

Review

# Electrochemical Sensors Coupled with Multivariate Statistical Analysis as Screening Tools for Wine Authentication Issues: A Review

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**Abstract:** Consumers are increasingly interested in the characteristics of the products they consume, including aroma, taste, and appearance, and hence, scientific research was conducted in order to develop electronic senses devices that mimic the human senses. Thanks to the utilization of electroanalytical techniques that used various sensors modified with different electroactive materials coupled with pattern recognition methods, artificial senses such as electronic tongues (ETs) are widely applied in food analysis for quality and authenticity approaches. This paper summarizes the applications of electrochemical sensors (voltammetric, amperometric, and potentiometric) coupled with unsupervised and supervised pattern recognition methods (principal components analysis (PCA), linear discriminant analysis (LDA), partial least square (PLS) regression, artificial neural network (ANN)) for wine authenticity assessments including the discrimination of varietal and geographical origins, monitoring the ageing processes, vintage year discrimination, and detection of frauds and adulterations. Different wine electrochemical authentication methodologies covering the electrochemical techniques, electrodes types, functionalization sensitive materials and multivariate statistical analysis are emphasized and the main advantages and disadvantages of using the proposed methodologies for real applications were concluded.

**Keywords:** wine authentication; electrochemical sensor; electronic tongue; multivariate data analysis

## 1. Introduction

Wine is one of the products most often subject to adultery all over the world, even if there are specific and strict regulations that protect its authenticity. Due to the fact that wine adulteration is occurring more and more often and to protect the health of consumers and avoid dishonest competition, which could create an unstable market, there is a need for appropriate analytical approaches that are capable of identifying some changes in the composition of wines induced by adulteration. The determination of wine authenticity through analytical laboratory investigations aims at confirming the inscriptions on the label and is of particular interest to consumers and authorities [1,2].

False declaration of wine geographical origin, variety, and year of production and the addition of exogenous substances represents the common adulteration practices in the wine industry. In order to protect the regional name and varietal labeling of wines, Commission Delegated Regulation (EU) 2019/33 indicated the geographical origins and varieties specific for the major wine-producing countries [3]. Wine marketing strategies associate the image of the product and the perception of quality with a particular region or variety, increasing the importance of regional and varietal characteristics [4]. There is an increasing interest for developing promising analytical methods for controlling wine

geographical and varietal origins and vintage year, and therefore, the research studies addressing these issues are encouraged.

Generally, numerous research papers address the wine authenticity aspects by targeted and nontargeted approaches using different instrumental techniques, including: elemental profile by Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma (ICP) techniques [5,6], isotopic fingerprints by Isotope Ratio Mass Spectrometry (IRMS) [7,8], and different classes of organic compounds (phenolic and volatile compounds, amino acids, organic acids) by different chromatographic techniques alone or coupled with mass spectrometry such as HPLC, HPLC-MS/MS, GC-MS [9–11], nuclear magnetic resonance ( $^1\text{H-NMR}$ ) [12,13], and DNA-based methods [14,15]. These techniques are very selective; therefore the instrumentation is very expensive, and the analytical investigations are time consuming and difficult to automate and implement in routine and on-site applications.

In search of simplicity, simple screening techniques such as UV-Vis spectroscopy [16], FT-IR spectrometry [17], and “electronic tongues” employing electrochemical devices based on different sensors/biosensors designs [18,19], combined with multivariate statistical data analysis (MVA), are used with admissible results to characterize wine produced in specific regions. In this context, electrochemical devices based on sensors and microsensors play an important role assuring fast and reproducible quantitative and qualitative measurement and offering the possibility to be implemented in portable systems [20]. MVA, called chemometrics, is required for the interpretation of screening data by extracting the information about wine quality attributes. The development of qualitative and quantitative MVA models such as PCA, cluster analysis (CA), linear discriminant analysis (LDA), soft independent modeling of class analogy (SIMCA), partial least squares (PLS) regression, etc. in combination with different pre-processing methods permits the discrimination of wines based on specific fingerprints.

In recent years, for the multicomponent qualitative and quantitative analysis of food, more and more attention has been paid to the use of electronic tongue (ET) devices that consist of non-specific cross-selectivity chemical sensor networks coupled to recognition software [21,22]. The principle is based on the construction of databases through the measurement of particular characteristics for a large number of samples and data processing by the use of multivariate analysis. The capability of ET to analyze and discriminate beverages has been reported for mineral waters, milks, teas, wines, or beers [23,24].

Voltammetry, amperometry, and potentiometry are the most used electrochemical techniques in ET devices, representing commonly used electrochemical techniques in analytical chemistry due to their high versatility, simplicity, and robustness [25,26]. Potentiometric measurements consist of the measurement of the oxidation–reduction potentials difference under static conditions, without any external excitation, using a working or indicator electrode and a reference electrode [27]. The most representative working electrodes are the ion-selective electrodes (ISEs) and membrane electrodes [20]. These sensors have good selectivity and sensitivity in particular for the charged chemical species [28].

In voltammetric and amperometric measurements, a potential is applied and depending on the working electrode, the wine electroactive compounds are either oxidized or reduced [29]. The resulted signal represents an overlap of the responses of all wine electroactive compounds that respond at potentials below the applied potential, which leads to a relative low selectivity of these techniques [22].

The performance of electrochemical multisensor systems can be improved by using electrodes chemically modified with electroactive materials, the peaks associated to the oxidation–reduction processes being associated with the analytes present in the test solution and the electroactive material [30]. In order to obtain a variety of electrodes with significant cross-selectivity and complementary electroactive properties that allow obtaining rich information to enhance the modeling capabilities of the signals, a series of modifiers/catalysts were used, including carbonaceous materials (multi- and single-walled carbon nanotubes, carbon microspheres, graphene, etc.) [31], conducting polymers [32,33], nanocomposites [34], metallophthalocyanines [35], and enzymes [36]. Screen-printed electrodes (SPEs) are widely used in various analytical chemistry applications such as biochemistry, medicine,

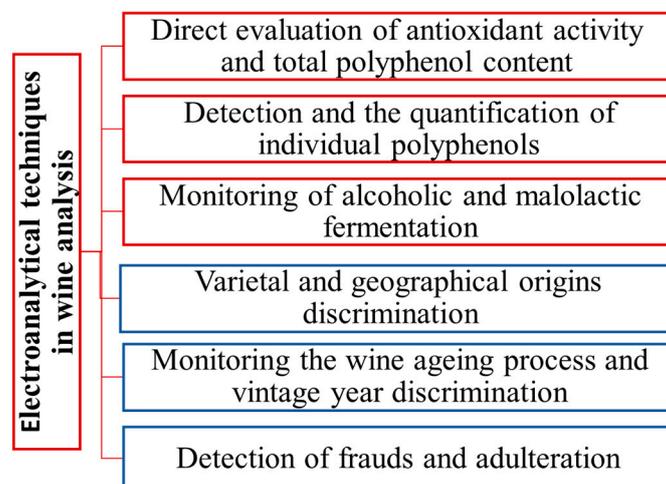
pharmacy, environmental protection, and food science due to their low cost, ease of use, size reduction, lack of contamination, allowing at the same time the development of sensitive, accurate, and high-reproducibility sensors [21,31,37,38]. One of the main challenges in ET is to find the appropriate sensing materials for each particular application, and for that, different complex molecular architectures or improved designs were adopted.

Wines contains numerous redox-active compounds (phenolic antioxidants) that can be oxidized and reduced at the electrode surface, and the resulted electrochemical profiles can be associated to specific wine types by using MVA techniques [18,39]. This review summarizes the main applications of electrochemical techniques for wine authentication assessments in term of varietal and geographical traceability, monitoring the wine aging process, vintage year prediction, and detection of adulteration. Relevant examples of different electrochemical techniques and different sensors functionalized with electroactive materials with enhanced properties coupled with qualitative and quantitative multivariate statistical tools were presented in order to configure a global view about the addressed issues.

## 2. General Consideration Regarding Application of Electrochemical Methodologies in Wine Authentication

Most often, electroanalytical techniques in wine analysis are used for: (1) the direct evaluation of antioxidant activity and total polyphenol content of wines [40–43]; (2) the detection and the quantification of individual polyphenols in wines [40,44,45]; and (3) the monitoring of alcoholic and malolactic fermentation [42], as well as monitoring grape ripening [46,47].

This review focus on the application of electroanalytical techniques for wine authentication in terms of geographical and varietal origins identification, monitoring the wine aging process and vintage year discrimination and detection of frauds and adulteration. Figure 1 indicates the main application of electroanalytical techniques in wine analysis, highlighting with blue color the applications related to wine authentication process, which are discussed in this review.



**Figure 1.** Principal application of electroanalytical techniques in wine analysis.

One of the most used electrochemical techniques in wine analysis is voltammetry, including cyclic voltammetry (CV) [19,48], differential pulse voltammetry (DPV) [49,50], linear sweep voltammetry (LSV) [51], and square wave voltammetry (SWV) [52,53], but potentiometry is used also [54–56].

Some studies indicate that SWV has some advantages versus CV such as the lower time per analysis and simplicity of the data treatment by providing single curves instead of bi-valuated curves [53]. Generally, in practical applications, multiparametric systems known as hybrid ETs consisting of an array of modified electrochemical sensors are preferred for wine discrimination [39,57,58]. Often, the electrochemical responses of ETs is associated with electronic nose (EN) and an e-eye (based on CIE Lab coordinates—CIE is the Commission Internationale de l’Eclairage, L is the luminance, a is the

red-green axis, and b is the blue-yellow axis.) [57], opto-fluidic system [59,60], and chromatographic information [56].

An ET device has the ability to obtain global information about the wine composition (fingerprint), due to their overall selectivity conferred by the utilization of non-specific modified chemical sensors with enhanced cross-sensitivity to numerous wine constituents [61]. Thus, the modification of an electrode surface with sensitive materials with different chemical properties, such as conducting polymers or molecularly imprinted polymers, nanomaterials (nanoparticles (NP) and carbon nanotubes (CNTs)), mediators (phthalocyanines, ferrocene), and biocatalysts (enzymes) allows obtaining complementary information that enhances the capability to discriminate among different wine categories [62,63].

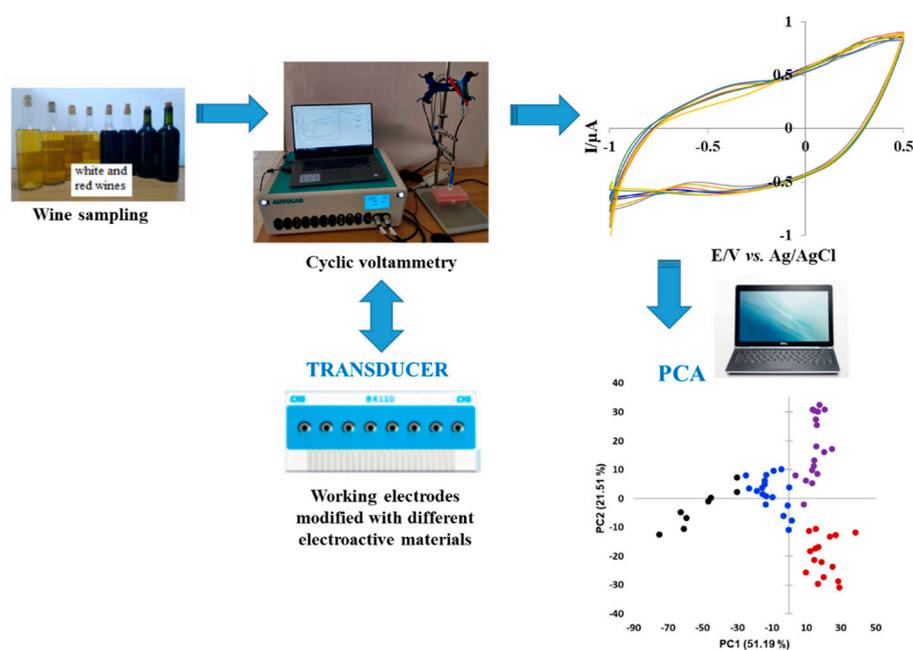
Introducing biosensors in the array can be advantageous, as they can show selectivity toward specific compounds such as phenols or sugars [64]. The specificity toward phenols can be assured by enzymes such as tyrosinase or laccase, while glucose oxidase or fructose dehydrogenase are specific for sugars [47]. The electroactive modifiers can be immobilized in graphite–epoxy electrodes [39], carbon paste electrodes (CPEs) [57,62], glassy carbon (GC) [58,65], thin films [64], or screen-printed carbon electrodes (SPCE) [47,51].

CV is generally used as a first approach to the electrochemical study of wines, giving indications about the redox behavior of the sample by locating the redox potentials of the electroactive species [65]. In the case of voltammetric ET, responses reflect the electrochemical processes that occur at the electrode surfaces, including (1) oxidation–reduction of redox-active molecules (wine antioxidants such as flavanols, flavanol derivatives, phenolic acids, SO<sub>2</sub>, and ascorbic acid) [51], (2) redox processes associated to the oxidation–reduction of the electroactive materials, and (3) diffusion of the counterions between the solution and the bulk material [52]. When no interferences occurs, the information of the anodic and the cathodic waves is complementary in reversible redox processes, the anodic wave being preferred as a data source, providing enhanced performances [53]. Due to the high number of individual oxidizable compounds having close oxidation potentials present in wines, the voltammograms are characterized by broad anodic waves [51]. The intensity and the positions of the redox processes registered in voltammetric experiments depend on the type of analyzed wines, thus making the discrimination of wines with different characteristics possible [57].

For CV measurements, the electrochemical cell consists of a standard three-electrode system including a voltammetric array, a reference double junction Ag/AgCl reference electrode, and a commercial platinum wire counter electrode. Wine samples were measured immediately after opening a bottle and a simple preparation step consisting of filtration and appropriate dilution with electrolytes (1 mM KCl) or synthetic wine is required before the electrochemical measurements of wine samples. Using some electrodes, the measurement procedure can be performed without sample pre-treatment.

In order to obtain stable voltammetric responses and to ensure reproducible ET signals, a conditioning step of the electrodes consisting of the application of several cycles in saline solution (i.e., 10 mM KCl) is required before performing the CV measurements for wine samples [39]. By performing multiple measurements using the same working electrode, some impurities can be adsorbed onto the working electrode surface, which can be removed by electrochemical cleaning or a simple wash with distillate water between each measurement, followed by the equilibration of the electrode in electrolyte solution so as to reach the initial response [39,53]. When glassy carbon, gold electrodes, and platinum electrodes were used, the active surface of the working electrodes must be regenerated by polishing with alumina slurry, followed by sonication in 1 M hydrochloric solution, ethanol, and water, in order to remove the residues [65]. In most cases, when using the SPE for wine analysis, a new sensor must be used for each sample [51].

A schematic illustration of the main steps required for the wine authentication process based on CV measurements with screen-printed electrodes modified with electroactive materials, including wine sampling, multiplexed electrochemical measurements, signal processing, and chemometric analysis is presented in Figure 2.



**Figure 2.** Schematic illustration of the methodology used for wine authentication in the case of ET based on screen-printed electrodes modified with electroactive materials.

The responses generated by the sensor array are not specific for certain wine compounds, but through the use of multivariate analysis, they can be associated with certain characteristics of wines. The electrochemical data that resulted from the ET devices is treated with supervised and unsupervised multivariate advanced tools for either the discrimination or quantification of some parameters [42,66].

As a red wine is a very complex media with many active compounds, the information comprised in the voltammograms is also very complex, and it is difficult to select the best input variables that will be further used for multivariate statistical analysis [53,67]. Thus, for the interpretation of the electrochemical responses, four sequential steps are required: signal pre-processing, dimensionality reduction, prediction, and validation [68].

The signal pre-processing procedures performed before pattern recognition techniques include drift compensation, scaling, and importing the registered currents [39], the extraction of representative parameters by derivatization of the raw signal [51], “bell-shaped-windowing” curves called “kernels” [53,69], and the Fast Fourier Transform (FFT) algorithm [39]. Derivatization of the raw signal greatly enhanced the differences existing across wines, providing representative fingerprints that can be used to discriminate among wine categories [51]. The pre-processing of voltammograms by autoscaling for the normalization of the units and ranges of the variables was followed by “bell-shaped-windowing” curves called the “kernels” technique, which allows capturing the information from the global response to obtain 10 representative values that are used as the input variable for multivariate statistical analysis [50,52,69]. The use of discrete wavelet transform also compresses the original information while keeping the relevant information of the original signals [70].

The dimensionality reduction step is mostly performed by PCA analysis, which projects significant information from multivariate input patterns onto a lower dimensional space (2D or 3D coordinates) consisting of a smaller number of variables called principal components (PCs). The resulted dimensional vectors were further used for the construction of classification and regression models. PCA represents a linear unsupervised exploratory technique that provides a visualization of the variability of the data, being used for checking the interrelationships between the different wine samples based on their chemical characteristics, detecting and interpreting sample patterns, groupings, similarities, or differences [50]. PCA analysis can be performed on raw (untreated) voltammograms or to

pre-processed voltammograms [51,53]. In addition, cluster analysis (CA) represents an unsupervised statistical tool used to establish a set of clusters containing similar objects and objects that are different from those located in another clusters. The resulted information is presented as a two-dimensional plot named a dendrogram [65].

By using classification models, such as LDA, SIMCA, artificial neural networks (ANN), K-nearest neighbors (KNN), and support vector machines (SVM), it is possible to develop a calibration model based on qualitative or quantitative data, which will be used for the identification and classification of unknown wine samples to previously categorized samples [25,70]. LDA analysis is used for the qualitative analysis of the data resulted from linear sensor response, while ANN permits the qualitative and quantitative modeling of the data resulted from non-linear sensor responses and is similar to human pattern recognition [39,49,71]. In order to construct and validate the LDA classification models, the investigated samples were divided randomly into two subsets, namely, a calibration set (containing 2/3 of the samples of each class) used to establish the model and a prediction set (containing 1/3 of samples for each class) used to verify the classification model [65]. Full cross-validation by the “leave-one-out” method is required for the LDA classification models. For ANN analysis, the data must be divided in three sets: a training set, an internal validation set, and an external validation set, which is used for the validation of the proposed model [65]. In SIMCA analysis, PCA models are constructed for each class from the calibration set, which is followed by the definition of the critical distance for classification at the 95% confidence level. Classification of an unknown sample in a certain class is performed by projecting the measurement vector into the proposed model. The KNN algorithm is a linear supervised pattern recognition method in which the samples from the prediction set are classified according to the K-nearest neighbors from the training set.

PLS regression models represent predictive models based on sensor responses and some quantitative parameters determined by another acceptable method [68]. The resulted PLS calibration equation can be applied for the quantification of several chemical and optical parameters of interest in wine quality. PLS regression analysis is mostly coupled with DA analysis resulting in the partial least squares-discriminant analysis (PLS-DA) pattern recognition technique, which is used for the construction and validation of classification models [50,59]. The performance of the PLS-DA classification models is estimated by sensitivity (SENS) and specificity (SPEC).

Different commercial software packages were used for multivariate statistical analysis of the electrochemical data, and the most used are Unscrambler (CAMO, Norway), MATLAB (MathWorks, USA), XLSTAT (Addinsoft, New York, USA), and SPSS (SPSS Inc., Chicago, IL, USA). There are also available commercial ETs such as Taste Sensing Systems commercialized by the company Intelligent Sensor Technology (INSENT) (Kanagawa, Japan), which is used in food analysis, and Astree manufactured by AlphaMOS, which includes ion-selective field effect transistors (ISFETs) that are used in the pharmaceutical industry and less for food analysis [20,72].

### 3. Applications of Electroanalytical Techniques for Wine Authentication

The use of electrochemical techniques for wine authentication in terms of varietal and geographical origins, monitoring the wine aging processes, vintage year discrimination, and detection of adulteration represent research topics mostly addressed in countries such as Spain, Italy, and China, while some studies were performed in Hungary and Russia. The papers reviewed in this manuscript were those published in the last 15 years in the field of electronic tongues based on electrochemical sensors used for the authenticity of wines.

#### 3.1. Discrimination of Wine Varietal and Geographical Origins

Most studies that address the discrimination of wine varietal and geographical origins were performed using ET devices containing different electrodes types (Pt disk, graphite–epoxy, gold, CPE, ion-sensitive field effect transistors (ISFETs) modified with electroactive materials, thus obtaining a complex wine fingerprint. Thanks to the different redox catalytic properties of the modifiers

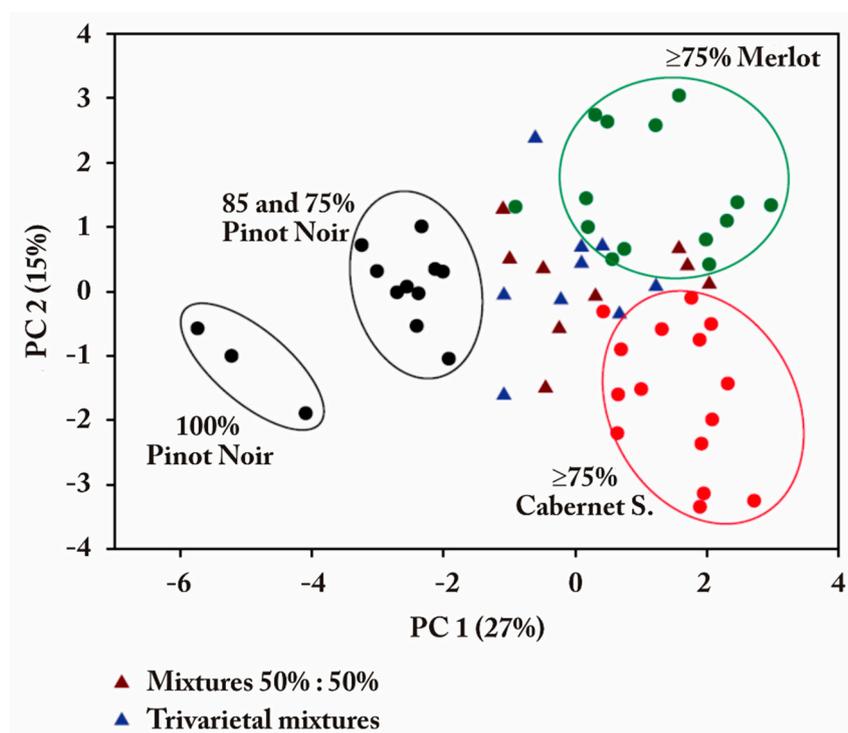
(conducting polymers, phthalocyanine complexes, composite materials, nanoparticles, enzymes, etc.), different oxidation and reduction peaks were obtained at the electrode surface, giving information of the different compounds present on the cava wine. A detailed description of the most representative studies is presented in Table 1.

Different types of Italian red wines of four different varieties (Sangiovese, Lambrusco, Montepulciano, and Primitivo) were classified by the chemometric analysis of voltammetric signals from a Pt disk electrode modified with poly (3,4-ethylenedioxythiophene) (PEDOT) using both DPV and CV techniques. Good classification capabilities were obtained when signals are recorded using DPV as the electrochemical technique. However, accumulating both DPV and CV data does not evidence significant classification improvement due to the large number of variables, making it difficult to extract the useful information [49]. Additionally, a Pt disk electrode modified with a PEDOT conducting polymer, Au and Pt composite materials incorporated in a PEDOT layer, showed excellent classification capabilities for the varietal discrimination of white wines. The modified electrodes were tested separately and coupled to each other in order to check the possible complementarity of the information brought by the different electrodes. Among the used electrodes, the PEDOT-modified electrode leads to the best classification models, giving results, in terms of SENS and SPEC, that are always equal to 100%. Thus, a PEDOT-modified electrode constitutes a convincing candidate as a sensing unit in ETs [50].

Similarly, an ET device consisting of glassy carbon (GC) potentiometric sensors modified with polyvinyl chloride (PVC) membranes doped with Co and Pt porphyrins demonstrate good capabilities for the discrimination of Italian Verdicchio appellation wines produced by different producers in different years. In addition, the proposed ET system has proven the capability to predict wine alcoholic content, volatile acidity, SO<sub>2</sub>, malic and lactic acids, and total polyphenols, which are parameters that were previously determined by classical methods [54].

Different hybrid voltammetric ETs were used for the discrimination of Spanish wines according to geographical and varietal origins or vintage year. The performances of the ET devices for the discrimination and classification of wines is assigned to the use of different sensitive materials deposited on working electrodes, which confer cross-selectivity and reproducibility of the response. Thus, graphite–epoxy electrodes modified with polyaniline, polypyrrole, and metallic nanoparticles in conjunction with chemometrics were used to discriminate different Cava wines [70], and an array of gold voltammetric electrodes modified with conducting polymers, phthalocyanins, and perylenes was used for the discrimination of red wines [69], while CPE sensors modified with rare-earth bisphthalocyanines and in combination with perylenes were used in voltammetric ET devices for the discrimination of Spanish white and red wines [52,53]. The sensor responses measured by CV or SWV were processed by PCA analysis in order to identify different wine categories.

A hybrid ET consisting of an array of different types of sensors: ion-sensitive field effect transistors (ISFETs) modified with polymeric membranes (for pH and Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> ions measurements), Pt sensors (for conductivity and redox potential), and amperometric microelectrodes has demonstrated the capability for the discrimination and classification of white and red wines according to the varietal and geographical origins and to differentiate bi- or trivarietal wine blends containing more than 75% of the main grape variety [20,59]. The monovarietal wines (100%) are discriminated from those containing 85% or 75% of the original grapes and from the bi- and trivarietal blends, which are located between the original groups in the PCA score plan (Figure 3).



**Figure 3.** Representation of the principal components analysis (PCA) results for the 20 triplicate blends of Cabernet Sauvignon, Merlot, and Pinot Noir red wines [20].

Furthermore, this ET system can predict some wine quality control parameters such as total acidity, alcoholic content, and pH, being a useful tool for the winemaking process [60].

In order to obtain the maximum sample information, the same proposed hybrid ET was coupled with a miniaturized optofluidic system and tested for the discrimination of monovarietal and bi- and trivarietal blends prepared from the Catalan white wines varieties and even the geographical origin. PCA, SIMCA, and PLS chemometric tools were used to characterize, classify, and quantify some parameters of interest. Good results are obtained both for discrimination and quantification methodologies, confirming the viability of the multisensor system [73].

A bioelectronic tongue consisting of nanostructured biosensors [64] and an array of electrochemical quartz crystal microbalances (EQCM) sensors functionalized with films containing iron, nickel, and copper phthalocyanines [74] sensible to sugars and polyphenols were tested for the discrimination of musts prepared from different varieties of grapes. Different statistical tools including PCA, PLS, Parallel Factor Analysis (PARAFAC), and Multi-way partial least squares (N-PLS) were used for this purpose. PLS analysis indicated good correlations with total polyphenol index and sugar concentration determined by classical methods.

Even if SPEs are extensively used for the discrimination of different foods, including beer [30,75] and olive oil [23], a few studies report the use of SPEs in the electrochemical experiments for wine authentication. The potential of linear sweep voltammetry (LSV) coupled with disposable screen-printed carbon paste electrochemical sensors for the analysis of the main white wine phenolic compounds as well as for the rapid fingerprinting and classification of white wines from different grape varieties was reported by Ugliano et al. [51].

A commercial device named Alpha ASTREE II (Toulouse, France) based on an IFSET ion-selective sensor array was reported for the discrimination of geographical and varietal origins of Hungarian wines [76]. Based on PLS regression models, some wine chemical parameters were predicted, including total acidity, alcohol content, volatile acidity, and pH.

### 3.2. Monitoring the Aging of Wines and Vintage Year Discrimination

The capability of the electrochemical sensors to predict the wine age is based on the modification induced in the wine phenolic composition due to oxidation and the condensation reaction that occurs during wine aging [56]. Wine polyphenols are labile substances subjected to various chemical transformations during wine-making and wine aging, and therefore, the oxidative aging process is more obvious at the beginning, and later, the process slows down as the body of the wine becomes more and more harmonious [65]. In order to improve the organoleptic characteristics, red wines are aged in oak barrels or using wood chips in micro-oxygenated stainless steel tanks, before bottling. ETs were successfully used to monitor or recognize the method of aging, control the fermentation, and discriminate between wines with different vintage years. The representative studies conducted in this direction are listed in Table 2.

Thus, an electronic panel test composed by an ET, an EN, and an e-eye was used to monitor the aging process of red wine matured by oak barrels or oak chips and micro-oxygenation. The voltammetric ET system consisting of CPEs modified with phthalocyanines and ferrocene, an unmodified CPE, and a platinum electrode demonstrated good discrimination capabilities, similar to those obtained by an EN system [57]. A hybrid ET based on potentiometric and voltammetric sensors was tested to control the wine fermentation process and to detect the wines altered by the improper storage conditions by identifying specific chemical markers [55]. The bioelectronic tongue proposed by Medina-Plaza et al. was used to monitor the ripening process of the grapes in order to identify the optimal date for harvesting [64].

A potentiometric ET multisensor system consisting of 26 potentiometric chemical sensors—plasticized PVC sensors displaying sensitivity to organic anions and phenols (9 sensors) and to organic cations (5 sensors), 11 chalcogenide glass sensors displaying redox response, and a conventional glass pH electrode tongue—has been able to predict the age of 160 Port wines of different ages (from 2 to 70 years) [77] and Madeira wines produced from different varieties of grape and lengths of aging [56]. The results indicated that the ET can predict the age of wines with an accuracy of 5 years for wines aged from 2 to 70 and with the accuracy of 1.8 years for the wines aged from 10 to 35. It is important that the results of age prediction of Port wines using the ET system cannot be automatically transferred to the other types of fortified wines such as Madeira, making it necessary to build new models. For the prediction of age of 14 Madeira wines (3, 6, 10, and 17 years old), the proposed ET multisensor system was associated with HPLC analysis of organic acids and phenolic compounds [56]. The ET device showed discrimination capabilities for the wine's age, but not for the discrimination of variety. PLS calibration models with respect to the wine age were capable of predicting wine age with accuracy in cross-validation of 2.6 and 1.8 years using HPLC and ET data, respectively. The main input to the discrimination of Madeira wines according to their age was from the anion-sensitive electrodes, which display cross-sensitivity to a wide range of phenolic compounds with acidic character such as phenolic acids [56].

A voltammetric ET composed by six bulk-modified graphite–epoxy electrodes was tested for the discrimination of cava wines according to the vintage year through the LDA qualitative classification model [39]. Similarly, ET devices consisting of gold, silver, platinum, palladium, tungsten, and titanium or glassy carbon, gold, and platinum operated by multi-frequency large amplitude pulse voltammetry (MLAPV) and CV techniques were successfully used to discriminate between Chinese rice wines with different marked ages: case 1 (wines with 1, 3, and 5 years) [78] and case 2 (wines with 3, 5, 8 and 10 years) [65]. PCA analysis allowed the discrimination of 5-year-old wines from the wines aged 1 and 3 years [78], while a non-linear BPANN (back-propagation artificial neural network) model was capable of distinguishing between young and older wines, but it was difficult to discriminate between older wines (8 and 10 years) [65].

**Table 1.** Discrimination of varietal and geographical origins.

Country	Wine Samples/Experiment Type	Electrochemical Technique	Working Electrode	Analyzed Parameters	Multivariate Statistical Analysis	Reference
Italy	Discrimination of nine different types of red wines: Sangiovese, Lambrusco, Montepulciano, Primitivo	CV and DPV	Pt disk electrode modified with PEDOT film	Voltammetric fingerprint	PCA PLS-DA	[49]
Italy	Varietal origin of white wines	DPV	Pt disk electrodes modified with PEDOT film with composite materials of Au and Pt nanoparticles	Voltammetric signals	PCA PLD-DA	[50]
Spain	21 sparkling wine (19 Spanish Cava DO and 2 Champagne (French)) from different regions	CV/ET	5 modified graphite–epoxy electrodes (modifiers: nanoparticles of Co and Pt, and conducting polymers (polyaniline and polypyrrole))	Cyclic voltammograms	PCA ANN	[70]
Spain	Denomination of origin, grape variety, and vintage of 12 red wines	CV/hybrid array of voltammetric sensors	voltammetric gold electrodes chemically modified with electroactive materials (conducting polymers, phthalocyanine complexes and perylenes)	Voltammetric fingerprint	PCA PLS-DA SIMCA	[69]
Spain	6 Tempranillo red wines with different DO origins and ageing stages	CV and SWV/sensor array	Carbon paste electrodes (CPEs) modified with rare-earth bisphthalocyaninate compounds (LnPc <sub>2</sub> ): LuPc <sub>2</sub> , GdPc <sub>2</sub> and PrPc <sub>2</sub>	Reproducible anodic and cathodic peaks; Cyclic voltammograms; SWV signals	PCA	[53]
Spain	Varietal origin of white wines (Tempranillo, Garnacha, Turrantes, Viura, and Malvasia)	SWV	Array of carbon paste electrodes (CPE) modified with three rare-earth bisphthalocyanines and three perylenes	voltammetric signals	PCA	[52]
Italy	Verdicchio white wines produced in different locations	Potentiometry	Glassy carbon with PVC solvent polymeric doped with several metallo-porphyrins porphyrin-based membranes	quantitative detection of total SO <sub>2</sub> , Total Polyphenols, Malic and Acetic Acids content	PCA	[54]
Spain	Varietal origin of 11 white wines (Macabeu, Parellada, Chardonnay, Xarello, Picapol) and 12 red wines (Trepal, Garnatxa, Cabernet Sauvignon, and Merlot)	Hybrid electronic tongue based on optical and electrochemical microsensors	The array: six ISFETs potentiometric sensors, a conductivity sensor, a redox potential (ORP) sensor and two amperometric electrodes (Au microelectrode and a microelectrode for sensing electrochemical oxygen demand (EOD)).	pH and Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Cl <sup>-</sup> , and NO <sub>3</sub> <sup>-</sup> ions; conductivity and redox potential (ORP)	PCA	[59]
Spain	18 white wines: 5 Macabeu, 5 Parellada, 4 Chardonnay, and 4 Xarello and 12 wines: 4 Merlot, 3 Cabernet Sauvignon, 3 Grenache and 2 Trepal. Analysis of monovarietal white wines and bi- and trivarietal mixtures	Flow multiparametric system consisting in a hybrid ET and a miniaturized opto-fluidic system	ISFET sensors modified with polymeric membrane, Pt conductivity, and ORP sensors and gold amperometric microelectrodes	pH and Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Cl <sup>-</sup> , and NO <sub>3</sub> <sup>-</sup> ions; conductivity and redox potential (ORP)	PCA SIMCA	[20,73]
Spain	Varietal origin of musts prepared from Tempranillo, Garnacha, Cabernet-Sauvignon, Prieto, Picudo, and Mencia varieties	CV/Array of biosensors	4 voltammetric biosensors based on Langmuir–Blodgett films containing glucose oxidase, D-fructose dehydrogenase, tyrosinase, and laccase, using LuPc <sub>2</sub> as electron mediator and arachidic acid as lipid	Polyphenols Sugars	PCA	[64]

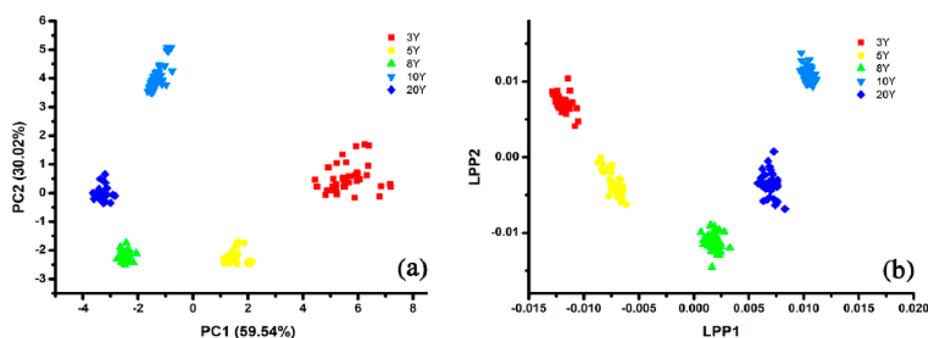
Table 1. Cont.

Country	Wine Samples/Experiment Type	Electrochemical Technique	Working Electrode	Analyzed Parameters	Multivariate Statistical Analysis	Reference
Italy	Varietal origin of commercial white wines (Riesling, Chardonnay, Viognier, Muscadet)	LSV	Screen-printed carbon paste electrode	Voltammetric fingerprint	PCA	[51]
Spain	Red musts: Juan García, Tempranillo, Prieto Picudo, Mencía Regadio, Cabernet, Garnacha	EQCM /Array of EQCM sensors	Pt/quartz crystals modified with iron, nickel, and copper phthalocyanines	voltammetric responses	PARAFAC	[74]
Hungary	Nine white wines with different varietal and geographical origins	Commercial Alpha ASTREE II (Alpha M.O.S., Toulouse, France) potentiometric electronic tongue	7 ISFET potentiometric sensors	Potentiometric responses	PCA LDA PLS	[76]

Table 2. Monitoring of wine aging and vintage year discrimination.

Country	Wine Samples	Electrochemical Technique	Working Electrode	Analyzed Parameters	Multivariate Statistical Analysis	Reference
Spain	Tempranillo red wines aged by different methods during the aging process	CV/ET	6 voltammetric sensors: 4 carbon paste electrodes (CPE) modified with electroactive materials (bisphthalocyanine molecules with lutetium and gadolinium central ions (LuPc <sub>2</sub> ), (GdPc <sub>2</sub> ), cobalt (II) monophthalocyanine (CoPc) and ferrocene), unmodified carbon paste, and platinum electrodes	Voltammetric responses	PCA PLS-DA	[57]
Spain	Tempranillo musts collected from grapes with different maturation stage	CV/Array of biosensors	4 voltammetric biosensors based on Langmuir–Blodgett films containing glucose oxidase, D-fructose dehydrogenase, tyrosinase and laccase, using LuPc <sub>2</sub> as an electron mediator and arachidic acid as lipid	Polyphenols Sugars	PCA	[64]
Spain	160 Port wines of different ages (from 2 to 70 years)	Potentiometric ET multisensor	14 plasticized PVC sensors, 11 chalcogenide glass sensors, and a conventional glass pH electrode	phenols and organic anions cations, redox and pH responses	PCA, PLS	[77]
	40 Madeira mono-varietal wines aged for 3, 6, 10, and 17 years				PCA, ANOVA	[56]
Spain	65 cava wine with different vintage time	CV/ET	6 graphite–epoxy voltammetric sensors made with different modifiers/catalysts: nanoparticles of Co and Pt, conducting polymers (polyaniline and polypyrrole), and cobalt(II) phtalocyanine	Cyclic voltammograms	PCA, LDA, ANN	[39]
China	120 Chinese rice wine of different marked ages (1, 3, and 5 years)	VE-tongue/ MLAPV	6 metallic electrodes (gold, silver, platinum, palladium, tungsten, and titanium)	Voltammetric responses	PCA, CA, PLS, ANN	[78]
China	120 Danyang Chinese rice wine with 3, 5, 8, and 10 marked ages	CV/ portable voltammetric ET	3 working electrodes: glassy carbon, gold, and platinum	Cyclic voltammograms	SIMCA, PLSDA, KNN, BPANN, SVM	[65]
China	200 Guyuelongshan rice wines of 3, 5, 8, 10, and 20 years old	ET and EN	GCE modified with conducting polymer nanocomposites	Voltammetric response	PCA and LPP	[58]

Recently, ET and EN devices, and also a combination of these, were used for the discrimination and classification of wines according to the vintage year. The ET system formed by GCE modified with nanocomposites materials embedded in the conducting polymer matrix demonstrate discrimination capabilities superior to those of EN. As observed in Figure 4, PCA and LPP (locality preserving projections) analyses allowed the discrimination and qualitative classification of wines with different ages, the clusters of each wine category being marked with different colors (3 years—3Y, 5 years—5Y, 8 years—8Y, 10 years—10Y, and 20 years—20Y).



**Figure 4.** PCA scores plot (a) and locality preserving projections (LPP) (b) plots of rice wine samples with different ages (3, 5, 8, 10, and 20 years (Y)) based on original feature data for ET [58].

### 3.3. Detection of Wine Frauds and Adulterations

Wine production must be performed according to the regulations indicated by their appellations and by national and international organisms. However, illegal practices such as dilution with water, the addition of exogenous substances (alcohol, sugars, preservatives, colorants), the use of grapes from different regions, or using forbidden aging methods are performed in order to minimize the costs and increase the profit [64]. In this regard, ETs can be a valuable tool in detecting wine adulteration. Some examples of the common adulteration practices and the proposed strategies for their detection are presented in Table 3.

Thus, an ET composed by a hybrid array of voltammetric CPEs chemically modified with phthalocyanines (3) and a conducting polymer (6), a bare CPE, and an Au disk electrode was used to identify wine adulterations associated with the addition of exogenous substances such as ethanol, tartaric and tannic acids, SO<sub>2</sub>, or sucrose. PCA analysis allowed the distinction between different categories of adulterated wines, while PLS analysis allowed the estimation of wine alcoholic content and acidity [62].

A multisensor array consisting of four thin-film metal oxide sensors surface-activated by Pt, Au, Pd, and Bi metal catalysts, combined to an ANN pattern recognition system has been used to recognize the white, red, and rose wines adulterated with up to 10% methanol and ethanol (1%, 5% and 10%) or adulterated by mixing wines with the same color [79]. The proposed multisensor array exhibits sensitivity for wine volatile compounds, which were sampled by the static headspace technique. The cross-validation of the non-linear pattern recognition system based on ANNs provides an overall accuracy of correct classification for the wine class recognition of 93.3% for wines adulterated with methanol, 70% wines adulterated with ethanol, and 83.3% and 100% for the mixed wines with the same color.

A miniaturized potentiometric ET based on an array of miniaturized potentiometric sensors was evaluated to detect adulterated wines counterfeited with SO<sub>2</sub>, H<sub>2</sub>S, and acetic acid adulterants and to predict the amount of each one [54]. Silicon-based potentiometric sensors prepared by depositing PVC membranes based on metalloporphyrins, corroles, and their analogues on the platinum electrode surface were introduced into a flow-injection cell and used to measure the wine samples. The sensors showed a good stability of response signal and a good reproducibility during several days of measurement. Based on constructed PLS regression models, the sensor array was able to predict low concentrations of H<sub>2</sub>S and SO<sub>2</sub> in adulterated wines, while for acetic acid, the correlation was satisfactory only at higher concentrations.

**Table 3.** Detection of wine frauds and adulterations.

Country	Wine Samples	Electrochemical Technique	Working Electrode	Analyzed Parameters	Multivariate Statistical Analysis	Reference
Spain	Red wines adulterated with ethanol, tartaric and tannic acids, SO <sub>2</sub> , acetic acid, sucrose, and acetaldehyde	CV/hybrid ET	Carbon paste (CPEs) voltammetric electrodes chemically modified with phthalocyanines, and conducting polypyrrole doped with a range of counterions	Voltammetric responses for pH and antioxidants	PCA PLS	[62]
Italy	Wines adulterated with SO <sub>2</sub> , H <sub>2</sub> S, and CH <sub>3</sub> CO <sub>2</sub> H	ET system based on an array of miniaturized potentiometric sensors	Miniaturized potentiometric sensors based on platinum electrode modified with PVC membranes based on metalloporphyrins, corroles, and their analogs	Potentiometric responses	PCA PLS	[54]
Italy	White (2), red (4) and rose (2) wines intentionally adulterated with methanol and ethanol or by mixing same-color wines	Chemoresistive e-tongue	Multisensor array based on four metal oxide semiconducting thin-film chemoresistive sensors (Pt, Au, Pd, and Bi metal catalysts)	Electrical resistance of each chemoresistive sensor	PCA, ANN	[79]
Hungary	Tokaj wines artificially adulterated with grape must concentrate and sucrose	Potentiometric e-tongue	Chemically modified field-effect transistor sensors	Potentiometric responses	PCA, LDA, and PLS	[80]
Russia Italy	Detection of markers of wine organoleptic faults: methionol, isoamyl alcohol, benzaldehyde, and acetic acid in a wide range of concentrations	Potentiometric ET	8 potentiometric chemical sensors obtained by the electrodeposition of substituted porphyrin polymeric coatings on flat Pt working electrodes	Potentiometric responses	PLS PCA SIMCA PLS-DA	[81]

A commercial potentiometric ET (Alpha Astree, Toulouse, France) in conjunction with PCA, LDA, and PLS regression chemometrics was tested for the rapid discrimination of lower grade Tokaj wines, which were artificially adulterated with grape must concentrate (GMC) to reach the sugar content of high-grade Tokaj [80]. The principle of measurement for the ET is based on the difference in the potential changes of several working electrodes (chemically modified field-effect transistor sensors from Alpha MOS (Toulouse, France)) against a reference electrode (Ag/AgCl) in zero-current condition. PCA analysis allowed the separation of non-adulterated wines and wines adulterated with GMC, although the wine sample adulterated with sugar before fermentation appeared to be closer to the non-adulterated wines. Thus, Tokaj wines adulterated with various levels of GMC were rapidly discriminated and classified with 100% accuracy using LDA analysis. However, more studies are required to build stronger models with defined limits of detection that can be adopted by regulatory authorities.

A potentiometric ET consisting of eight porphyrin electropolymer coatings was applied for the quantitative detection of benzaldehyde and isoamyl alcohol adulteration markers associated with the yeast activity and vinegar formation, respectively [81].

#### 4. Conclusions and Perspectives

This paper presents a comprehensive literature review of the most representative papers addressing the wine authenticity assessments in terms of varietal and geographical origins discrimination, monitoring the wine aging processes, vintage years discrimination, and detection of adulteration based on different electrochemical techniques coupled with appropriate pattern recognition methods.

Thanks to the use of different families of sensitive materials with enhanced cross-selectivity, the capability of discrimination of the multisensory systems was considerably improved, making it possible to detect small amounts of exogenous compounds and some chemical characteristics of the wines underlying the discrimination of wine varietal and geographical origins or vintage year.

By handling electrochemical data with appropriate pattern recognition methods, it can be possible to obtain qualitative and quantitative models for wine authentication and the prediction of some wine quality parameters. In order to improve the reliability of the statistical models, it is essential to process a high number of wines covering all the possible sources of variability (different varieties, origins, vintage years, and storage time).

The ET devices could be considered as attractive alternative methods to the sensory panels or classical methods, being suitable for screening purposes and the development of cost-effective wine authentication methodologies, but nevertheless, the vast flexibility of choice among different electrodes types in the electrochemical cell, different instrumental operational parameters, and sample protocol preparation has prevented these methodologies from being used in practical applications to date. In order to appear more convincing for wine authenticity assessment approaches, future research should focus on demonstrating the practical applicability of the authentication electrochemical methodologies for numerous samples, rather than on the development of new sensors and different sensors combinations for wine analysis. Clear protocols should be first implemented, followed by the development of large databases with the electrochemical behavior of different wine types.

Minimal sample preparation, rapidity, measurements in one step, and possibilities for the development of portable equipment and in situ monitoring should be considered as advantages of the electrochemical authentication methodologies, offering the possibility to be used by official organisms to certify the authenticity of wines.

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