




Review

Voltammetric Electronic Tongues in Food Analysis

Clara Pérez-Ràfols ¹, Núria Serrano ^{1,2}, Cristina Ariño ^{1,2}, Miquel Esteban ^{1,2}
and José Manuel Díaz-Cruz ^{1,2,*}

¹ Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, Martí i Franquès 1-11, E08028 Barcelona, Spain; claraperezrafols@ub.edu (C.P.-R.); nuria.serrano@ub.edu (N.S.); cristina.arino@ub.edu (C.A.); miquelEsteban@ub.edu (M.E.)

² Institut de Recerca de l'Aigua (IdRA) of the University of Barcelona. Martí i Franquès 1-11, E08028 Barcelona, Spain

* Correspondence: josemanuel.diaz@ub.edu; Tel.: +34-93-402-1796

Received: 9 September 2019; Accepted: 28 September 2019; Published: 30 September 2019



Abstract: A critical revision is made on recent applications of voltammetric electronic tongues in the field of food analysis. Relevant works are discussed dealing with the discrimination of food samples of different type, origin, age and quality and with the prediction of the concentration of key substances and significant indexes related to food quality.

Keywords: voltammetric electronic tongues; food analysis; food authentication

1. Introduction

Electronic noses and electronic tongues are bioinspired devices created during the 1980's as a successful encounter of electronics and electrochemistry with chemometrics. As suggested by their names, they try to mimic the ability of human noses and human tongues to identify characteristic odors and tastes [1–6]. For this purpose, an array of non-specific sensors is used to mimic the role of the diverse bio-receptors present in the human nose/tongue and a chemometric model is used to mimic the processing of the bio-receptor's signals by the human brain, as Figure 1 shows. Regarding the sensors, they must present different sensitivities (cross response) with respect to the substances related to the odor/taste, so that these sensors are able to provide complementary, non-redundant information. As for chemometric models, they can be used to classify the samples (e.g., according to different protected designations of origin, PDO) or to quantitatively determine the concentrations of target species (e.g., major components, adulterants, pollutants) or the values of parameters related to some food properties (e.g., antioxidant capacity, bitterness).

Although electronic noses and tongues are employed in many research fields such as environmental monitoring [7], pharmacy [8] or biotechnology [9], these devices have been mostly focused on food analysis [10–13]. This is not strange, since they try to mimic human noses and tongues, which are frequently busy smelling and tasting food products. As a consequence, a large number of works have been published in recent years dealing about the application of electronic noses and tongues to food analysis, as the reviews in [10–13] show.

In this work we will focus on voltammetric electronic tongues, proposed by Winqvist et al. in 1997 [14] as an alternative/complement to the existing potentiometric electronic tongues, mostly based on measurements with ion-selective electrodes and frequently applied in food analysis [12]. Figure 1 shows an example of voltammetric electronic tongue constituted by three screen-printed devices acting as sensing units. Although every screen-printed unit includes all electrodes needed for a voltammetric measurement (working, reference and auxiliary), the tongue shown in the picture also has conventional reference and auxiliary electrodes for a more accurate control of the potential applied.

Then, a multichannel potentiostat simultaneously registers the current of the three working electrodes of the screen-printed devices as a function of the potential. The voltammograms measured by all three sensors (depicted in blue, green and red) are integrated into a data matrix (where the position of the datasets coming from the different sensors is indicated with the same colors). Then, the matrix is submitted to a chemometric strategy to get qualitative and/or quantitative information.

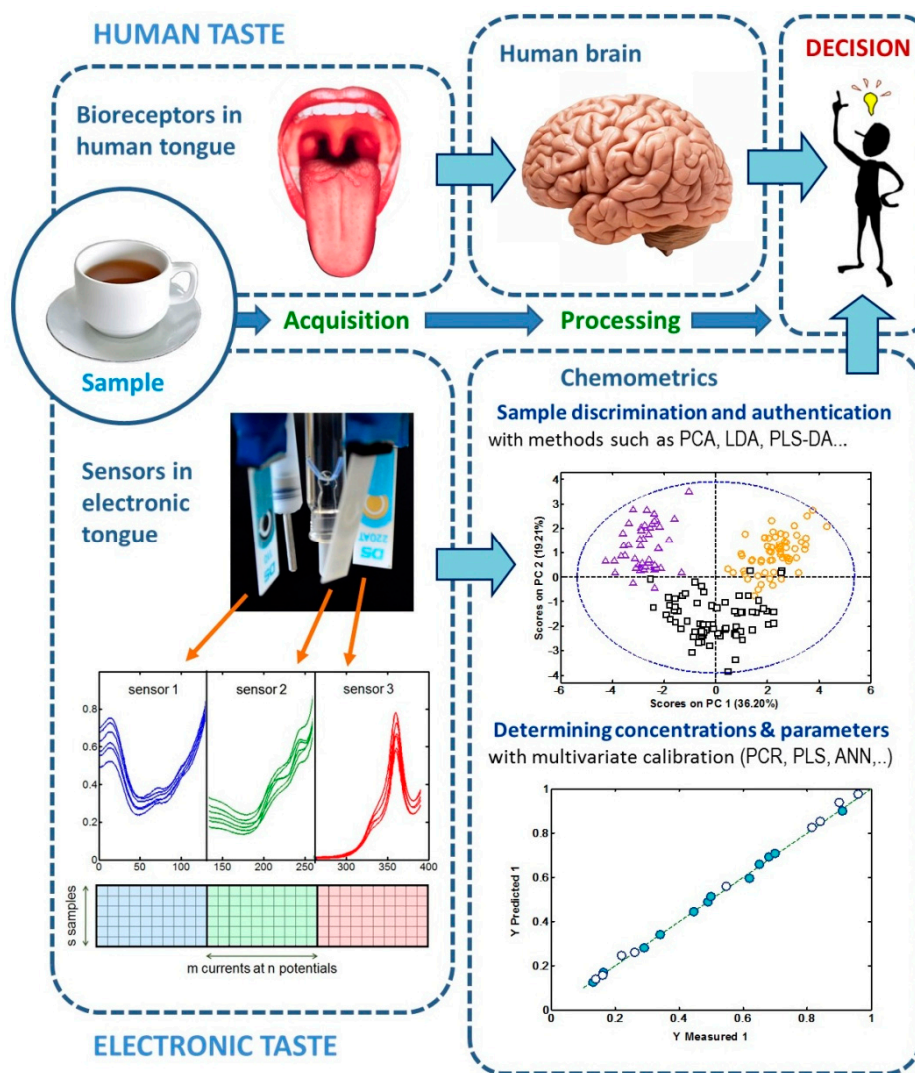


Figure 1. General scheme of voltammetric electronic tongues.

In the first case, a pattern recognition tool like principal component analysis (PCA) can be applied to detect groups of samples with common properties (clusters). In the PCA scores plot shown in the figure above, three clusters are visible, which agree very well with the previous information about the origin of the samples (denoted with purple, yellow and black colors). If the PCA model can identify the origin of known samples (training set), then it can be used to identify unknown samples. In the case of quantitative information, a calibration model is built with a method like partial least squares (PLS) applied to a training set of samples with known values of the properties to be determined. Then, if the predictions of the calibration model are right (as shown by the predicted versus measured plot in Figure 1) it can be used to predict the desired properties in unknown samples from the voltammograms acquired by the tongue.

As compared to potentiometric devices, the advantages of voltammetric electronic tongues include the higher amount of information achieved (a full voltammogram instead of a single potential per sensor) and the higher sensitivity (especially when electrochemical preconcentration is possible),

which allows one to consider not only major components of the sample but also trace substances that can be very informative about the origin and quality of food products. However, the main drawbacks of voltammetric devices are the higher complexity of the experimental design and, especially, of the datasets, which usually require sophisticated chemometric models for the data treatment. Thus, although it is clear that potentiometric tongues are a simple, compact and user-friendly solution in many cases, voltammetric tongues can be a more powerful solution for complicated problems. The real power of the ‘voltammetric way’ is conditioned, on the one hand, by the sensitivity and (cross) selectivity of the sensors integrating the array and, on the other hand, by the performance of the chemometric method used for the data treatment.

Concerning the sensors integrating the array, two main trends can be identified. Some research groups prefer arrays of bare metals such as silver, gold, platinum, or iridium combined with high and low amplitude pulsed signals at different frequencies [15], whereas other groups select electrode substrates chemically modified with substances that present certain affinity for the target species combined with the potential scans typically used in voltammetry (e.g., linear sweep, differential pulse, square wave). In the last case, modifications can be made on many substrates such as carbon paste [16], graphite–epoxy composites [17], glassy carbon [18] or screen-printed electrodes [19].

As for the chemometric tools, methods like PCA, linear discriminant analysis (LDA) or partial least squares discriminant analysis (PLS-DA) are applied for sample discrimination, whereas multivariate calibration methods like principal component regression (PCR) or PLS are used for determining concentrations and quality parameters in the case of reasonably linear data [20–24]. When measurements behave in a strongly non-linear way, more sophisticated methods like artificial neural networks (ANN) or support vector machine (SVM) are employed [23–26]. Figure 1 summarizes how both sensing and data treatment strategies applied to voltammetric electronic tongues converge to mimic human tongues.

The main body of this review is divided into two parts, a first one dedicated to the characterization, classification and authentication of food products and a second part regarding the determination of chemical species and other quantitative parameters. For more general information about the use of voltammetric electronic tongues in food analysis we refer to the more extensive review by Wei et al. [27].

2. Characterization, Classification and Authentication of Food Products

As already pointed out, voltammetric electronic tongues can provide valuable qualitative information about food samples when combined with a chemometric method of pattern recognition. Table 1 summarizes some relevant applications found in references [14–17] and [28–71] focused on the characterization, classification and authentication of food products.

In general terms, voltammetric tongues are mostly applied to liquid samples, with especial predominance of wine, but they can also operate with more consistent food products such as honey, yogurt, meat or fish. The number of working electrodes ranges from two to eight and includes bare metals, carbon paste electrodes modified with phthalocyanine and other substances, graphite–epoxy based electrodes and screen-printed electrodes. As already mentioned, arrays of bare metals usually are submitted to multi-pulse excitation signals whereas the rest of the sensors mostly work with cyclic (CV), square wave (SW) or differential pulse voltammetric (DPV) scans. In some cases (especially CV), the scans generate a large amount of data and some compression is needed to increase the speed of calculations. The simplest solution is to replace the full voltammogram by a few parameters describing relevant features. For instance, Bougrini et al. [60] used the difference between the maximum and minimum values of the current and the maximum slope of the current curve in the anodic and cathodic scans. In this way, the measurements of a honey sample with an array of seven working electrodes produces just a set of 21 numbers. The PCA treatment of these roughly compressed data allowed a quite satisfactory discrimination among 13 types of honey. However, in some cases this method of compression can lead to the loss of valuable information and it is better to resort to more sophisticated compression strategies like fast Fourier transform (FFT) or discrete wavelet transform (DWT) which preserve most of the information of the voltammogram with a significant decrease in

the amount of data. For instance, Cetó et al. [37] obtained good results with the DWT compression of CV data from five sensors in the PCA discrimination of different cava wine varieties (results that were further refined by means of ANN).

In many situations, a relatively simple and unsupervised data treatment by means of PCA is sufficient to visually discriminate groups of samples in the scores plot. However, more complex problems require supervised classification methods like LDA or PLS-DA where the classes of the known samples are included in a model that will be used to assign unknown samples to the predefined classes. This is the case, for instance, of the work by Blanco et al. [48] that will be further discussed.

As for the discrimination purposes, most studies are focused either on the authentication of both local origin (typically PDO) and quality of food products or on the detection of adulterations. Nevertheless, there is an increasing interest on the evolution of products with time (e.g., grape ripening, spoilage of meat and fish during storage) in order to detect the samples that are not in good conditions to be consumed. Especially interesting is the work by Haddi et al. [70], which used measurements by CV in a tongue of seven working electrodes to discriminate the type of meat (beef, goat or sheep) and the degree of spoilage, measured in terms of number of storage days.

The same data sets used for sample discrimination can be processed by multivariate calibration methods like PLS to predict certain parameters related to food quality. For this purpose, it is necessary to measure the target parameter in the known samples and include the resulting values in the calibration model. Anyway, these quantitative implications of electronic tongues will be discussed in Section 3.

Table 1. Selected works dealing about the characterization, classification and authentication of food products with voltammetric electronic tongues.

| Food Product | Working Electrodes | Data Analysis | Comments | Ref. |
|-----------------------|-----------------------------------------------------------------------------------------------------------------------------------|---------------|---------------------------------------------------------------------------------|------|
| Orange juice and milk | Pt and Au | PCA | First voltammetric e-tongue | [14] |
| Milk | Au, Pt, Rh, stainless steel | PCA | Monitoring of milk in dairy industry | [28] |
| | Au, Cu, Au modified with Prussian blue | PCA | Recognition of milk adulteration with hydrogen peroxide | [29] |
| | Au, Cu, Pt | PCA | Recognition of milk adulteration with urea, formaldehyde and melamine | [30] |
| | Au, Pd, Pt | MPCA, NPLS-DA | Recognition of milk adulteration with urea | [31] |
| | Au, Pt, Ag | PCA, PLS-DA | Discrimination of various brands of pure milk | [32] |
| | Au, Ag, Pt, Pd | PCA, CA | Monitoring of quality and storage time of unsealed pasteurized milk | [15] |
| Yogurt | Au, Ag, Pt, Pd | SVM | Monitoring the fermentation, post-ripeness and storage processes of set yogurts | [33] |
| | Au, Ag, Pt, Pd | PCA, CA | Evaluation of varieties of set yogurts | [34] |
| Wines and liqueurs | Phthalocyanine-based carbon paste electrodes and electrodes covered with conducting polypyrrole doped with different counter ions | PCA | Detection of adulterations in wines | [16] |
| | Au, Cu | PCA | Discrimination of wines and whiskies of different quality | [35] |
| | Au, Ag, Pt, Pd, W, Ti | PCA, CA | Classification of rice wines of different ages | [36] |
| | Five bulk-modified graphite-epoxy electrodes | PCA, ANN | Cava wine authentication | [37] |
| | Six bulk-modified graphite-epoxy electrodes | LDA | Cava wine authentication | [17] |
| | Five different graphite-epoxy composite electrodes | PCA, ANN | Discrimination of wines of different types and PDO | [38] |

Table 1. Cont.

| Food Product | Working Electrodes | Data Analysis | Comments | Ref. |
|--------------------|---------------------------------------------------------------------------------------------------------------------------------------------|------------------|----------------------------------------------------------------------------------------------------------------------------|---------|
| Wines and liqueurs | Sensors based on metallic and bulk-modified graphite electrodes | LDA | Classification of wines of different PDO | [39] |
| | Four carbon paste electrodes chemically modified in different ways | PCA | Discrimination between red wines aged in oak barrels and matured in steel tanks in contact with oak wood chips | [40] |
| | Three nanocomposites modified electrodes prepared with Au and Cu nanoparticles in the presence of conducting polymers and carbon nanotubes. | PCA, LDA | Classification of rice wines of different geographical origins | [41] |
| | Six modified epoxy-composite electrodes | LDA | Classification of brandies according to their taste category and ageing method | [42] |
| | Four carbon paste electrodes: one unmodified and the others chemically modified with Co, Fe and Zn phthalocyanines | PCA | Discrimination of apple liqueurs | [43] |
| Grapes | Eight metallic electrodes housed inside a stainless steel cylinder | PCA | Study of grape ripening | [44] |
| | Poly-ethylendioxythiophene modified Pt electrode and sonogel carbon electrode | PCA | Study of grape ripening | [45] |
| Beer | Three enzymatic biosensors based on tyrosinase and phthalocyanines as mediators | PCA, LDA | Monitoring of the aging of beers | [46] |
| | Six bulk-modified graphite-epoxy electrodes | PCA, LDA, PLS-DA | Classification of three types of beer: Lager, Stout and IPA | [47] |
| | Four commercial screen-printed electrodes made of carbon, Au, carbon/Co-Phtahlocyanine and Pt | PCA, LDA | Classification of different types of beer | [48] |
| Coffee | Six graphite-epoxy electrodes modified in different ways | LDA, SVM | Geographical classification of Mexican coffees | [49] |
| | Au wire and graphite rod | PCA | Discrimination of civet coffee | [50] |
| Tea | Ir, Pt, Rh | PCA | Discrimination of nine different teas | [51] |
| | Au, Ir, Pd, Pt, Rh | PCA, LDA | Tea quality assessment | [52,53] |
| | Pt and glassy C | PCA, LDA | Classification of black tea liquor | [54] |
| | Metallic oxide-modified nickel foam electrodes (SnO ₂ , ZnO, TiO ₂ , Bi ₂ O ₃) | PCA, SVM | Classification of green and black teas | [55] |
| | Au, Ir, Pd, Pt, Rh | PCA | Monitoring the fermentation process of black tea | [56,57] |
| Honey | Au, Ag, Pt, Pd, W, Ti | PCA, CA, DFA | Classification of mono-floral honeys | [58] |
| | Au, Ag, Pt, Pd, W, Ti | PCA, DFA | Tracing floral and geographical origins of honey | [59] |
| | Pt, Au, glassy C, Ag, Pd, Ni, Cu | PCA, SVM, HCA | Classification of Moroccan and French honeys according to geographical and botanical origins and detection of adulteration | [60,61] |
| | Au, Ag, Pt | PCA, LDA | Authentication of mono-floral and honeydew Romanian honeys | [62] |
| | Ir, Rh, Pt, Au | PCA | Monitoring honey adulteration with sugar syrups | [63] |
| | Au, Ag, Pt, glass electrode | PLS-DA | Monitoring honey adulteration | [64] |
| | | | | |
| Oil | Six electrodes based on polypyrrole | PCA, PLS-DA | Discrimination of extra virgin olive oils according to their degree of bitterness | [65] |
| | Pt, Au, glassy C, Ag, Ni, Pd, Cu | PCA, DFA, SVM | Detection of adulteration in argan oil | [66] |
| | Modified carbon paste electrodes | PLS-DA | Detection of virgin olive oil adulteration | [67] |
| | Cu, glassy C, Au, Ni, Pd, Pt, Ag | PCA, SVM, HCA | Identification of Portuguese olive oils | [68] |

Table 1. Cont.

| Food Product | Working Electrodes | Data Analysis | Comments | Ref. |
|---------------|---------------------------------------------------------------------------|---------------|------------------------------------------------------------------|------|
| Meat and fish | Screen-printed electrodes modified with bisphthalocyanine and polypyrrole | PCA, PLS-DA | Beef freshness monitoring by detection of ammonia and putrescine | [69] |
| | Pt, Au, Ag, glassy C, Pd, Cu, Ni | PCA | Assessment the origins of red meats and their storage time | [70] |
| | Ir, Rh, Pt, Au, Ag, Co, Cu, Ni | PCA | Shelf-life assessment of fresh cod in cold storage | [71] |

As a first example of sample discrimination with voltammetric electronic tongues, we will briefly discuss the work by M. Sliwinska et al., published in [43] and focused on apple liqueurs (Nalewka). In this study, an array of four working electrodes was used, including an unmodified carbon paste electrode (C-CPE) and three electrodes chemically modified with cobalt, iron and zinc phthalocyanines (denoted as CoPc-CPE, FePc-CPE and ZnPc-CPE, respectively). Figure 2 compares the cyclic voltammograms registered for liqueurs prepared with five different apple varieties (Ligol, Kosztela, Grey Reinette, Rubin and Cox Orange). Notorious differences can be observed between the responses obtained with different electrodes and in different types of liqueur.

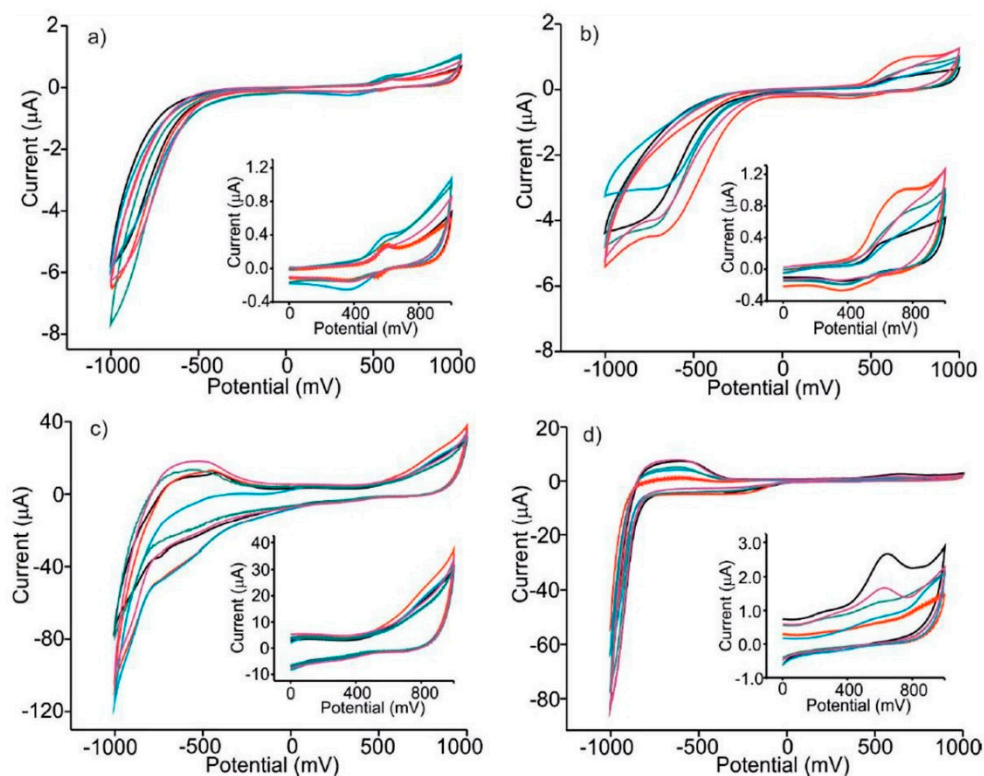


Figure 2. Cyclic voltammograms registered using four different carbon paste electrodes (CPEs) immersed in liqueur samples made from different varieties of apples. (a) Unmodified CPE; (b) ZnPc-CPE; (c) FePc-CPE; (d) CoPc-CPE. Apple varieties: Ligol (black), Kosztela (red), Grey Reinette (blue), Rubin (green), Cox Orange (purple). Reproduced from [43].

The application of PCA to this kind of data allowed the authors to clearly discriminate among liqueurs made from different varieties of apple, as shown by Figure 3. This is a 3D plot of the scores achieved by the three samples of every apple variety for the three first principal components of the model (PC1, PC2 and PC3). As it can be seen, the three replicates of each variety are very close with each other in the graph and quite far from the groups of replicates of the other varieties, which makes it possible to identify unknown samples from the position of their scores in the diagram.

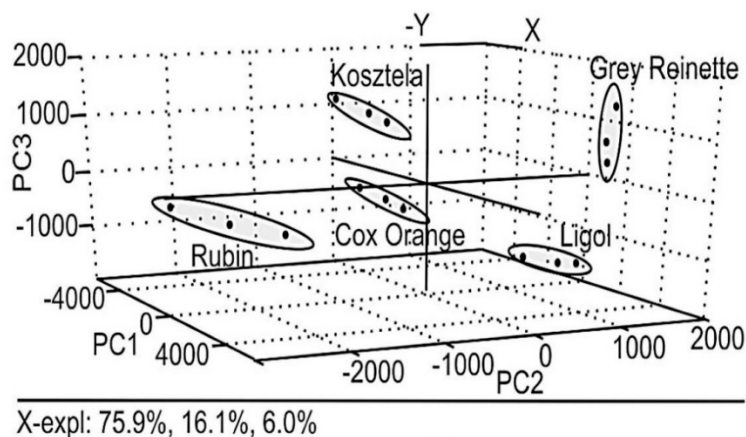


Figure 3. Scores plot obtained in the PCA treatment of cyclic voltammetric (CV) data (see Figure 2) acquired with four working electrodes in three replicates of five types of apple liqueur (from Ligol, Kosztela, Grey Reinette, Rubin and Cox Orange apples). Reproduced from [43].

As pointed out before, supervised classification methods like LDA and PLS-DA can improve the performance of PCA in more intricate situations, as it happens in our second example. Blanco et al. [48] applied LDA to CV data from four commercial screen-printed electrodes (Figure 4) to classify beer samples in four categories: free alcohol, Pilsener, doppelbock and European strong lager. In LDA, new optimized variables (discrimination functions, DFs) are obtained from the original variables but, unlike the principal components (PCs) used in PCA, such variables do not try to explain most of the data variance. They are constructed to get the maximum discrimination between the predefined classes. Then, a plot of the scores of the discriminant functions (Figure 5) allows a satisfactory classification of the beers which was not possible with PCA (data not shown).

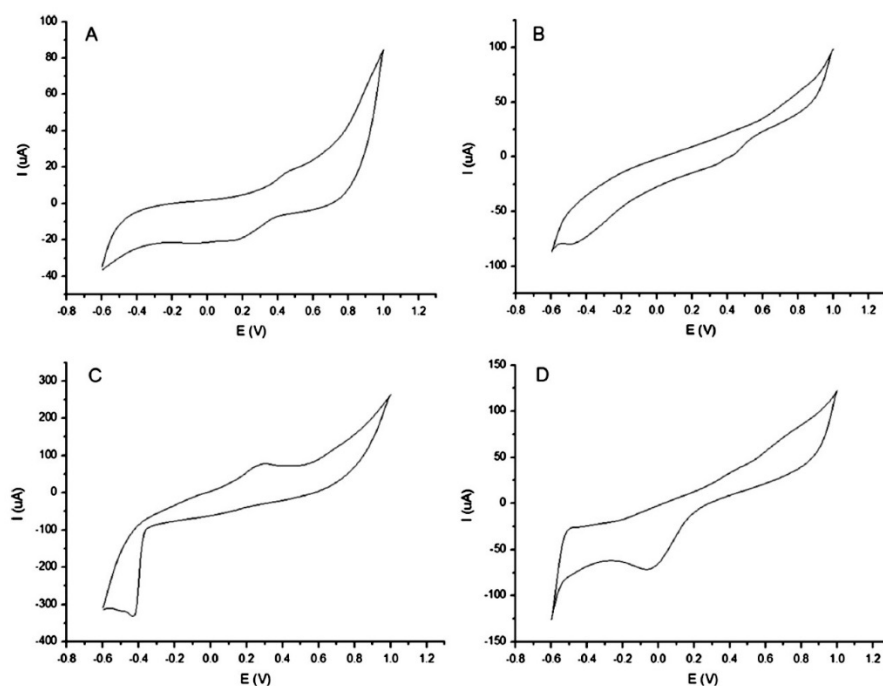


Figure 4. Cyclic voltammograms registered with an array of four commercial screen-printed sensors exposed to a beer sample. (A) DS-110; (B) DS-250AT; (C) DS-410; and (D) DS-550. Reproduced from [48] with permission.

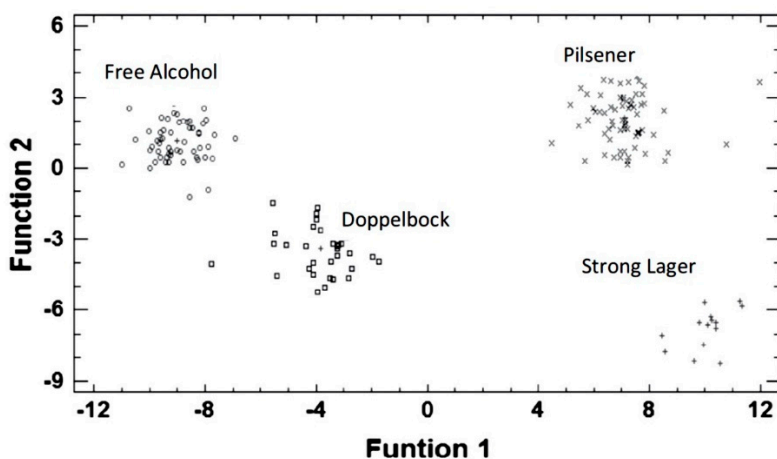


Figure 5. Scores plot obtained in the LDA treatment of CV data (see Figure 4) acquired with four commercial screen-printed sensors in beer belonging to three different categories. Reproduced from [48] with permission.

3. Determination of Chemical Species and Other Quantitative Parameters Related to Food Analysis

Unlike human tongues, voltammetric electronic tongues can be used for quantitative purposes if their signals are submitted to a multivariate calibration method such as PLS or ANN. For instance, they can be applied to determine pollutants like nitrophenols [72], heavy metal ions [73] or glyphosate [74] in different samples. In the case of food analysis, predictions can be made not only of the concentrations of relevant species, but also of a large deal of parameters informing about the quality of food products. Table 2 summarizes some representative contributions in this field, corresponding to references [75–90]. It can be seen that the working electrodes used are essentially the same employed for sample discrimination (Table 1). Among the substances determined we can mention theaflavine and thearubigin in tea, several sugars in fruits and sugar cane bagasse, bisulfite and ethylphenol metabolites in wine, some anions in meat and antibiotic residues in milk. As for the quality parameters, the determination of bitterness, polyphenol indexes and antioxidant capacity in wines, beers and olive oils deserves special attention. Concerning chemometric tools, PLS (and, eventually, PCR) is the main choice, but non-linearity problems quite often demand more sophisticated methods like ANN or SVM.

As an example of these studies, we will summarize the work by Apetrei, who in [65] not only classified different extra virgin olive oils according to their degree of bitterness, but also applied a multivariate calibration model to predict the corresponding bitterness indexes. For this purpose, six polypyrrole-based screen-printed electrodes were used to measure quite different cyclic voltammograms as these shown in Figure 6. Then, a PLS model was constructed with the voltammograms of calibration samples whose bitterness indexes had been previously determined by means of a chemical method. PLS is amongst the most popular multivariate calibration methods and is present in commercial software. It is based on a calibration between the experimental data matrix and that containing the parameters to be predicted, where both matrices have been ‘compressed’ in terms of a set of optimized variables called latent variables (LVs). The main difference of LVs with the PCs of PCA is that they are optimized to maximize the covariance between both matrices involved in the calibration. Although PLS processing provides many useful graphs, most authors just provide the errors of the calibration (RMSEC) and the validation (RMSEV) in a table. Fortunately, a few authors like Apetrei also provide the plot of the predicted values as a function of the real ones (Figure 7). In a good PLS model the points of this graph should be placed in a straight line, not very far from the theoretical line of slope 1 and intercept 0. As Figure 7 shows, the PLS model in [65] is quite successful in predicting bitterness indexes.

Table 2. Selected works dealing with the determination of chemical species and other quantitative parameters in food analysis by using voltammetric electronic tongues.

| Application | Working Electrodes | Data Analysis | Ref. |
|-------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|---------------|---------|
| Prediction of bitterness and alcoholic strength in beers | Polypyrrole polymerized onto Pt disks and doped with different modifiers | PLS | [75] |
| Determination of total polyphenol index in wines | Five graphite-epoxy electrodes modified in different ways | PLS, ANN | [76] |
| Determination of theaflavin and thearubigin in black tea | Au, Ir, Pd, Pt, Rh | PLS, SVM, ANN | [77,78] |
| Evaluation of sugar content and firmness of non-climacteric pears | Au, Ag, Pt, Pd, W, Ti | PLS, PCR, SVM | [79] |
| Evaluation of the antioxidant capacity of red wines | Graphite-epoxy composite electrodes and modified carbon paste electrodes | PLS, ANN | [80] |
| Evaluation of oxygen exposure levels and polyphenolic content of red wines | Modified carbon paste electrodes based on bisphthalocyanines and perylenes | PLS | [81] |
| Quantification in rosé cava wines of different indexes related to total phenolic content and other specific phenolic features | Four graphite-epoxy voltammetric (bio)sensors with different modifiers such as tyrosinase, laccase and copper nanoparticles | ANN | [82] |
| Determination of galactose, glucose, xylose and mannose in sugar cane bagasse | Glassy carbon electrodes modified with multi-walled carbon nanotubes containing metal (Pd, Au, Cu, Ni, Co) | ANN | [18] |
| Determination of spring water quality parameters | Ir, Rh, Pt, Au | PLS | [83] |
| Determination of bisulphites in wines | Au, Rh, Pt, stainless steel | PLS | [84] |
| Determination of ethylphenol metabolites in wines | Six graphite-epoxy modified composite electrodes | ANN | [85] |
| Determination of nitrate, nitrite and chloride in minced meat | Au, Pt, Rh, Ir, Ag, Ni, Co, Cu | PLS | [86] |
| Determination of Tl(I) and In(III) in tonic water by using a multivariate standard addition method | A screen-printed carbon nanofibers electrode modified with selenocystine and a screen-printed carbon electrode modified with a Bi film | PLS | [19] |
| Determination of the polyphenolic content of extra virgin olive oils | Twelve sensors: five of them based on lanthanide bisphthalocyanines, six based on polypyrrole and one unmodified carbon paste electrode. | PLS | [87] |
| Determination of bitterness index in olive oils | Six polypyrrole-based screen-printed electrodes | PLS | [65] |
| Quantification of total polyphenol content in olive oils | Polypyrrole modified screen-printed electrodes | PLS | [88] |
| Detection of antibiotic residues in bovine milk | Au, Ag, Pt, Pd, Ti | PCR, PLS, SVM | [89] |
| Determination of the antioxidant activity of camu camu and tumbo juices | Au, Pt, Ir, Rh, Ag, Cu, Ni, Co | PLS | [90] |

In general terms, PLS method works well for reasonably linear data. However, for strongly non-linear data PLS fails and more sophisticated data treatments are required, like ANN or SVM. In our last example, taken from ref. [85], González-Calabuig and del Valle used ANN to predict the content in wine samples of the metabolites related to the Brett defect: 4-ethylphenol (4-EP), 4-ethylguaiacol (4-EG) and 4-ethylcatechol (4-EC). For this purpose, they registered CV scans in wine samples spiked with different concentrations of metabolites by using a voltammetric electronic tongue integrated by six bulk-modified graphite-epoxy composites and obtained signals like those shown in Figure 8. The original data (2490 inputs per sample) were compressed by means of DWT with a 93.5% compression ratio (132 numbers per sample) to keep the maximum information with the minimum data size. Then, an ANN model was built with 27 standards containing different proportions of the three analytes (according to a 3³ factorial design). The model is composed by neurons, i.e., calculation units organized in layers (usually three) which use transfer functions that operate the numbers in the preceding layer to generate the numbers in the next layer. A critical point in ANN strategy is to

design the architecture of the network (e.g., the neurons per layer or the type of transfer functions). In this case, a network was built with 132 neurons in the input layer, 3 neurons in the hidden layer and 3 neurons in the output layer. The training of the ANN consists on the optimization of the coefficients of the transfer functions to get results in the output layer (the concentrations of the three analytes) as close as possible to the real ones when the compressed measurement of the 27 standards are fed to the input layer. As Figure 9 shows, the trained ANN produced good predictions for all three analytes not only in the standard solutions (denoted with black circles), but also in 10 additional solutions used for external validation (empty circles).

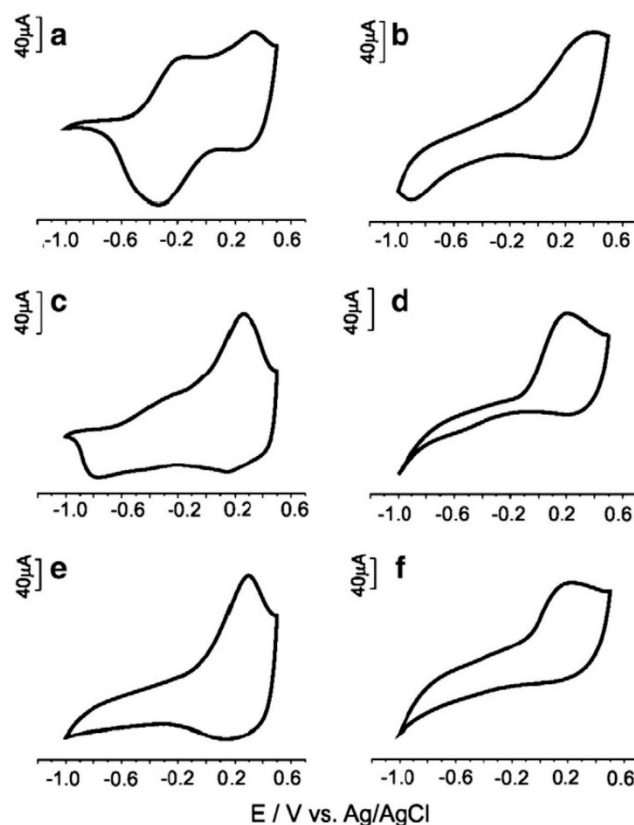


Figure 6. Cyclic voltammograms measured with the six working electrodes described in [65] in the same emulsion of extra virgin olive oil. (a) Ppy/FCN; (b) Ppy/MO; (c) Ppy/NP; (d) Ppy/AQS; (e) Ppy/H₂SO₄; (f) Ppy/PWA. Reproduced with permission.

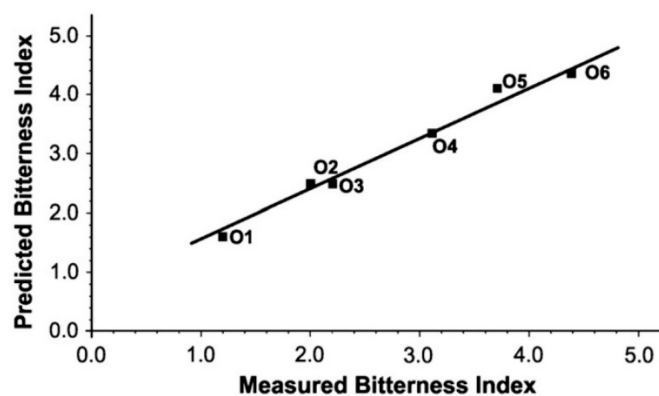


Figure 7. Plot of the bitterness index predicted with the electronic tongue in [65] by means of PLS calibration for different olive oil samples as a function of the corresponding bitterness index obtained by a chemical method. Reproduced with permission.

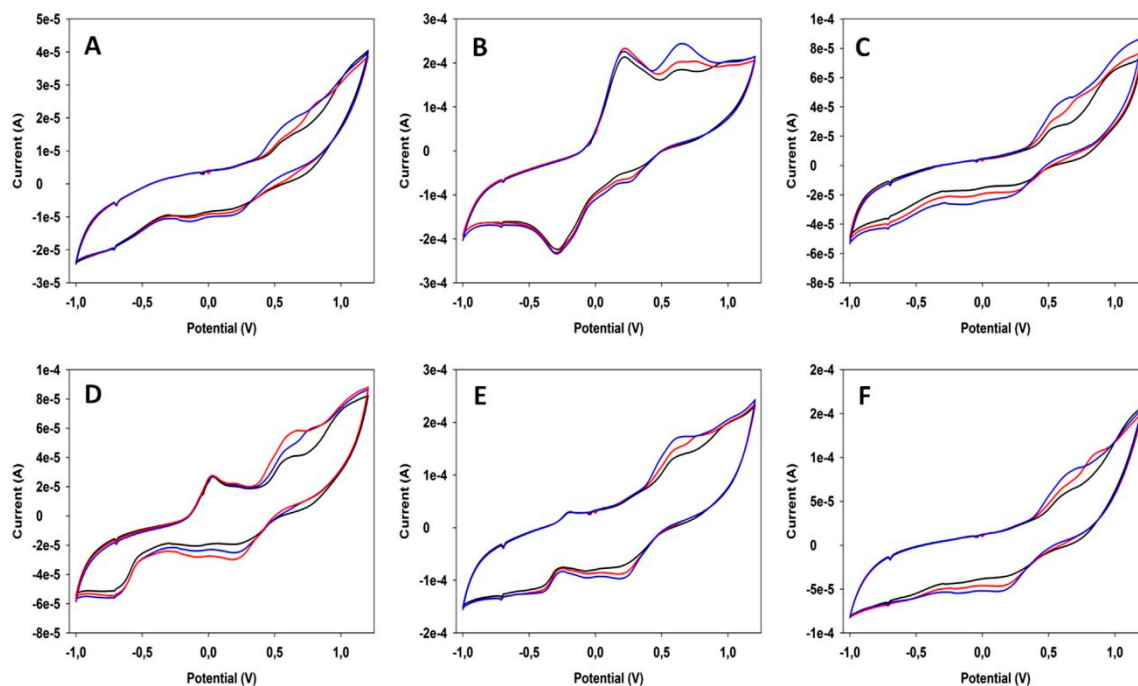


Figure 8. CV signals obtained for 25 ppm of 4-EP (black), 4-EG (red) and 4-EC (blue) in a wine matrix for (A) a bare epoxy-graphite electrode; and electrodes modified with (B) Cu nanoparticles; (C) WO_3 nanoparticles; (D) Bi_2O_3 nanoparticles; (E) polypyrrole; and (F) Co(II) phthalocyanine. Reproduced from [85] with permission.

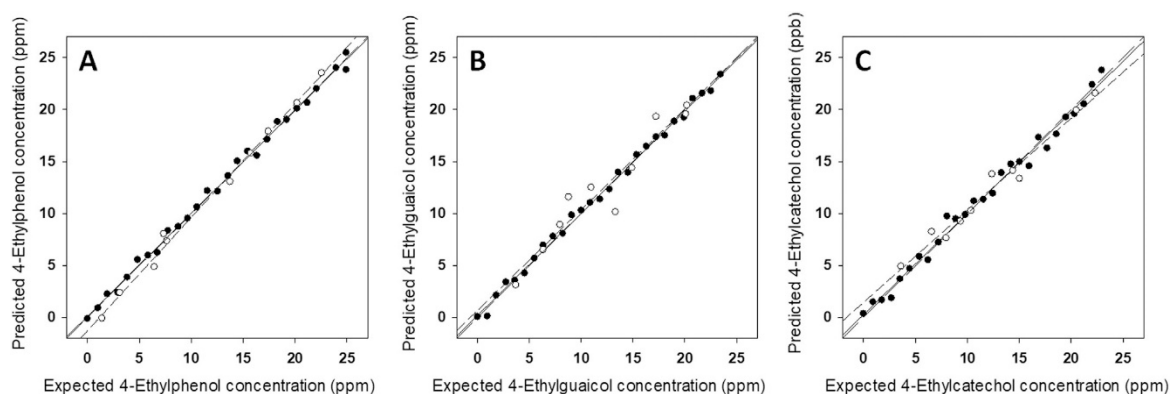


Figure 9. Modeling ability of the developed ANN: expected vs. predicted concentrations for (A) 4-EP; (B) 4-EG; and (C) 4-EC, both for training (●, solid line) and testing subsets (○, dashed line). Dotted line corresponds to theoretical diagonal line. Reproduced from [85] with permission.

4. Conclusions

In the field of food control, voltammetric electronic tongues are a promising complement for the more widely used potentiometric electronic tongues and electronic noses, especially in these really complex situations demanding a higher amount of information. For data sets not too far from linearity, conventional chemometric methods such as PCA, LDA, PLS or PLS-DA can be applied to build models that are able to discriminate between samples of different origin and freshness or to determine the concentration of key substances and relevant indexes related to food quality. In the presence of strongly non-linear data, more sophisticated chemometric methods such as ANN or SVM can be applied instead. The problem of these methods, however, is that their use is not obvious. For instance, ANNs require a careful design of their architecture, which usually is made by means of the trial and error strategy. As a consequence, models are built for particular situations and datasets, and are rarely accessible as supplementary materials of the papers or in the webs of research groups. Then, hey

promote a sensation of ‘black box’ that, unlike PCA or PLS, prevents their dissemination as a common practice in the treatment of voltammetric tongue data.

Nowadays there is a great diversity of designs and applications of voltammetric electronic tongues, recently enhanced by the popularization of screen-printed electrodes. In our view, the initial strategy of pulse activation signals and metallic electrodes has been progressively replaced by conventional voltammetric scans (mainly CV) and chemically modified electrodes which enhance the (cross) selectivity of the sensors constituting the tongue. We believe that this is a positive trend, since chemical interactions of significant components of the sample with the modified electrodes are more likely to produce sample discrimination than just the different electrochemical behavior of electrodes made of different metals. Nevertheless, in our opinion, an effort is required to achieve the maximum simplicity and economy in both the electrode selection and the strategy for data treatment. This means that statistic tools should be applied to confirm that all the sensors used are really necessary (eight sensors for a tongue predicting a single parameter sounds a bit excessive). Additionally, powerful compression methods like DWT or FFT should be extensively applied to the data sets to reduce the computing time (in their competition with chromatographic methods, voltammetric tongues should not spend in calculations the time saved for the absence of separation). Finally, an effort should be made to adapt calibration models to matrix effects and signal drifts in order to improve their reliability in real operating conditions. For this purpose, multivariate adaptations of the univariate methodologies of standard addition and inner standard would be highly welcome.

Just to conclude, only with robust and reproducible electrode arrays susceptible to cost-effective mass production and with programs for data treatment implemented in commercial software voltammetric electronic tongues will be able to cross the frontier between the proof of concept and the market for an effective assessment of food provenance and quality.

Author Contributions: C.P.-R., N.S., C.A., M.E. and J.M.D.-C. collected and evaluated, in a coordinated way, all the publications mentioned in the paper. With this material, J.M.D.-C. wrote a preliminary version of the review that was further enriched with suggestions and contributions by the rest of the authors.

Funding: The authors gratefully acknowledge the support of the Generalitat of Catalonia, Spain, under the project 2017SGR-311. Clara Pérez-Ráfols also acknowledges the Spanish Ministry of Education, Culture and Sports for a Ph.D. grant (reference FPU15/02140) and the financial support of the Water Research Institute (IdRA) of the University of Barcelona.

Conflicts of Interest: The authors declare no conflict of interests.

References

1. Persaud, K.C.; Dodd, G. Analysis of discrimination mechanisms in the mammalian olfactory system using a model nose. *Nature* **1982**, *299*, 352–355. [[CrossRef](#)] [[PubMed](#)]
2. Otto, M.; Thomas, J.D.R. Model studies on multiple channel analysis of free magnesium, calcium, sodium, and potassium at physiological concentration levels with ion-selective electrodes. *Anal. Chem.* **1985**, *57*, 2647–2651. [[CrossRef](#)]
3. Gardner, J.W.; Bartlett, P.N. A brief history of electronic noses. *Sens. Actuators B Chem.* **1994**, *18*, 210–211. [[CrossRef](#)]
4. Vlasov, Y.; Legin, A. Non-selective chemical sensors in analytical chemistry: From “electronic nose” to “electronic tongue”. *Fresenius J. Anal. Chem.* **1998**, *361*, 255–260. [[CrossRef](#)]
5. Ciosek, P.; Wróblewski, W. Sensor arrays for liquid sensing—electronic tongue systems. *Analyst* **2007**, *132*, 963–978. [[CrossRef](#)] [[PubMed](#)]
6. del Valle, M. Electronic tongues employing electrochemical sensors. *Electroanalysis* **2010**, *22*, 1539–1555. [[CrossRef](#)]
7. Krantz-Rülcker, C.; Stenberg, M.; Winqvist, F.; Lundström, I. Electronic tongues for environmental monitoring based on sensor arrays and pattern recognition: A review. *Anal. Chim. Acta* **2001**, *426*, 217–226. [[CrossRef](#)]
8. Woertz, K.; Tissen, C.; Kleinebudde, P.; Breitzkreutz, J. Taste sensing systems (electronic tongues) for pharmaceutical applications. *Int. J. Pharm.* **2011**, *417*, 256–271. [[CrossRef](#)] [[PubMed](#)]

9. Rudnitskaya, A.; Legin, A. Sensor systems, electronic tongues and electronic noses, for the monitoring of biotechnological processes. *J. Ind. Microbiol. Biotechnol.* **2008**, *35*, 443–451. [[CrossRef](#)] [[PubMed](#)]
10. Deisingh, A.K.; Stone, D.C.; Thompson, M. Applications of electronic noses and tongues in food analysis. *Int. J. Food Sci. Technol.* **2004**, *39*, 587–604. [[CrossRef](#)]
11. Escuder-Gilabert, L.; Peris, M. Highlights in recent applications of electronic tongues in food analysis. *Anal. Chim. Acta* **2010**, *665*, 15–25. [[CrossRef](#)] [[PubMed](#)]
12. Ciosek, P.; Wróblewski, W. Potentiometric electronic tongues for foodstuff and biosample recognition—An overview. *Sensors* **2011**, *11*, 4688–4701. [[CrossRef](#)] [[PubMed](#)]
13. Peris, M.; Escuder-Gilabert, L. Electronic noses and tongues to assess food authenticity and adulteration. *Trends Food Sci. Technol.* **2016**, *58*, 40–54. [[CrossRef](#)]
14. Winqvist, F.; Wide, P.; Lundström, I. An electronic tongue based on voltammetry. *Anal. Chim. Acta* **1997**, *357*, 21–31. [[CrossRef](#)]
15. Wei, Z.; Wang, J.; Zhang, X. Monitoring of quality and storage time of unsealed pasteurized milk by voltammetric electronic tongue. *Electrochim. Acta* **2013**, *88*, 231–239. [[CrossRef](#)]
16. Parra, V.; Arrieta, A.A.; Fernández-Escudero, J.A.; Rodríguez-Méndez, M.L.; De Saja, J.A. Electronic tongue based on chemically modified electrodes and voltammetry for the detection of adulterations in wines. *Sens. Actuators B Chem.* **2006**, *118*, 448–453. [[CrossRef](#)]
17. Cetó, X.; Capdevila, J.; Puig-Pujol, A.; del Valle, M. Cava wine authentication employing a voltammetric electronic tongue. *Electroanalysis* **2014**, *26*, 1504–1512. [[CrossRef](#)]
18. de Sá, A.C.; Cipri, A.; González-Calabuig, A.; Stradiotto, N.R.; del Valle, M. Resolution of galactose, glucose, xylose and mannose in sugarcane bagasse employing a voltammetric electronic tongue formed by metals oxy-hydroxide/MWCNT modified electrodes. *Sens. Actuators B Chem.* **2016**, *222*, 645–653. [[CrossRef](#)]
19. Pérez-Ràfols, C.; Puy-Llovera, J.; Serrano, N.; Ariño, C.; Esteban, M.; Díaz-Cruz, J.M. A new multivariate standard addition strategy for stripping voltammetric electronic tongues: Application to the determination of Tl(I) and In(III) in samples with complex matrices. *Talanta* **2019**, *192*, 147–153. [[CrossRef](#)]
20. Esbensen, K.H.; Guyot, D.; Westad, F. *Multivariate Data Analysis in Practice: An Introduction to Multivariate Data Analysis and Experimental Design*, 4th ed.; Camo: Oslo, Norway, 2000.
21. Brown, S.D.; Tauler, R.; Walczak, B. *Comprehensive Chemometrics: Chemical and Biochemical Data Analysis*; Elsevier: Amsterdam, The Netherlands, 2009.
22. Esteban, M.; Ariño, C.; Díaz-Cruz, J.M. Chemometrics for the analysis of voltammetric data. *Trends Anal. Chem.* **2006**, *25*, 86–92. [[CrossRef](#)]
23. Oliveri, P.; Casolino, M.C.; Forina, M. Chemometric brains for artificial tongues. *Adv. Food Nutr. Res.* **2010**, *61*, 57–117. [[CrossRef](#)] [[PubMed](#)]
24. Cetó, X.; Céspedes, F.; del Valle, M. Comparison of methods for the processing of voltammetric electronic tongues data. *Microchim. Acta* **2013**, *180*, 319–330. [[CrossRef](#)]
25. Despagne, F.; Massart, D.L. Neural networks in multivariate calibration. *Analyst* **1998**, *123*, 157R–178R. [[CrossRef](#)] [[PubMed](#)]
26. Burges, C.J. A tutorial on support vector machines for pattern recognition. *Data Min. Knowl. Discov.* **1998**, *2*, 121–167. [[CrossRef](#)]
27. Wei, Z.; Yang, Y.; Wang, J.; Zhang, W.; Ren, Q. The measurement principles, working parameters and configurations of voltammetric electronic tongues and its applications for foodstuff analysis. *J. Food Eng.* **2018**, *217*, 75–92. [[CrossRef](#)]
28. Winqvist, F.; Bjorklund, R.; Krantz-Rülcker, C.; Lundström, I.; Östergren, K.; Skoglund, T. An electronic tongue in the dairy industry. *Sens. Actuators B Chem.* **2005**, *111*, 299–304. [[CrossRef](#)]
29. Paixão, T.R.; Bertotti, M. Fabrication of disposable voltammetric electronic tongues by using Prussian Blue films electrodeposited onto CD-R gold surfaces and recognition of milk adulteration. *Sens. Actuators B Chem.* **2009**, *137*, 266–273. [[CrossRef](#)]
30. Bueno, L.; de Araujo, W.; Salles, M.; Kussuda, M.; Paixão, T. Voltammetric electronic tongue for discrimination of milk adulterated with urea, formaldehyde and melamine. *Chemosensors* **2014**, *2*, 251–266. [[CrossRef](#)]
31. Li, L.A.; Yu, Y.; Yang, J.; Yang, R.; Dong, G.; Jin, T. Voltammetric electronic tongue for the qualitative analysis of milk adulterated with urea combined with multi-way data analysis. *Int. J. Electrochem. Sci.* **2015**, *10*, 5970–5980.

32. Yu, Y.; Zhao, H.; Yang, R.; Dong, G.; Li, L.; Yang, J.; Jin, T.; Zhang, W.; Liu, Y. Pure milk brands classification by means of a voltammetric electronic tongue and multivariate analysis. *Int. J. Electrochem. Sci.* **2015**, *10*, 4381–4392.
33. Wei, Z.; Zhang, W.; Wang, Y.; Wang, J. Monitoring the fermentation, post-ripeness and storage processes of set yogurt using voltammetric electronic tongue. *J. Food Eng.* **2017**, *203*, 41–52. [[CrossRef](#)]
34. Wei, Z.; Wang, J.; Jin, W. Evaluation of varieties of set yogurts and their physical properties using a voltammetric electronic tongue based on various potential waveforms. *Sens. Actuators B Chem.* **2013**, *177*, 684–694. [[CrossRef](#)]
35. Novakowski, W.; Bertotti, M.; Paixao, T.R. Use of copper and gold electrodes as sensitive elements for fabrication of an electronic tongue: Discrimination of wines and whiskies. *Microchem. J.* **2011**, *99*, 145–151. [[CrossRef](#)]
36. Wei, Z.; Wang, J.; Ye, L. Classification and prediction of rice wines with different marked ages by using a voltammetric electronic tongue. *Biosens. Bioelectron.* **2011**, *26*, 4767–4773. [[CrossRef](#)] [[PubMed](#)]
37. Cetó, X.; Gutiérrez, J.M.; Moreno-Barón, L.; Alegret, S.; del Valle, M. Voltammetric electronic tongue in the analysis of cava wines. *Electroanalysis* **2011**, *23*, 72–78. [[CrossRef](#)]
38. Gutiérrez, J.M.; Moreno-Barón, L.; Pividori, M.I.; Alegret, S.; del Valle, M. A voltammetric electronic tongue made of modified epoxy-graphite electrodes for the qualitative analysis of wine. *Microchim. Acta* **2010**, *169*, 261–268. [[CrossRef](#)]
39. Cetó, X.; González-Calabuig, A.; Capdevila, J.; Puig-Pujol, A.; del Valle, M. Instrumental measurement of wine sensory descriptors using a voltammetric electronic tongue. *Sens. Actuators B Chem.* **2015**, *207*, 1053–1059. [[CrossRef](#)]
40. Apetrei, C.; Apetrei, I.M.; Nevares, I.; Del Alamo, M.; Parra, V.; Rodríguez-Méndez, M.L.; De Saja, J.A. Using an e-tongue based on voltammetric electrodes to discriminate among red wines aged in oak barrels or aged using alternative methods: Correlation between electrochemical signals and analytical parameters. *Electrochim. Acta* **2007**, *52*, 2588–2594. [[CrossRef](#)]
41. Wang, J.; Zhu, L.; Zhang, W.; Wei, Z. Application of the voltammetric electronic tongue based on nanocomposite modified electrodes for identifying rice wines of different geographical origins. *Anal. Chim. Acta* **2019**, *1050*, 60–70. [[CrossRef](#)]
42. Cetó, X.; Llobet, M.; Marco, J.; del Valle, M. Application of an electronic tongue towards the analysis of brandies. *Anal. Methods* **2015**, *5*, 1120–1129. [[CrossRef](#)]
43. Śliwińska, M.; Garcia-Hernandez, C.; Kościński, M.; Dymerski, T.; Wardencki, W.; Namieśnik, J.; Śliwińska-Bartkowiak, M.; Jurga, S.; Garcia-Cabezon, C.; Rodriguez-Mendez, M. Discrimination of apple liqueurs (nalewka) using a voltammetric electronic tongue, UV-Vis and Raman spectroscopy. *Sensors* **2016**, *16*, 1654. [[CrossRef](#)] [[PubMed](#)]
44. Campos, I.; Bataller, R.; Armero, R.; Gandia, J.M.; Soto, J.; Martínez-Mañez, R.; Gil-Sánchez, L. Monitoring grape ripeness using a voltammetric electronic tongue. *Food Res. Int.* **2013**, *54*, 1369–1375. [[CrossRef](#)]
45. Pigani, L.; Simone, G.V.; Foca, G.; Ulrici, A.; Masino, F.; Cubillana-Aguilera, L.; Calvini, R.; Seeber, R. Prediction of parameters related to grape ripening by multivariate calibration of voltammetric signals acquired by an electronic tongue. *Talanta* **2018**, *178*, 178–187. [[CrossRef](#)] [[PubMed](#)]
46. Ghasemi-Varnamkhasti, M.; Rodríguez-Méndez, M.L.; Mohtasebi, S.S.; Apetrei, C.; Lozano, J.; Ahmadi, H.; Razavi, S.H.; de Saja, J.A. Monitoring the aging of beers using a bioelectronic tongue. *Food Control* **2012**, *25*, 216–224. [[CrossRef](#)]
47. Cetó, X.; Gutiérrez, J.M.; Mimendia, A.; Céspedes, F.; del Valle, M. Voltammetric electronic tongue for the qualitative analysis of beers. *Electroanalysis* **2013**, *25*, 1635–1644. [[CrossRef](#)]
48. Blanco, C.A.; De la Fuente, R.; Caballero, I.; Rodríguez-Méndez, M.L. Beer discrimination using a portable electronic tongue based on screen-printed electrodes. *J. Food Eng.* **2015**, *157*, 57–62. [[CrossRef](#)]
49. Domínguez, R.B.; Moreno-Barón, L.; Muñoz, R.; Gutiérrez, J.M. Voltammetric electronic tongue and support vector machines for identification of selected features in Mexican coffee. *Sensors* **2014**, *14*, 17770–17785. [[CrossRef](#)]
50. Lopetcharat, K.; Kulapichitr, F.; Suppavorasatit, I.; Chodjarusawad, T.; Phatthara-aneksin, A.; Pratontep, S.; Borompichaichartkul, C. Relationship between overall difference decision and electronic tongue: Discrimination of civet coffee. *J. Food Eng.* **2016**, *180*, 60–68. [[CrossRef](#)]
51. Ivarsson, P.; Holmin, S.; Höjer, N.E.; Krantz-Rülcker, C.; Winqvist, F. Discrimination of tea by means of a voltammetric electronic tongue and different applied waveforms. *Sens. Actuators B Chem.* **2001**, *76*, 449–454. [[CrossRef](#)]

52. Palit, M.; Tudu, B.; Dutta, P.K.; Dutta, A.; Jana, A.; Roy, J.K.; Bhattacharyya, N.; Bandyopadhyay, R.; Chatterjee, A. Classification of black tea taste and correlation with tea taster's mark using voltammetric electronic tongue. *IEEE Trans. Instrum. Meas.* **2010**, *59*, 2230–2239. [[CrossRef](#)]
53. Palit, M.; Tudu, B.; Bhattacharyya, N.; Dutta, A.; Dutta, P.K.; Jana, A.; Bandyopadhyay, R.; Chatterjee, A. Comparison of multivariate preprocessing techniques as applied to electronic tongue based pattern classification for black tea. *Anal. Chim. Acta* **2010**, *675*, 8–15. [[CrossRef](#)] [[PubMed](#)]
54. Bhattacharyya, R.; Tudu, B.; Das, S.C.; Bhattacharyya, N.; Bandyopadhyay, R.; Pramanik, P. Classification of black tea liquor using cyclic voltammetry. *J. Food Eng.* **2012**, *109*, 120–126. [[CrossRef](#)]
55. Liu, N.; Liang, Y.; Bin, J.; Zhang, Z.; Huang, J.; Shu, R.; Yang, K. Classification of green and black teas by PCA and SVM analysis of cyclic voltammetric signals from metallic oxide-modified electrode. *Food Anal. Methods* **2014**, *7*, 472–480. [[CrossRef](#)]
56. Ghosh, A.; Bag, A.K.; Sharma, P.; Tudu, B.; Sabhapondit, S.; Baruah, B.D.; Tamuly, P.; Bhattacharyya, N.; Bandyopadhyay, R. Monitoring the fermentation process and detection of optimum fermentation time of black tea using an electronic tongue. *IEEE Sens. J.* **2015**, *15*, 6255–6262. [[CrossRef](#)]
57. Ghosh, A.; Sharma, P.; Tudu, B.; Sabhapondit, S.; Baruah, B.D.; Tamuly, P.; Bandyopadhyay, R. Detection of optimum fermentation time of black CTC tea using a voltammetric electronic tongue. *IEEE Trans. Instrum. Meas.* **2015**, *64*, 2720–2729. [[CrossRef](#)]
58. Wei, Z.; Wang, J. Classification of monofloral honeys by voltammetric electronic tongue with chemometrics method. *Electrochim. Acta* **2011**, *56*, 4907–4915. [[CrossRef](#)]
59. Wei, Z.; Wang, J. Tracing floral and geographical origins of honeys by potentiometric and voltammetric electronic tongue. *Comput. Electron. Agric.* **2014**, *108*, 112–122. [[CrossRef](#)]
60. Bougrini, M.; Tahri, K.; Saidi, T.; El Hassani, N.E.A.; Bouchikhi, B.; El Bari, N. Classification of honey according to geographical and botanical origins and detection of its adulteration using voltammetric electronic tongue. *Food Anal. Methods* **2016**, *9*, 2161–2173. [[CrossRef](#)]
61. El Hassani, N.E.A.; Tahri, K.; Llobet, E.; Bouchikhi, B.; Errachid, A.; Zine, N.; El Bari, N. Emerging approach for analytical characterization and geographical classification of Moroccan and French honeys by means of a voltammetric electronic tongue. *Food Chem.* **2018**, *243*, 36–42. [[CrossRef](#)]
62. Oroian, M.; Ropciuc, S. Romanian honey authentication using voltammetric electronic tongue. Correlation of voltammetric data with physico-chemical parameters and phenolic compounds. *Comput. Electron. Agric.* **2019**, *157*, 371–379. [[CrossRef](#)]
63. Sobrino-Gregorio, L.; Bataller, R.; Soto, J.; Escriche, I. Monitoring honey adulteration with sugar syrups using an automatic pulse voltammetric electronic tongue. *Food Control* **2018**, *91*, 254–260. [[CrossRef](#)]
64. Oroian, M.; Paduret, S.; Ropciuc, S. Honey adulteration detection: Voltammetric e-tongue versus official methods for physicochemical parameter determination. *J. Sci. Food Agric.* **2018**, *98*, 4304–4311. [[CrossRef](#)] [[PubMed](#)]
65. Apetrei, C. Novel method based on polypyrrole-modified sensors and emulsions for the evaluation of bitterness in extra virgin olive oils. *Food Res. Int.* **2012**, *48*, 673–680. [[CrossRef](#)]
66. Bougrini, M.; Tahri, K.; Haddi, Z.; Saidi, T.; El Bari, N.; Bouchikhi, B. Detection of adulteration in argan oil by using an electronic nose and a voltammetric electronic tongue. *J. Sens.* **2014**, *2014*, 245831. [[CrossRef](#)]
67. Apetrei, I.M.; Apetrei, C. Detection of virgin olive oil adulteration using a voltammetric e-tongue. *Comput. Electron. Agric.* **2014**, *108*, 148–154. [[CrossRef](#)]
68. Tahri, K.; Duarte, A.A.; Carvalho, G.; Ribeiro, P.A.; da Silva, M.G.; Mendes, D.; El Bari, N.; Raposo, M.; Bouchikhi, B. Distinguishment, identification and aroma compound quantification of Portuguese olive oils based on physicochemical attributes, HS-GC/MS analysis and voltammetric electronic tongue. *J. Sci. Food Agric.* **2018**, *98*, 681–690. [[CrossRef](#)]
69. Apetrei, I.M.; Apetrei, C. Application of voltammetric e-tongue for the detection of ammonia and putrescine in beef products. *Sens. Actuators B Chem.* **2016**, *234*, 371–379. [[CrossRef](#)]
70. Haddi, Z.; El Barbri, N.; Tahri, K.; Bougrini, M.; El Bari, N.; Llobet, E.; Bouchikhi, B. Instrumental assessment of red meat origins and their storage time using electronic sensing systems. *Anal. Methods* **2015**, *7*, 5193–5203. [[CrossRef](#)]
71. Ruiz-Rico, M.; Fuentes, A.; Masot, R.; Alcañiz, M.; Fernández-Segovia, I.; Barat, J.M. Use of the voltammetric tongue in fresh cod (*Gadus morhua*) quality assessment. *Innov. Food Sci. Emerg. Technol.* **2013**, *18*, 256–263. [[CrossRef](#)]

72. González-Calabuig, A.; Cetó, X.; del Valle, M. A Voltammetric electronic tongue for the resolution of ternary nitrophenol mixtures. *Sensors* **2018**, *18*, 216. [[CrossRef](#)]
73. Pérez-Ráfols, C.; Serrano, N.; Díaz-Cruz, J.M.; Ariño, C.; Esteban, M. A screen-printed voltammetric electronic tongue for the analysis of complex mixtures of metal ions. *Sens. Actuators B Chem.* **2017**, *250*, 393–401. [[CrossRef](#)]
74. Bataller, R.; Campos, I.; Laguarda-Miro, N.; Alcañiz, M.; Soto, J.; Martínez-Mañez, R.; Gil, L.; García-Breijo, E.; Ibáñez-Civera, J. Glyphosate detection by means of a voltammetric electronic tongue and discrimination of potential interferents. *Sensors* **2012**, *12*, 17553–17568. [[CrossRef](#)] [[PubMed](#)]
75. Arrieta, A.A.; Rodríguez-Méndez, M.L.; De Saja, J.A.; Blanco, C.A.; Nimubona, D. Prediction of bitterness and alcoholic strength in beer using an electronic tongue. *Food Chem.* **2010**, *123*, 642–646. [[CrossRef](#)]
76. Cetó, X.; Gutiérrez, J.M.; Gutiérrez, M.; Céspedes, F.; Capdevila, J.; Mínguez, S.; Jiménez-Jorquera, C.; del Valle, M. Determination of total polyphenol index in wines employing a voltammetric electronic tongue. *Anal. Chim. Acta* **2012**, *732*, 172–179. [[CrossRef](#)] [[PubMed](#)]
77. Ghosh, A.; Tudu, B.; Tamuly, P.; Bhattacharyya, N.; Bandyopadhyay, R. Prediction of theaflavin and thearubigin content in black tea using a voltammetric electronic tongue. *Chemom. Intell. Lab. Syst.* **2012**, *116*, 57–66. [[CrossRef](#)]
78. Ghosh, A.; Tamuly, P.; Bhattacharyya, N.; Tudu, B.; Gogoi, N.; Bandyopadhyay, R. Estimation of theaflavin content in black tea using electronic tongue. *J. Food Eng.* **2012**, *110*, 71–79. [[CrossRef](#)]
79. Wei, Z.; Wang, J. The evaluation of sugar content and firmness of non-climacteric pears based on voltammetric electronic tongue. *J. Food Eng.* **2013**, *117*, 158–164. [[CrossRef](#)]
80. Cetó, X.; Apetrei, C.; del Valle, M.; Rodríguez-Méndez, M.L. Evaluation of red wines antioxidant capacity by means of a voltammetric e-tongue with an optimized sensor array. *Electrochim. Acta* **2014**, *120*, 180–186. [[CrossRef](#)]
81. Rodriguez-Mendez, M.L.; Apetrei, C.; Gay, M.; Medina-Plaza, C.; de Saja, J.A.; Vidal, S.; Aagaard, O.; Ugliano, M.; Wirth, J.; Cheynier, V. Evaluation of oxygen exposure levels and polyphenolic content of red wines using an electronic panel formed by an electronic nose and an electronic tongue. *Food Chem.* **2014**, *155*, 91–97. [[CrossRef](#)]
82. Cetó, X.; Capdevila, J.; Mínguez, S.; del Valle, M. Voltammetric BioElectronic Tongue for the analysis of phenolic compounds in rosé cava wines. *Food Res. Int.* **2014**, *55*, 455–461. [[CrossRef](#)]
83. Carbó, N.; López Carrero, J.; Garcia-Castillo, F.J.; Tormos, I.; Olivas, E.; Folch, E.; Alcañiz-Fillol, M.; Soto, J.; Martínez-Mañez, R.; Martínez-Bisbal, M.C. Quantitative Determination of Spring Water Quality Parameters via Electronic Tongue. *Sensors* **2017**, *18*, 40. [[CrossRef](#)] [[PubMed](#)]
84. Labrador, R.H.; Olsson, J.; Winquist, F.; Martínez-Mañez, R.; Soto, J. Determination of bisulfites in wines with an electronic tongue based on pulse voltammetry. *Electroanalysis* **2009**, *21*, 612–617. [[CrossRef](#)]
85. González-Calabuig, A.; del Valle, M. Voltammetric electronic tongue to identify Brett character in wines. On-site quantification of its ethylphenol metabolites. *Talanta* **2018**, *179*, 70–74. [[CrossRef](#)] [[PubMed](#)]
86. Campos, I.; Masot, R.; Alcaniz, M.; Gil, L.; Soto, J.; Vivancos, J.L.; García-Breijo, E.; Labrador, R.H.; Barat, J.M.; Martínez-Mañez, R. Accurate concentration determination of anions nitrate, nitrite and chloride in minced meat using a voltammetric electronic tongue. *Sens. Actuators B Chem.* **2010**, *149*, 71–78. [[CrossRef](#)]
87. Rodríguez-Méndez, M.L.; Apetrei, C.; De Saja, J.A. Evaluation of the polyphenolic content of extra virgin olive oils using an array of voltammetric sensors. *Electrochim. Acta* **2008**, *53*, 5867–5872. [[CrossRef](#)]
88. Apetrei, I.M.; Apetrei, C. Voltammetric e-tongue for the quantification of total polyphenol content in olive oils. *Food Res. Int.* **2013**, *54*, 2075–2082. [[CrossRef](#)]
89. Wei, Z.; Wang, J. Detection of antibiotic residues in bovine milk by a voltammetric electronic tongue system. *Anal. Chim. Acta* **2011**, *694*, 46–56. [[CrossRef](#)]
90. Baldeón, E.O.; Alcañiz, M.; Masot, R.; Fuentes, E.M.; Barat, J.M.; Grau, R. Voltammetry pulse array developed to determine the antioxidant activity of camu-camu (*Myrciaria dubia* (HBK) McVaugh) and tumbo (*Passiflora mollissima* (Kunth) LH Bailey) juices employing voltammetric electronic tongues. *Food Control* **2015**, *54*, 181–187. [[CrossRef](#)]

