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Review

Electrochemical Sensor-Based Devices for Assessing Bioactive Compounds in Olive Oils: A Brief Review

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Abstract: Electrochemical bioinspired sensor devices combined with chemometric tools have experienced great advances in the last years, being extensively used for food qualitative and quantitative evaluation, namely for olive oil analysis. Olive oil plays a key role in the Mediterranean diet, possessing unique and recognized nutritional and health properties as well as highly appreciated organoleptic characteristics. These positive attributes are mainly due to olive oil richness in bioactive compounds such as phenolic compounds. In addition, these compounds enhance their overall sensory quality, being mainly responsible for the usual olive oil pungency and bitterness. This review aims to compile and discuss the main research advances reported in the literature regarding the use of electrochemical sensor based-devices for assessing bioactive compounds in olive oil. The main advantages and limitations of these fast, accurate, bioinspired voltammetric, potentiometric and/or amperometric sensor green-approaches will be addressed, aiming to establish the future challenges for becoming a practical quality analytical tool for industrial and commercial applications.

Keywords: electrochemical devices; sensor technology; olive oil; bioactive compounds; chemometrics

1. Introduction

Olive tree (*Olea europaea* L.), native to the Mediterranean basin and parts of Asia, is now cultivated worldwide to produce olive oil and table olives. The traditional "Mediterranean diet", recognized by United Nations Educational, Scientific, and Cultural Organization (UNESCO) as an element of the Intangible Cultural Heritage of Humanity, in which olive oil is the main dietary fat, is considered one of the healthiest since it has been associated to the reduction of incidence of cardiovascular diseases and to the prevention of diseases that may be related to oxidative damages [1–6]. Olive tree products are a rich source of valuable and bioactive compounds that possess several nutritional and health properties. Besides, Virgin Olive Oil (VOO) has a delicate aroma and flavor that are highly appreciated by the consumers, being that its consumption is an ancient tradition. Olive oil contains a triglyceride fraction (up to 90–99% of the olive oil) and a non-glycerol or unsaponifiable fraction (0.4–5% of the olive oil), containing this latter several phenolic compounds [7–11]. The consumption of olive oil highly contributes to the daily intake of phenolic compounds [12], including a group of phenolic compounds of the secoiridoid family [13], which is absent in other Mediterranean diet foods, such as fruits, vegetables, and cereals [14]. The complex family of secoiridoids derived from oleuropein and ligstroside, are characterized by the presence of elenolic acid or its derivatives in their molecular structure [7–10,15]. Breakdown products of the major phenolic constituents namely oleuropein and ligstroside aglycones together with hydroxytirosol and tyrosol, form the majority of the phenolic fraction [10,15,16]. Also, the phenolic compounds are exogenous antioxidants that protect food from lipid oxidation and organisms by enhancing their endogenous antioxidant defense system [17]. In fact, in vitro studies showed that the VOO phenols had antimicrobial, anti-inflammatory, or chemopreventive activities on gastric or intestinal cells, which are dose-dependent [18–23]. However, the benefic properties related to the phenolic compounds intake due to VOO consumption is dependent on the concentration of these compounds in the olive oil [19–24]. The olive cultivar the geographical origin and the climacteric conditions [25–31], the agronomic practices [32–39], olive tree diseases [40,41] the maturity of the olive fruit at harvest [42,43], the olive oil extraction [20,31] and filtration [23], and production processes (malaxation, milling, and crushing) [31,36,44–48], the storage conditions and time since harvest, are several of factors that influence the phenolic contents of VOO [14].

Recently, the European Commission (EC) Regulation n°432/2012 regulated the possible use of health claims of olive oils based on their polyphenolic contents and the olive oil daily intake. The regulation states that " … *the claim may be used only for olive oil which contains at least 5 mg of hydroxytyrosol and its derivatives (e.g., oleuropein complex and tyrosol) per 20 g of olive oil. In order to bear the claim information shall be given to the consumer that the beneficial effect is obtained with a daily intake of 20 g of olive oil*" [49].

On the other hand, the intake of other bioactive olive oils compounds, such as α-tocopherol or vitamin E, has also been linked to beneficial health effects, namely at the cardiovascular level, being related to the significantly decrease of the risk of coronary artery disease [50].

Phenolic compounds are also important due to their influence on the sensory attributes of olive oil. The increased demand for high-quality VOO is not only related to the previously mentioned health benefits but also to its unique organoleptic characteristics. The phenolic compounds of the VOO are responsible for the appreciated and desirable bitter and pungent sensations [51–53]. Nevertheless, depending on the bitterness and pungency intensities, these attributes can influence consumer's preferences, being usually appreciated at low to moderate levels, but rejected at high intensities. The health promoting and organoleptic properties of the phenolic compounds led to their use as quality markers for VOO and also as a desirable trait in the selection of new cross-breeding programs [54].

Usually, the determination of the total polyphenolic content is carried out by spectrophotometric [10,55] or chromatographic [56,57] methods. Although most of the official methods for assessing the quality of oils and fats are relatively simple, some of them are time-consuming, quite expensive, often requiring the use of toxic chemicals and solvents as well as of skilled technicians [58,59].Thus, sensor-based techniques coupled with chemometric tools, namely, electronic noses (E-noses), and tongues (E-tongues) have recently emerged as alternative/complementary fast, cost-effective, portable, reliable, and robust approaches for olive oil and olive table chemical and sensory analysis [60,61].

An E-tongue is an analytical tool that includes one or more arrays of non-specific, low selective chemical sensors with partial specificity (cross-sensitivity) to different compounds in solution, usually combined with pattern recognition methods and/or multivariate quantitative approached used for data-processing [62]. Since these devices show an electrochemical response towards the basic taste compounds (i.e., acid, bitter, salty, sweet, and umami sensations), mimicking the responses of the human tongue, they are also known as "taste sensors". In a broader sense, the signal profiles generated (potentiometric, voltammetric, etc.) depend on the solution composition, namely on the capability of establishing electrostatic interactions between the sensors and the compounds present in the solution or due to the redox characteristics of those specific compounds. Similarly, E-noses are bioinspired electronic devices that mimic the biological sense of smell, by using gas sensors or biosensors combined with multivariate statistical tolls, with this concept dating back to 1994 [63].

The type of sensors usually used in E-noses and E-tongues and the detection principles are summarized in Figure 1.

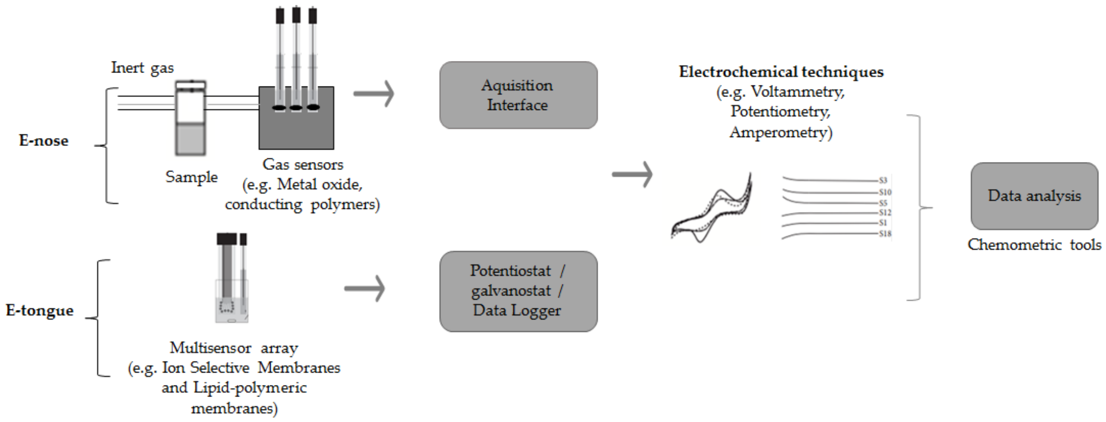


Figure 1. Schematic representation of an electrochemical sensor framework: E-nose and E-tongue devices.

The literature shows that the use of these electrochemical tools has been successfully demonstrated for:

(i) Assessing olive oils' geographical origin, cultivar, chemical, and sensory (positive and negative attributes) characteristics [64–75], which brings benefits for the olive sector due the possible economic impact.

(ii) Monitoring the quality and oxidative resistance of olive oils during storage [76,77], as well as the evaluation of their shelf life [78,79], which is of utmost importance for olive oil producers and consumers, allowing to include a possible "best consume until" information on the label, guaranteeing the olive oil quality during that time-period.

(iii) Detecting olive oil adulterations with other vegetable oils or with low-quality olive oils. The detection of olive oil adulteration is still a challenge due to the diverse composition of cultivars and the drawbacks of existing detection methods [80,81]. The use of E-noses or E-tongues, for olive oil sensory evaluation or olive oil discrimination according to the olive cultivar or geographical origin, olive oil quality and authenticity has been recently reviewed [63,64]. In this context, E-noses [82–84] as well as voltammetric [85,86] and potentiometric [87] E-tongues approaches have been developed.

(iv) Classifying the quality commercial grade of table olives considering the intensity of the sensory defect predominantly perceived (DPP), to quantify the DPP intensity as well as to evaluate table olives' positive gustatory notes (acid, bitter and salty sensations) using a potentiometric E-tongue [88–90].

(v) Quantifying total polyphenolic, flavonoids, and phenolic acids contents in olive oils using voltammetry [91–97], potentiometry [98,99] or amperometry [100,101] as electroanalytical methods.

Since the bioactive compounds present in olive oil contribute for the positive health and sensory attributes, this review aims to compile and discuss the main research findings reported in the literature regarding the use of electrochemical devices, based on bioinspired sensors, which, in combination with chemometric tools, have been developed and applied as practical tools for assessing the bioactive compounds in olive oils and olive fruits.

2. Electrochemical Sensors

2.1. Electrochemical Apparatus

Electrochemical sensors have been widely used in different industries and have been gaining an important space as powerful analysis tools, namely for the pharmaceutical/biomedical and food science and technology fields, as well as in environmental applications.

2.1.1. Electronic Tongue

The E- tongue is an electrochemical device for which several definitions have been proposed in the literature, being the broader accepted definition that proposed by Vlasov et al. [62]. The E-tongue working principle has been inspired in the human recognition of taste sensations. In the human tongue, the information regarding the basic tastes (i.e., acid, bitter, salty, sweet, and umami) is gathered by sensors located in the tongue (in the form of 10,000 taste buds of 50–100 taste cells each), and the information is processed in the human brain (Figure 2a). Similarly, E-tongues (Figure 2b) also gather the overall chemical fingerprint of a specific liquid matrix through an array of non-specific sensors. Then the generated electrochemical profiles are treated using chemometric tools and artificial intelligence to fulfill a similar goal, i.e., to qualitatively or quantitatively evaluate the physicochemical or sensory profile of the sample under analysis and so, to be able to classify the samples according (or not) to a pre-specific attribute or quality [102,103]. Briefly, the E-tongue allows one to generate a set of electrochemical data (e.g., potentiometric, voltammetric, amperometric, etc.), representative of the physicochemical and sensory attributes of a liquid or semi-solid sample, such as food or environmental samples, which, coupled with multivariate statistical tools, may be further used for qualitative and/or quantitative evaluation of the sample matrix of interest [104].

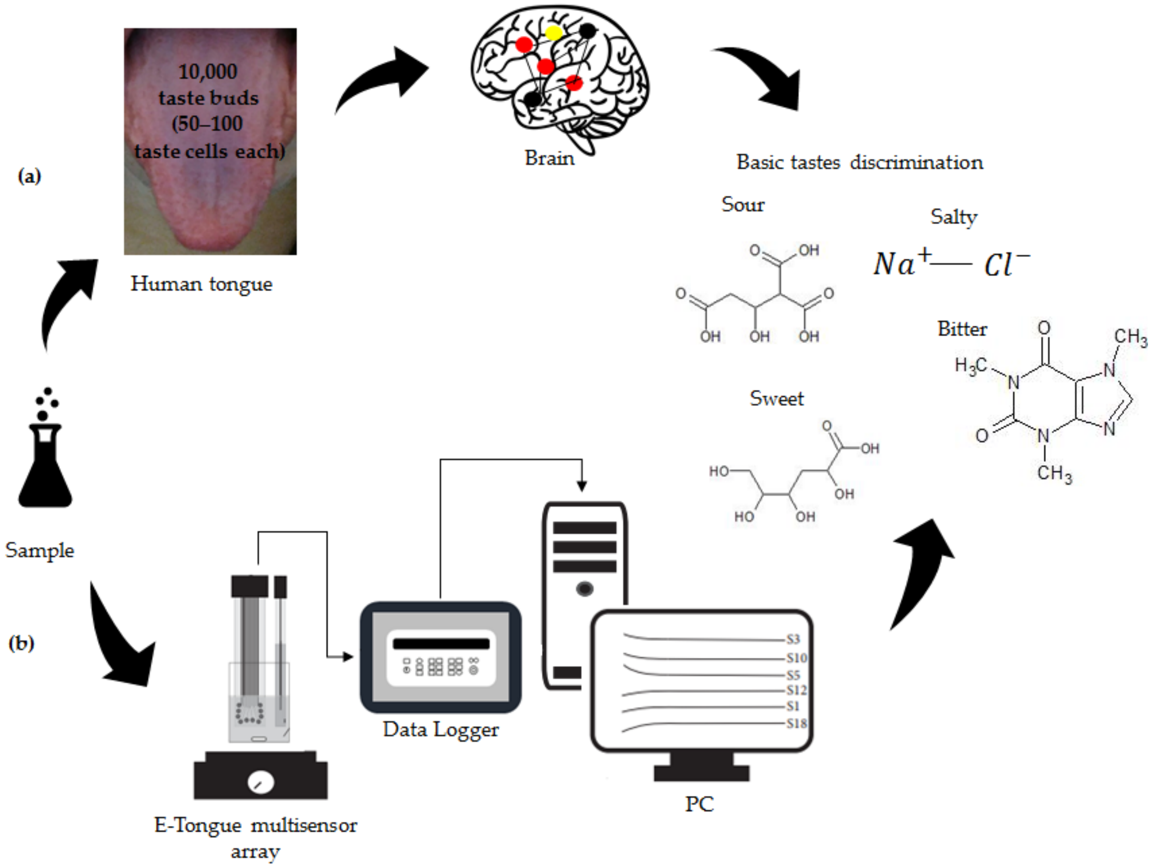


Figure 2. (**a**) Scheme of the taste human recognition framework and (**b**) scheme of an E-tongue working principle.

The first research works reporting the development and use of E-tongues (or taste sensor devices) go back to the 1990's and were mainly focused on the analysis of ions and heavy metals [105,106], taste sensations [107], and spoilage [108] of food products.

2.1.2. E-nose

The term "electronic nose" (E-nose) was first used in 1994 by Gardner and Bartlett [63]. The E-nose allows obtaining a digital signature of a sample, which is accomplished by applying pattern recognition methods, instead of delivering specific information of the sample composition.

The E-nose includes three major instrumental components: (i) a sample delivery system; (ii) a detection system; and (iii) a data acquisition/processing computing system. The sample delivery system allows obtaining a gas sample containing the volatile compounds of the sample. This headspace is then injected or put in contact with a detection system, which is the "reactive" part of the instrument, consisting of a multi-sensor array. When the sensor array is in contact with the volatile compounds, the sensors suffer a chemical interaction leading to a change of electrical properties of the sensor membrane. In the majority of the E-nose systems, an array of sensors is used, being each sensor sensitive to most of the volatile molecules, although showing different sensitivities. The specific response is recorded by the electronic interface being the signal transformed into a digital value. The recorded data are then computed using appropriate statistical multivariate tools [109].

2.2. Electrochemical Principles

According to the type of signal transduction, electrochemical sensors can use different modes of detection being the most common the potentiometric and voltammetric ones. Each detection principle requires a specific design of the electrochemical cell, being the potentiometric and voltammetric sensors the most used for food analysis.

2.2.1. Potentiometric Sensors

Potentiometric sensors operate at thermodynamic equilibrium conditions. The equilibrium potential of an indicator electrode is measured against a selected reference electrode at zero current using a high impedance millivoltmeter.

When using potentiometric sensors, the analytical data is gathered after converting the recognition process into a potential signal, which is logarithmically proportional to the concentration (activity) of the species analyzed during the recognition process. The Nernst Equation (1) logarithmically relates the electrode potential measured between the indicator electrode and the reference electrode, E, to the relative activities of the species to be analyzed:

$$E = constant + \frac{RT}{nF} \ln a_M \tag{1}$$

Where the *constant* includes the standard electrode potential (quoted relative to the idealized Standard Hydrogen Electrode) and the constant potential contribution of the reference electrode, a_M is the activity of the species analyzed, R is the universal gas constant; T is the absolute temperature; F is the Faraday constant; and n is the number of moles of electrons exchanged in the electrochemical reaction [110]. The potential of the indicator electrode is obtained from the equilibrium established at the interfaces of the membrane generated from the differences between the internal interface containing a known fixed concentration (if it has an internal solution) and the external interface, the unknown concentration of the sample solution to be determined. Considering the fixed sample solution's ionic strength, resulting from adding an inert salt with high concentration, the activity coefficient of any ion present in the sample is fixed, allowing to determine the concentration, [M], directly, as in the following equation:

$$E = constant + \frac{RT}{nF} \ln[M] \tag{2}$$

Polymeric membranes have been widely used as the chemical recognition elements in the design of chemical sensors. Ionophores are often incorporated into the polymeric membranes aiming to increase the selectivity and the fairly low partition of the hydrophilic ions into the lipophilic membrane phase. The ionophores are mobile lipophilic, organic or inorganic substances with electrically neutral or charged character, that allow a selective interaction with the analyte ions through the establishment of electrostatic interactions [111]. Two kinds of interactions may occur, namely covalent (very stable [112]) and non-covalent (weaker electrostatic interactions and hydrogen bonds [113]). In this case, a large number of functional monomers is randomly grafted in the matrix. The non-covalent approach has been the most used due to its simplicity and re-usable character, allowing an easy removal of the adsorbed analyte [114].

The polymeric membrane response mechanism is determined by its chemical composition. A direct chemical interaction is established between the ionophore and the analyte ion, mediating the ion transport from the liquid sample to the outer phase boundary of the membrane. The ion extraction is limited to the membrane/aqueous solution interface due to the electroneutrality principle. If the membrane is selective to the analyte ion of interest, the analyte ion is partitioned into the outer phase boundary of the membrane generating a potential difference [111]. This membrane is used as the chemical recognition element for constructing potentiometric sensors. In the literature, it is possible to find potentiometric sensors comprising ion-selective membranes (ISMs) [115] and/or cross-sensitive membranes. The cross-sensitivity is related to the capability of a sensor to respond to different analytes in solution and/or to produce a stable integrated response when multicomponent solutions are being analyzed [62].

2.2.2. Voltammetric Sensors

Voltammetry is based on the premise that the current is linearly dependent of the concentration of the electroactive species (analyte) involved in a chemical or biological recognition process (at a scanned or fixed potential), implying a varying voltage. Among the different voltammetric techniques the most commonly used are the cyclic voltammetry (CV), the square wave voltammetry (SWV) and the differential pulse voltammetry (DPV) [116,117]. Amperometry can be seen as a sub-class of voltammetry in which, during the analysis, the electrode is held at a constant potential during several periods of time. However, with the raising of new potentiostats, the instrumental differences between these two techniques has been substantially reduced [118].

The majority of the voltammetric techniques are based on the use of mercury, carbonaceous materials and noble metals as working electrodes (WEs). The toxicity of mercury combined with some limitations related to its use has led to the elimination of its usage. Carbon–based WEs include all allotropic forms of carbons (graphite, glassy carbon, amorphous carbon, fullerenes, and nanotubes), Nowadays, most electrochemical sensors employ screen-printed carbon-paste electrodes as the WE. Nowadays, the use of novel materials, especially nanomaterials, has gained an increased interest within the design of new electrochemical sensors [119,120].

Cyclic Voltammetry

Cyclic voltammetry (CV) is the most frequently used technique for the qualitative evaluation of the properties and characteristics of an electrochemical process. With CV, it is possible to obtain information regarding the thermodynamics of the redox processes and kinetics of heterogeneous electron-transfer reactions, as well as on coupled chemical reactions or adsorption processes. It consists of measuring the current change in a WE (in an unstirred solution) using a triangular potential waveform scanning. Single or multiple scan cycles can be used. The potentiostat/galvanostat measures the current generated by the redox process resulting on a plot of the current versus the applied potential [121–123]. Figure 3a (reprinted with permission from [97] ©Elsevier, Amsterdam, The Netherlands, 2018) shows an example of the CV curve obtained by Enache et al. [97] regarding the analysis of the total phenol contents of VOO using screen-printed electrodes.

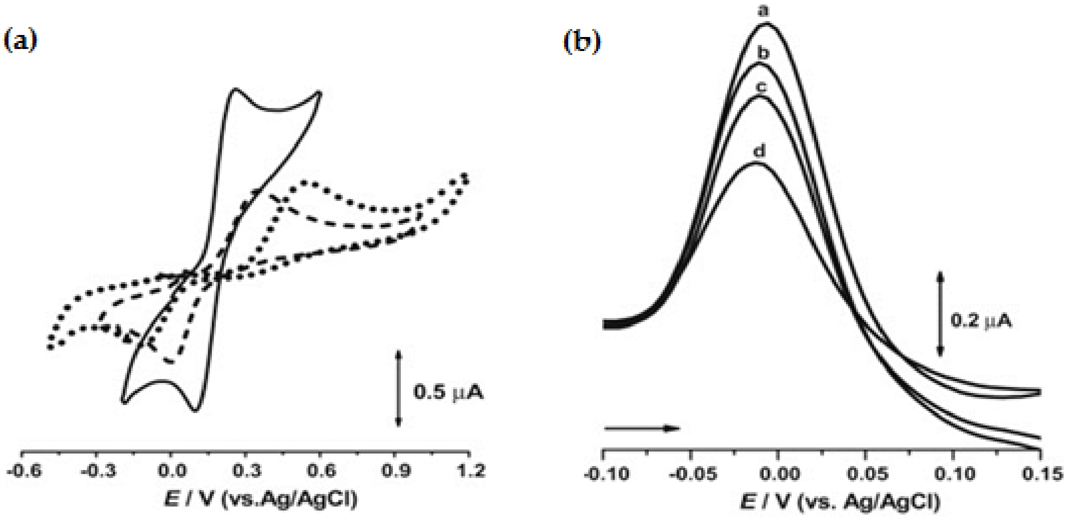


Figure 3. (**a**) Cyclic voltammograms of 50 μM catechol in 0.1 M phosphate buffer (pH = 7.0) using three different activation procedures. (**b**) Square wave voltammograms of 10 μM HT in 0.1 M phosphate buffer (pH = 7.0) using screen printed electrodes in the presence of mono-phenols: **a**-0, **b**-10 μM phenol + 10 μM tyrosol, **c**-30 μM phenol + 30 μM tyrosol and **d**-50 μM phenol + 50 μM tyrosol (adapted with permission from [97] ©Elsevier, Amsterdam, The Netherlands, 2018).

Square Wave Voltammetry

Square Wave Voltammetry (SWV) is a large-amplitude differential technique in which the applied potential follows a symmetrical square wave, superimposed on a base staircase potential, at the WE [124]. This technique exhibits an excellent sensitivity since the net current is larger than either the forward or the reverse components. Indeed, the SWV net current is higher than that of differential pulse voltammetry (in which the no reverse current is used), being possible to attain very low detection limits (~1 × 10^{-8} M) [80]. Figure 3b (reprinted with permission from [97] ©Elsevier, Amsterdam, The Netherlands, 2018) shows an example of SWV curves during the analysis of phenol compounds, usually found in olive oils [103].

Differential Pulse Voltammetry

In differential pulse voltammetry (DPV), fixed-magnitude pulses are superimposed on a linear potential ramp. The current intensity is measured before each potential change and its current difference is plotted versus the applied potential. The pulse length usually is set equal to 40 or 60 ms, and the interval between pulses varies from 0.5 to 5 s. By sampling the current just before the potential change, the amount of capacitive current (from the charging of the electrochemical double layer) is minimized in the current measurement [125]. Figure 4 (reprinted with permission from [126] ©Elsevier, Amsterdam, The Netherlands, 2018) shows an example of differential pulse voltammograms reported by Vasilescu et al. [126] for (a) 0.1 mol L^{-1} tetrabutylammonium tetrafluoroborate (TBATFB)/Methanol and (b) 0.033 mol L^{-1} KCl/Methanol. In this case, and according to the authors, the analytical parameters of the method were optimized using DPV since it was more sensitive compared to CV.

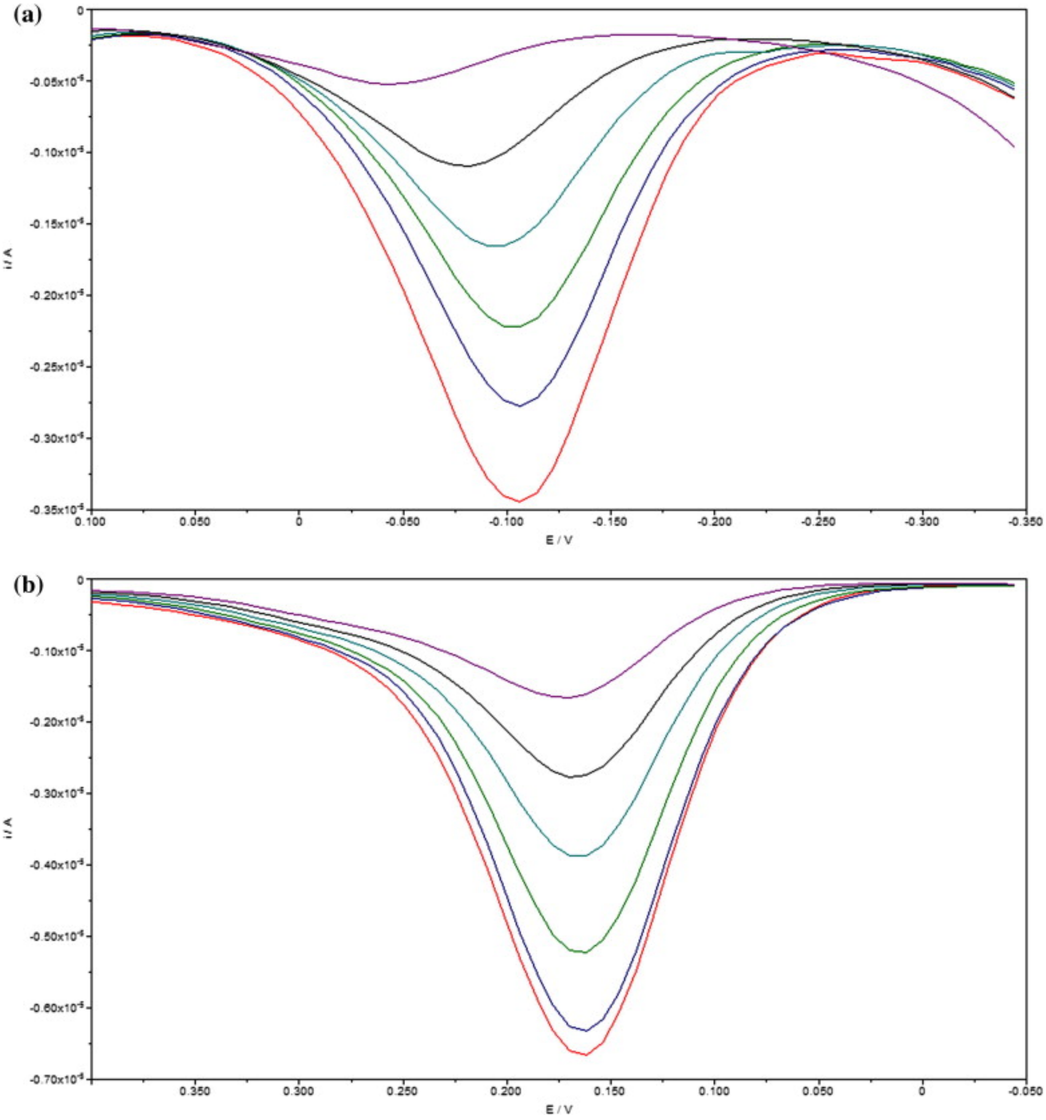


Figure 4. Differential pulse voltammograms for 1 mmol L^{-1} of 2,2′-diphenyl-1-picrylhidrazyl free radical (DPPH•) solution in the presence of different concentrations of α-tocopherol, measured at Pt-SPE in (**a**) 0.1 mol L^{-1} TBATFB/Methanol and (**b**) 0.033 mol L^{-1} KCl/Methanol (reprinted with permission from [126] ©Elsevier, Amsterdam, The Netherlands, 2018).

2.3. Data Processing–Chemometric Methods

Chemometrics was initially defined as the science of obtaining information from chemical systems by using data mathematical modeling [127]. More recently, Massart and co-workers suggested a wider definition: " … *chemometrics is a chemical discipline that uses mathematics, statistics and formal logic (a) to design or select optimal experimental procedures; (b) to provide maximum relevant chemical information by analyzing chemical data; and (c) to obtain knowledge about chemical systems*" [128].

Thus, chemometrics is an inter-disciplinary field that combines multivariate statistics, mathematics and computer sciences for chemical data analysis. Both qualitative and quantitative approaches are under the scope of chemometrics as well as the design of experiments (DOE) [129].

The use of electrochemical methods and especially E-sensor devices results in a dataset of signals, which may be not necessarily specific of any particular chemical species. Instead, the pattern of responses generated is, in some cases, when non-specific cross-sensitivity sensor membranes are used, an electrochemical fingerprint of the sample under study. This pattern can be related to certain features or characteristics of the sample by means of chemometric tools [73]. In some cases, feature extraction strategies or data preprocessing methods must be applied in order to transform an initial larger redundant and complex dataset into a better and reduced data input, which may be achieved by applying pattern recognition tools or variable selection algorithms [130]. Indeed, heuristic or meta-heuristic variable selection algorithms are frequently used allowing reducing the number of variables to be included in the final regression/predictive qualitative or quantitative statistical models, enabling minimizing noise effects or overcoming signal collinearity issues. Afterwards, E-tongue/nose devices are then combined with linear and non-linear qualitative and quantitative techniques, which enable verifying the capability and versatility of these electrochemical devices.

Amongst the available linear pattern recognition approaches [131], Principal Component Analysis (PCA) [91,92,94,95,98,124,132,133], K-Nearest Neighbor (KNN) [134] and Linear Discriminant Analysis (LDA) [97,99,132] are widely applied. For quantitative assessment [131], Multiple Linear Regression (MLR) [100], Principal Component Regression (PCR) [77] and Partial Least-Squares (PLS) [91–93,95,100,122,132,133,135] models are often used. Regarding qualitative and/or quantitative non-linear strategies, Artificial Neural Networks (ANNs) are the most common approaches [134]. Figure 5 summarizes some statistical chemometrics methods commonly used for E-devices data processing.

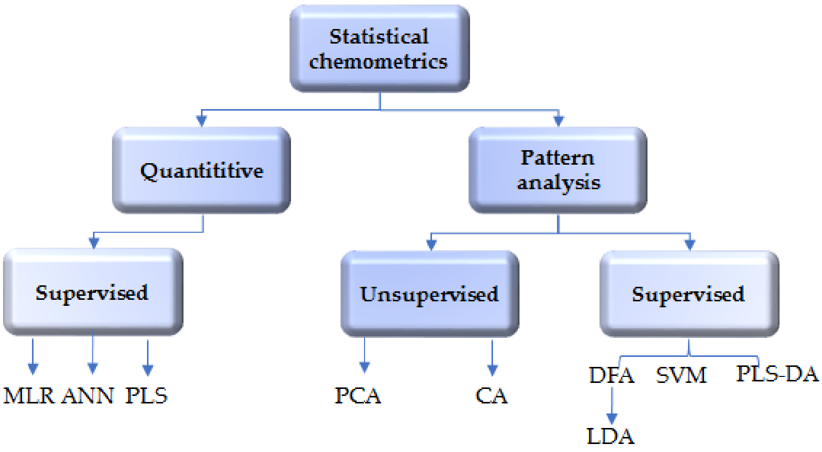


Figure 5. Statistical chemometric methods for data processing (MLR: multiple linear regression, PLS: partial least squares, PCA: principal component analysis, CA: cluster analysis, DFA: discriminant function analysis, LDA: linear discriminant analysis, ANN: Artificial neural networks, SVM: support vector machine, PCR: principal component regression, PLS-DA: partial least squares - discriminant analysis).

3. Bioactive Compounds of VOO

Among vegetable oils, virgin olive oils (VOO) and extra-virgin olive oils (EVOO) possess high contents of minor compounds extracted from the live fruits, due to the absence of refining, which have known bioactive properties. These minor compounds include polar phenols and their derivatives, and non-polar (unsaponifiable) compounds, such as squalene and other triterpenes, sterols, tocopherols (e.g., α-, β- and γ-tocopherols), and pigments (e.g., β-carotene and chlorophylls). Olive oil bioactive compounds, including polyphenols, tocopherols, and pigments, are being intensively studied aiming to evaluate their effects on health as well as their impact at a nutritional level. Indeed, the recognized antioxidant activity of VOO is mainly attributed to the presence of carotenoids and phenolic compounds [1–6,136,137].

3.1. Phenolic Compounds of VOO

The polar phenolic fraction of olive oils contains different chemical compounds that can be grouped into five phenolic groups, namely, phenolic alcohols, flavonoids, secoiridoids aglycons derivatives, dihydroxybenzoic acids derivatives, and phenolic acids. These compounds are responsible for the antioxidant capacity and health-promoting properties attributed to VOO [138]. Thus, in the last years several review papers have focused on the nutritional properties of the phenolic compounds of VOO [139–147]. Figure 6 shows the molecular formulas of selected phenolic compounds which may be found in VOO, from each of the referred five phenolic groups.

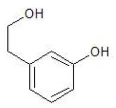
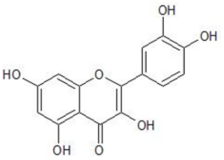
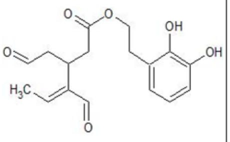
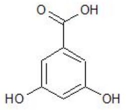
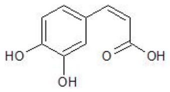
Phenolic Alcohol	**Flavonoid**	**Secoiridoid Aglycon**	**Dihydroxybenzoic Acid**	**Phenolic Acid**
				
Name: Tyrosol **Molecular formula:** $C_8H_{10}O_2$	**Name:** Quercetin **Molecular formula:** $C_{15}H_{10}O_7$	**Name:** Oleuropein-aglycone di-aldehyde **Molecular formula:** $C_{17}H_{20}O_6$	**Name:** 3,5 Dihydroxybenzoic **Molecular formula:** $C_7H_6O_4$	**Name:** Caffeic Acid **Molecular formula:** $C_9H_8O_4$

Figure 6. Molecular formulas of Virgin Olive Oil (VOO) phenolic compounds.

The phenolic compounds capability to donate an electron or hydrogen from the phenolic hydroxyl groups, resulting a phenoxy radical that tends to be less reactive because of electron delocalization in the aromatic ring, explains their antioxidant properties. It also explains the possibility of carrying out their analysis using electrochemical devices based, for example, on the voltammetric detection principle. Indeed, polyphenols are redox-active compounds. On the other hand, potentiometric devices may comprise arrays of lipid-polymeric membranes with both negative and positive polarities as well as with polar and non-polar regions. This fact allows the establishment of electrostatic or hydrophobic interactions between the sensor membranes and the phenolic compounds (or other polar compounds) enabling their potentiometric assessment. For example, the use of a plasticizer and a polymer matrix with low dielectric constant favors the detection mechanism making the signal more stable [111]. As previously reported, lipid-polymeric membranes comprising different combinations of lipid additives (e.g., methyltrioctylammonium chloride, oleic acid, oleyl alcohol, and octadecylamine) and plasticizers (e.g., bis(1-butylpentyl) adipate, dibutyl sebacate, dioctyl phenylphosphonate, 2-nitrophenyl-octylether, and tris(2-ethylhexyl)phosphate) were able to detect and quantitatively interact with different chemical compounds including phenolic aldehydes, esters, alcohol, and aldehydes [71], acids, salts, caffeine, and quinine [88,89]. Moreover, the sensor-analyte interaction may be enhanced by functionalizing the membranes with electrocatalytic activity materials or nanomaterials, or by using nanostructured thin films.

3.2. Other Bioactive Compounds of VOO

Besides the hydrosoluble phenolics, other lipophilic phenolics, like vitamin E, are also relevant from a nutritional and health point of view. In olive oils, α-tocopherol is the main contributor for the vitamin E concentrations, which may vary between 1.2 to 43 mg/100 g [148–150]. Indeed, one tablespoon of olive oil may contain 1.9 mg of vitamin E, which is 10% of the daily intake amount of a 2000-calorie diet. Obviously, like with other compounds, the amounts of tocopherols, and so, of vitamin E, present in olive oil depend of several factors, like agro-climacteric conditions, olive cultivar, and olive oil age [148–150].

The virgin olive oil colour may vary from greenish-yellow to gold, depending on the olive maturation level. Colour is an organoleptic parameter of VOO influencing the consumer's perception of quality. Chlorophylls and carotenoids are the main pigments responsible for VOO colour. During VOO storage, chlorophyll undergoes specific changes leading to changes of the pigment profile usually associated with recently extracted VOO [151] with chlorophyll pheophytinization, already initiated during the extraction process, as a consequence of the released acidity. As to carotenoids, lutein is the major component, followed by β-carotene. Lutein has antioxidant activity and contributes for preventing age-related macular degeneration and cataract formation [152].

Several factors may influence the chlorophyll and carotenoid composition, such as the olive fruit variety, the geographical origin, the degree of fruit ripeness, the extraction process, and the storage conditions of the oil [153]. Additionally, chlorophylls and carotenoids greatly influence the VOO stability, due to their antioxidant nature in the dark and pro-oxidant activity in the light, which levels found in the oils dependent on their concentration in the fruit [154,155]. Below, Figure 7 presents the molecular formulas of selected bioactive compounds, in which may be found in VOO, namely α-tocopherol and Lutein.

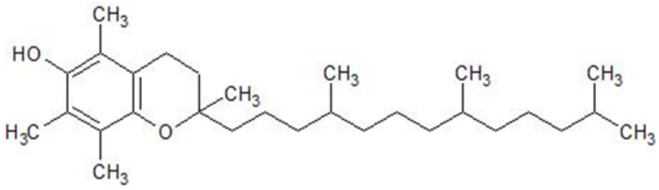
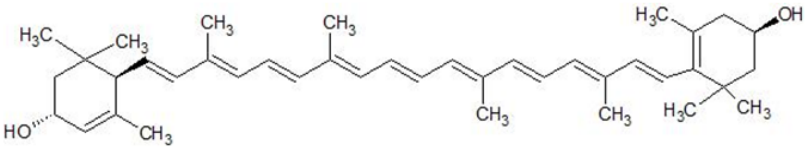
	**Name: α-tocopherol** **Molecular formula:** **$C_{29}H_{50}O_2$**
	**Name: Lutein** **Molecular formula:** **$C_{40}H_{56}O_2$**

Figure 7. Molecular formulas of Virgin Olive Oil (VOO) bioactive compounds.

As described in the previous section, it can be seen through the chemical structure shown in Figure 7, that these bioactive compounds have the common capability to donate an electron or hydrogen from the phenolic hydroxyl groups, resulting in a stable phenoxy radical, with an unpaired electron on the oxygen atom, that tends to be less reactive [156] (less likely to initiate further chain reactions) compared to the initial structure, because of electron delocalization in the aromatic ring, explaining their antioxidant properties as well as the possibility of carrying out their analysis using electrochemical devices.

For this reason, numerous researches have been carried out, searching for new analytical devices and techniques, aiming to develop fast, accurate, green, and user-friendly tools for assessing the quality grade of VOO, namely in which concerns their composition in bioactive compounds, mainly responsible for the organoleptic, healthy, and nutritional properties of the olive oils.

4. Electrochemical Evaluation of Olive Oils Bioactive Compounds: Applications

In the last years, multisensor devices, based on electrochemical detection principles, have been developed and used for olive oil analysis including assessing olive oils' geographical origin olive cultivar, chemical and sensory (positive and negative attributes) quality [64–75], monitoring olive oil quality physicochemical changes during storage [77–80], and detecting olive oil adulterations [81–84,87]. On the other hand, these devices have also been applied for assessing the levels of bioactive compounds in olive oils, which have been related with positive sensory attributes, health and nutritional effects, contributing to the olive oil recognized richness.

Table 1 summarizes the current literature on electrochemical tools (amperometric, potentiometric, or voltammetric E-noses and E-tongues) used in the identification and/or quantification of bioactive compounds in olive oils, namely phenolic compounds, tocopherols, carotenoids, and chlorophyll derivatives, as well as the chemometric tools used in each case.

Table 1. Summary of the current literature on electrochemical tools used evaluation of bioactive compounds in olive oils.

Electrochemical Methods	Apparatus	Techniques	Electrochemical Data Analysis	Application	Results	Reference
Amperometry	Electrochemical cell	Flow injection system	PLS	Evaluation of the bitter taste intensity of monovarietal EVOOs using amperometric detection at two fixed potentials (+0.4 and +0.9 V).	Amperometric signal at + 0.9 V was correlated with the total phenols contents of the samples (R^2 = 0.810) Amperometric signal at + 0.4 V was correlated with oleuropein aglycone (3,4 DHPEA-EDA) contents (R^2 = 0.790).	[100]
Potentiometry	E-tongue	Lipid polymeric membranes	PCA LDA-SA	Determination of olive oil total phenolic contents and sensory sensations trends during oven and microwave heating processes.	Bitter, pungent, fruity and green sensations intensities showed linear trends with the total phenolic contents (0.8075 ≤ *R*-Pearson ≤ 0.9694) LDA sensitivities of 94 ± 4%, for repeated *K*-fold cross-validation (internal-validation procedure). The total phenolic concentrations range from: 304 ± 83 to 581 ± 100 mg caffeic acid/kg olive oil.	[98]
Potentiometry	E-tongue	Lipid polymeric membranes	MLR-SA	Assessing phenolic and volatile compounds of Arbequina EVOO.	Satisfactory E-tongue-MLR-SA correlation coefficients for the phenolic contents of olive oils: $R^2 \geq 0.914$.	[99]
Potentiometry	E-tongue	Polymeric sensor membranes	PCA PLS	Simultaneous numerical assessment of peroxide values, anisidine index and lipophilic phenol contents.	Multivariate regression tools yielded RMSE for cross-validation of: 0.5 meq/kg for peroxide values (R^2 = 0.890); 0.8 arbitrary units for anisidine index (R^2 = 0.67); and, 10 mg/100 g for total tocopherols concentrations (R^2 = 0.830).	[133]
Voltammetry	E-tongue	CV SWV	PCA PLS-DA	Evaluation of EVOO with different degree of bitterness	High correlation between the response of the sensors versus the values of bitterness intensity obtained by a trained sensory panel (R^2 = 0.920).	[95]
Voltammetry	E-tongue	CV SWV	PCA PLS-DA	Discrimination of olive oils bitterness using an array of voltammetric sensors, which allowed analyzing the polyphenolic fraction extracted from the oils.	Linear correlation between: - polyphenolic content vs. traditional chemical analysis (R^2 = 0.990); - voltammetric data vs. the bitterness index obtained by chemical method (R^2 = 0.996); - voltammetric data vs. bitterness values assessed by a sensory panel (R^2 = 0.992).	[94]
Voltammetry	E-tongue	CV	PCA PLS-DA	Discrimination of EVOO with different bitterness degrees.	Quantitative performance of the voltammetric tool: (i) the bitterness perceived by the panelists and the bitterness index obtained from chemical methods, R^2= 0.990; (ii) the bitterness index obtained with the sensors versus the bitterness index obtained by chemical methods, R^2 = 0.997; (iii) the bitterness index assessed by the sensors versus the bitterness perceived by the panelists, R^2 = 0.993.	[122]

Table 1. *Cont.*

Electrochemical Methods	Apparatus	Techniques	Electrochemical Data Analysis	Application	Results	Reference
Voltammetry	Electrochemical cell	CV SWV	LR	Electroanalytical method for the determination of VOO oxidation of ortho-phenols and mono-phenols.	Hydroxytyrosol contents determined: 3 mg/kg for 2-year-old VOO; 6–7 mg/kg for 1-year-old VOO; and 30 mg/kg for fresh VOO. Recoveries: 78–93% for samples spiked with hydroxytyrosol standard.	[97]
Voltammetry	Electrochemical cell	CV	LDA	Evaluation of the hydrophilic phenolic fraction in olive oils.	Working ranges and quantitative performance achieved with the voltammetry device, Caffeic acid: linearity between 0.075 and 2.5 mg L^{-1} (R = 0.998, N = 7) Tyrosol: linearity between 0.075 and 3 mg L^{-1} (R = 0.999, N = 8).	[96]
Voltammetry	Electrochemical cell	CV	PCA PLS-DA	Qualitative and quantitative determination of phenolic compounds found in extra virgin olive oils.	Results of the voltammetric approach obtained for the training and test datasets compared to those obtained by conventional analytical methods: $R^2_{\text{calibration}} = 0.9976$ $R^2_{\text{prediction}} = 0.9884$.	[91]
Voltammetry	Electronic panel system: E-tongue E-nose E-eye	SWV	PCA PLS-DA	Evaluation of different olive cultivars and different degrees of bitterness.	Quantification of polyphenolic contents determined by HPLC, using the proposed voltammetric tool: $R^2 \geq 0.900$	[92]
Voltammetry	Glassy carbon electrode	CV DPV	PLS	Determination of nordihydroguaiaretic acid (synthetic antioxidant) in olive oil due to the migration from the package material, in presence of other natural antioxidants.	Recovery values in the analysis: 97.2 to 106.7%.	[135]
Voltammetry	E-tongue	CV	PCA LDA PLS	Quantification of Free Fatty Acid, chlorophyll and carotenoid content in Portuguese olive oils.	The best models established with the voltammetric data allowed a satisfactory quantification of the chemical parameters, Free Fatty Acid content: R = 0.962 Carotenoids contents: R = 0.923 Chlorophyll contents: R = 0.810	[132]
Voltammetry	Screen-printed electrode	CV DPV	LR	Determination of the antiradical vitamin E properties of commercial olive oils, being the antiradical activity correlated with the lipophilic phenol contents.	Quantitative performance of the voltammetric analytical proposed approach. Concentration range (µmol L^{-1}): α-Tocopherol: 1.00–100.00; $R^2 = 0.995$ δ-Tocopherol: 5.00–150.00; $R^2 = 0.998$ λ-Tocopherol: 5.50–125.00; $R^2 = 0.989$	[126]
Voltammetry/Amperometry	Graphite screen-printed and carbon paste electrodes	CV Flow injection analysis	LR	Detection of o-diphenolic content of phenolic extracts obtained from olive oil samples.	Quantitative performance of the voltammetric procedure developed for catechol: $R^2 = 0.999$. Calibration using the amperometric system for assessing catechol: $R^2 = 0.998$.	[157]

E-tongue: Electronic tongue; E-nose: Electronic nose; E-eye: Electronic eye; CV: Cyclic Voltammetry; SWV: Square Wave Voltammetry; DPV: Differential Pulse Voltammetry; PCA: Principal Component Analysis; LDA: Linear Discriminant Analysis; LR: single Linear Regression; PLS: Partial Least-Squares; MLR: Multiple Linear Regression; HPLC: High performance liquid chromatography; V: Volt; RMSE: root mean square errors.

As can be inferred from Table 1, several works described the application of electrochemical devices for assessing bioactive profile of olive oils, together with tentative estimation of quality (peroxide, anysidine, and free fatty acids) and sensorial perceptions (bitterness index).

Regarding polyphenolic evaluation in olive oils, an array of polypyrrole modified screen-printed electrodes allowed the quantitative discrimination of total polyphenol content in 18 extra virgin olive oil samples [97]. Similar successful results were reported when applying voltammetric E-tongues or combined electrochemical devices, merging voltammetric E-tongues and E-noses. In fact, voltammetric E-tongues were previously successfully applied to assess, in a single assay, the bitterness index of EVOO as well as to quantify the contents of total phenols and phenolic compounds in EVOO, which are directly related to positive sensory attributes [91,92,94,95,97]. Furthermore, the E-tongue combined with an E-nose allowed assessing the levels of total polyphenols, flavonoids, phenolic acids, and other phenolic fractions [96], extracted from EVOO. Indeed, the voltammetric E-tongues quantitative accuracy was similar to the standard spectrophotometric and liquid chromatography techniques.

Potentiometry is an electrochemical technique that has also been used in this research field. For instance, Borges et al. [99] used a potentiometric E-tongue-MLR-SA model to quantify the olive oil polyphenolic compounds. The results obtained by the authors showed that the proposed E-tongue-chemometric approach could be used to quantify the total phenolics, flavonoids, phenolic acids and phenolic alcohols found in Arbequina EVOO. Satisfactory R^2 values ($R^2 \geq 0.914$) were achieved when comparing the predicted phenolic contents based on the E-tongue with the results from the chromatographic conventional technique, confirming the predictive overall quantitative performance of the E-tongue-MLR-SA [99]. In the same work, the authors reported that the E-tongue based strategy should be used with caution for assessing the total contents of certain volatiles families, as alcohols, aldehydes, esters or terpenes, and so, the E-tongue could not be used as an alternative tool to the chromatographic analysis. This less positive performance could be partially attributed to the fact that, contrary to the assessment of the phenolic compounds, which contents are directly related to the concentration found in the liquid extracts, the volatile levels were indirectly evaluated through the analysis of the same liquid extract, which may not be an accurate representation of the olive oil volatile fractions [99].

Olive oils are naturally resistant to thermal oxidation due to their rich composition in monounsaturated fatty acids and phenolic compounds. However, when subjected to high temperatures (from 160 to 190 °C) during prolonged times, they suffer a progressive degradation due to oxidation, hydrolysis, and polymerization reactions [158]. Indeed, triacylglycerols are hydrolyzed, the free fatty acids contents change, peroxide values increase, total polar compounds amounts increase, cyclic fatty acid monomers and low molecular weight volatile aldehydes are formed, the contents of some olive oil phenolic fractions are reduced or completely degraded, and phytosterols are oxidized [158]. For examples, Prata et al. [98] used a homemade potentiometric E-tongue together with multivariate statistical techniques to discriminate EVOOs after subjecting them to different heating cooking procedures, during different time periods. The E-tongue successful performance was tentatively related to the related to the reduction of total phenolic contents and loss of sensory positive sensations after subjecting the olive oils to the different heat-induced processes.

Lately, tocopherols attracted much attention namely due to their antioxidant properties, contributing to the nutraceutical characteristics of foods, such as olive oils effects. On the other hand, the detection of specific tocopherols may be used as authentication/adulteration markers. Indeed, according to Chen et al. [159], λ-tocopherol presence in olive oil is correlated with the fraudulent addition of oils from other sources. Vasilescu et al. [97] used a platinum screen-printed electrode with optimized analytical parameters to determine the antiradical properties of olive oils. These authors also described the development of an electrochemical method based on differential pulse voltammetry (DPV) and using 2,2′-diphenyl-1-picrylhidrazyl free radical (DPPH), which allowed correlating the antiradical activity to the tocopherols contents in olive oils.

Still within the scope of olive oils bioactive compounds, Tahri et al. [132] showed that a multisensor system combined with chemometric techniques, could be satisfactorily used for olive oil discrimination and identification. These authors used a voltammetric electronic tongue to determine chlorophyll and carotenoids content in olive oils. It is interesting to note that, despite being a minority compound, chlorophylls are among the compounds that present more influential parameters in the organoleptic and chemical characteristics of the olive oils.

It should be noticed that, regardless of the satisfactory performances reported by different research groups regarding the applications of electrochemical sensor-based devices for olive oil analysis, the implementation of these devices as routine analytical tools remains far from being a reality. The commercial exploitation of such sensor devices is scarce, being necessary to further demonstrate their advantageous to overcome the skepticism of the olive oil industry. Indeed, for turning electrochemical sensor devices a future trend at the industrial level as well as for the official food control and safety agencies several limitations and drawbacks should be overcome. For instance, some sensor-arrays can only be used as a single-use disposable procedure due to the poisoning of the electrodes/membranes surface [160]. In fact, passivation phenomena may occur due to the adsorption of oxidation products on the sensor surface leading to the formation of non-compact monolayers that highly condition the sensor re-use, since depending on the nature of the target molecules and on the type of sensor membrane, the subsequent desorption may be slow or impossible [161–163]. Besides, signal temperature dependent effects may also be observed, which may condition the in-situ sensors use [163]. In addition, since, the molecular mechanisms explaining the redox properties of some compounds (e.g., phenolics) are still unclear, together with the fact that peak potentials highly depend on the experimental conditions, being sensitive to diffusion coefficients of the analytes, the study of novel samples would require a calibration step for determining key electrochemical parameters [164]. Additionally, when natural samples are being evaluated, the presence of other compounds or natural polymers besides the target analytes could hinder the experimental manipulation and interfere with the interpretation of the sensor signal profiles recorded [165]. Nevertheless, in general, the use of this type of electrochemical devices does not require complex sample pre-treatments, neither complex sensors surface cleaning or polishing steps in order to guarantee the removal of samples leftovers between assays [166,167], showing long-term signal stability and repeatability although some devices may exhibit signal drifts, requiring signal statistical treatments for ensuring drift corrections [168,169]. Indeed, signal drift and signal noise effects constitute a major obstacle that has precluded the wider use of electrochemical devices as routine techniques [169]. Finally, the difficulty of using a single unified calibration model for different devices that are sensitive towards the same analytes or to transfer calibration models from one sensor array or one type of sensor to another, poses a deep limitation to their routine and commercial application [170,171]. In fact, as pointed out by Rudnitskaya [171] the frequent reduced temporal validity of the calibration models, the need of recurrent recalibrations, the temporal signal drift and the sensors' membranes alterations during their use, and the subsequent need of replacing sensors constitute the main obstacles for a broader practical use of these sensor devices. These drawbacks may be partially overcome by implementing drift correction procedures, calibration standardization and calibration update techniques. So, as recently pointed out by Veloso et al. [172] the most relevant challenges in the near future include the capability to design sensor devices able to deliver repeatable electrical or electrochemical signal responses, negligible ageing and temperature effects, as well as a limited or null irreversible binding of substances on the materials used as sensing units. The capacity of overcoming these main drawbacks would allow a broader commercial use of these fast, cost-effective, and user-friendly green analytical devices.

5. Conclusions, Future Trends, and Perspectives

The capability to deal with complex, changing background and diminish the impact of interferents, together with the practical, fast, accurate and green- tool characteristics constitute the main reasons for the relevance of the electrochemical sensors. Different sensing techniques, possible use of unconventional fabrication methods and numerous data treatment procedures indicate that electrochemical tools can be tailored to various application areas. Precise and rapid analysis not requiring skilled trained technicians make them a promising alternative for time-consuming and expensive analytical methods. The electrochemical sensor-based devices discussed in this review are developed for the determination, identification, and quantification of bioactive compounds in olive oils. The fact that these tools are not yet heavily present on an industrial scale makes the food industry still dependent on costly and time-consuming analytical conventional techniques, for sensory analysis, detection, and quantification of olive oil compounds, assessing the individual and overall chemical composition profile as well as for quality control issued. In the coming years, it is expected that the electrochemical sensor devices coupled with chemometric tools may become a recognized practical routine analytical procedure for olive oil analysis, gaining commercial and industrial application.

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