oil, soybean oil and corn oil were measured using modified carbon paste based sensors. The square wave voltammetric signals were processed using kernel method. Chemometric methods applied allows discrimination and classification of oils in agreement with botanical origins. Excellent correlations between voltammetric signals and polyphenolic content was obtained by PLS regression. PLS-DA and PLS regression demonstrated the feasibility of detecting adulterations of olive oil with percentages lower than 10% of sunflower, soybean and corn oils. These results indicate that e-tongue can be a useful tool for the detection of olive oil adulteration with seed oils.

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1. Introduction

Extra virgin olive oil (EVOO) is obtained from the olive fruit named *Olea europaea*. EVOO is extracted by only mechanical procedure without application of refining process. The quality of olive oil ranges from the high quality EVOO to the low quality olive–pomace oil (Tsimidou, 2006). It is one of the primary ingredients of the Mediterranean diet (Psaltopoulou et al., 2004). Different factors such as cultivar, environment and cultural practices determine the quality and uniqueness of specific EVOOs (Tura et al., 2009). The agreeable taste and aroma with the health benefits of EVOOs are important reasons for consumers to consume this product (Amirante et al., 2012). Oil pureness is a very important aspect of the quality edible oil for special reasons of the sensory properties, perceived health values and the confidence of the health foods (Cozzolino, 2012). Because of the high value of EVOO, it can be adulterated with other oils of lower commercial value. The most common adulterants found in EVOO are refined olive oil, seed oils and nut oils (Dourtoglou et al., 2003).

The detection of adulteration in EVOOs is a particular concern in the food industry. The adulteration of extra virgin olive oil with other cheaper oils can lead to significant profits for the unscrupulous vendor or raw material supplier. Therefore, continuous caution is required to control the adulteration of EVOOs and to protect the interests of the consumers.

In order to detect VOO adulteration, a number of chromatographic and spectroscopic methods, including fluorescence (Kunz et al., 2011), near-infrared (NIR) (Özdemir and Öztürk, 2007), Fourier transform infrared spectroscopy (FT-IR), FT-Raman (Heise et al., 2005), nuclear magnetic resonance (NMR) (Xu et al., 2014), mass spectrometry (MR) (Calvano et al., 2012), mid-infrared spectroscopy (MIR) (Gurdeniz and Ozen, 2009) and high-performance liquid chromatography (HPLC) (Lísa et al., 2009) were used.

All these methods were applied with some success. However, there are also some shortcomings. Chromatographic, mass and NMR spectroscopy methods need expensive instruments. Fluorescence spectroscopy and chromatography methods require preprocessing of the samples. Furthermore, these methods are not suitable for on-line, in-line or real time analysis.

The multivariate data analysis like linear discriminant analysis (LDA), principal component analysis (PCA), partial least square regression (PLS), machine learning (ML), and artificial neural networks (ANN) are applied to further analyze the oil spectroscopy data for oil adulteration detection (Xu et al., 2014; Gurdeniz and Ozen, 2009).

Nowadays there is an increasing interest for simple and fast techniques called e-nose and e-tongue for various applications in food industry (Peris and Escuder-Gilabert, 2013). An e-tongue is an device, which consists of an array of chemical sensors and an appropriate pattern recognition method, for recognition (identification, classification, discrimination) of quantitative multicomponent analysis and artificial assessment of taste and flavour of various liquids. In the case of e-tongues, their capability to analyse

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and discriminate a variety beverages such as mineral waters, milks, teas, wines or beers has already been established (Cetó et al., 2014; Yaroshenko et al., 2014; Gutiérrez-Capitán et al., 2013; Ghasemi-Varnamkhasti et al., 2012; Apetrei et al., 2012). However, few works have been focused to the analysis of olive oils using e-tongues (Cosio et al., 2007; Haddi et al., 2013; Apetrei and Apetrei, 2013). In previous works we have developed different strategies in order to use an voltammetric e-tongue to discriminate oils of different origins and qualities (Apetrei et al., 2007, 2010, 2012). In one method, the olive oil is binder used for preparation of carbon paste-based sensor. The characteristics of the voltammograms observed when the sensor is immersed in different electrolytic solutions reflect the electroactive properties of the oils (Apetrei et al., 2007, 2010).

The aim of this work is to evaluate the feasibility of e-tongue (based on modified EO carbon paste-based sensors) to detect the adulteration qualitatively and precisely of EOs with different seed oils based on their tasting fingerprints. Based on our knowledge, it is the first time that a voltammetric e-tongue is employed for detection of adulteration of extra virgin olive oil. Various chemometric methods were performed for discrimination and classification of adulteration levels.

2. Experimental

2.1. Reagent and chemicals

Potassium chloride (KCl) was obtained from Sigma–Aldrich. Hydrochloric acid (HCl) was purchased from S.C. Chemical Company S.A. (Romania). Water was purified on a Milli-Q Simplicity® Water Purification System (Millipore Corporation) with resistivity of 18.2 MΩ. Electrolyte solutions were prepared using ultrapure water. Carbon nanopowder, <50 nm particle size (TEM), ⩾99% trace metals basis from Aldrich was used for fabrication of carbon paste electrodes modified with edible oils.

2.2. Samples

Four kinds of edible vegetable oil were purchased from local supermarkets, including the extra virgin olive oil, the sunflower oil, the soybean oil and the corn (maize) oil.

The oil samples were stored in the fridge at 4 °C until the day of analysis. The adulterant oil is considered the seed oil at different level of concentrations. For e-tongue measurements, mixtures of seed and extra virgin olive oils, with concentration of seed oil at different levels (2%, 5%, 10%, 20% and 25%) were prepared (Table 1). The mixtures of oils were prepared using an Elmasonic S10H ultrasonic bath.

Total phenolic content was determined spectrophotometrically following the Folin–Ciocalteu spectrophotometric method (Herchi et al., 2011). The results are presented in Table 2.

2.3. e-Tongue system

For electronic tongue measurements carbon paste electrodes (CPE) modified with edible oils were prepared as previously described (Apetrei et al., 2007, 2010). Voltammetric measurements were carried out in an Biologic Science Instruments SP 150 potentiostat/galvanostat (EC-Lab Express software) using a conventional three-electrode cell. The modified EO carbon paste-based sensors were used as working electrodes. The reference electrode was an Ag/AgCl KCl 3M and the counter electrode was a platinum wire. The electrochemical experiments were performed at a controlled temperature of 25 °C.

Three identical EO carbon paste-based sensors were prepared for each oil under study. Each replicate sensor was immersed in one electrolytic solution (0.1 mol × L^{-1} HCl or 0.1 mol × L^{-1} KCl) and the voltammetric response was registered. Voltammetric measurements were carried out by means of SWV (Square wave voltammetry). SWV were recorded using a frequency of 15 Hz, an amplitude of 0.10 V and a step high of 0.005 V. The SWV curves were registered in the potential range from −0.2 to +1.3 V. Seven measurement replicates were carried out with each sensor (measured after the conditioning step) in both electrolyte solutions.

2.4. Data analysis

Several steps were carried out in order to obtain the input matrix for multivariate data analysis. SWV curves were pre-processed using the adaptation of a data reduction technique based on predefined response "bell shaped-windowing" curves called "kernels" (Apetrei et al., 2010). Using this method, ten parameters per each SWV were obtained. Because in this case, the variables are the edible oils from the sensors, the initial input matrix was transposed. In this way, the variables are the electrolyte solutions and the samples are the edible oils from the carbon paste-based sensors.

Table 1
Edible oil samples under study.

Sample	Edible oil	Concentration/%				
EVOO	Olive oil	100				
Sf	Sunflower oil	100				
S	Soybean oil	100				
C	Corn oil	100				
EVOO + Sf	Olive oil/sunflower oil	98/2	95/5	90/10	80/20	75/25
EVOO + S	Olive oil/soybean oil	98/2	95/5	90/10	80/20	75/25
EVOO + C	Olive oil/corn oil	98/2	95/5	90/10	80/20	75/25

Table 2
Total phenolic content of oil samples determined spectrophotometrically.

Sample	EVOO	EVOO + Sf					EVOO + S					EVOO + C				
		98/2	95/5	90/10	80/20	75/25	98/2	95/5	90/10	80/20	75/25	98/2	95/5	90/10	80/20	75/25
Total polyphenols content (mg × kg^{-1})	275.43	271.92	261.63	249.80	220.75	208.23	270.75	260.54	250.18	221.24	207.41	272.43	260.74	250.17	219.94	208.95

RSD = 4.5%.