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Review

Review: Highlights in recent applications of electronic tongues in food analysis

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A B S T R A C T

This paper examines the main features of modern electronic tongues (e-tongues) and their most important applications in food analysis in this new century. The components of an e-tongue (automatic sampler, array of chemical sensors, and data processing system) are described. Applications commented include process monitoring, freshness evaluation and shelf-life investigation, authenticity assessment, foodstuff recognition, quantitative analysis, and other quality control studies. Finally, some interesting remarks concerning the strengths and weaknesses of e-tongues in food analysis are also mentioned.

Contents

1. Introduction

In the present decade, many papers have appeared in the literature describing the use of the so-called electronic tongues (e-tongues), most notably in the field of food analysis [1–7]. These devices are typically array of sensors coupled to chemometric processing used to characterize complex samples, and can be considered as analytical instruments that artificially reproduce the taste sensation. Arrays of gas sensors are termed 'electronic noses' [8] while arrays of liquid sensors are referred to as 'electronic tongues' [9]. This paper will focus on the use of e-tongues in quality control and process operations in the food industry along the present century. The principles behind the design of this type of devices will be also discussed.

2. Why an electronic tongue in food analysis?

In food analysis, a wide range of traditional methodologies are used to determine or detect compounds characteristics of food. These methodologies show good precision, accuracy, and reliabil-

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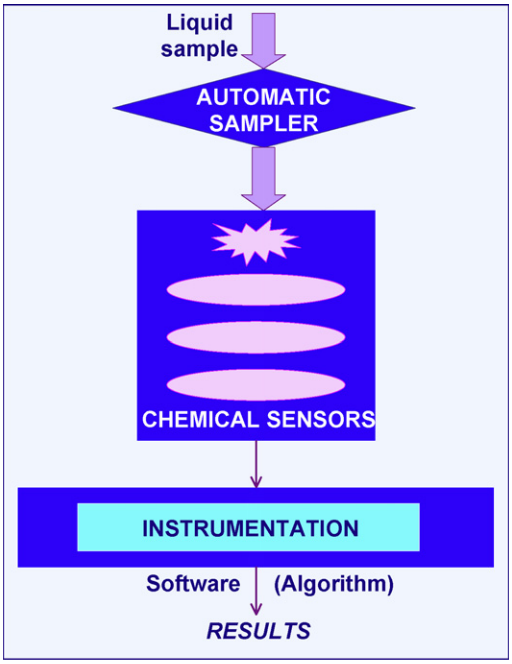

Fig. 1. Components of an electronic tongue.

ity but they are destructive, time-consuming, require expensive equipment, and are unsuitable for *in situ* or *at site* monitoring. To overcome these drawbacks, e-tongues have emerged as rapid and easy-to-use tools very promising for evaluation of food quality, especially in such situations in which only qualitative or semi-quantitative information is required (i.e., in places where foods are prepared, commercialized, or stored).

Although e-tongues still stray considerably from natural taste sense, they have shown good correlations with organoleptic scores given by human panellists. Comparing both taste systems, artificial senses are not subjective, do not become tired or infected and can be used in a wider range of samples (i.e., toxic samples). Moreover, e-tongues can have better sensitivity than the human tongue and can detect substances undetectable by their natural counterparts. This is because the taste system in humans is not as highly developed as the olfactory system. As Legin et al. [10] pointed out, 'the electronic tongue can be thought of as analogous to both olfaction and taste and it can be used for the detection of all types of dissolved compounds, including volatile compounds which give odors after evaporation'. This device can be used for the recognition, classification and quantitative determination of multiple component concentrations.

3. Description and structure of an e-tongue

E-tongues have been developed on the basis of mechanisms of biological systems. In a gustatory system, substances producing taste are received by the biological membrane of gustatory cells in non-specific taste buds on the tongue. Information on taste substances is transduced into an electric signal, which is transmitted along the nerve fibre to the brain, where the taste is perceived. In an e-tongue, the output of the non-specific sensor array shows different patterns for the different taste-causing chemical substances and such data is statistically processed.

The e-tongue can be defined as 'a multisensory system for liquid analysis based on chemical sensor arrays and a suitable pattern recognition method'. Nevertheless, and in a broader sense, an e-tongue is composed of four elements (Fig. 1): (i) automatic sampler (although it is not a necessary component), (ii) array of chemical sensors with different selectivity, (iii) instrumentation to obtain the signal, and (iv) software with the appropriate algorithm to process the signal and get the results. All of them will be described thereafter.

The autosampler allows several samples to be evaluated automatically once the sample has been prepared. No special sample pre-treatment is required but filling the corresponding beakers. One beaker position is usually reserved for cleaning the sensor array after the analysis of each individual sample. The automatic sampler also includes fluidic pumps for cleaning out the beaker for sensor rinsing when needed. Sample temperature may also be controlled to ensure analytical reproducibility of measurements.

The use of mechanized flow techniques – mainly flow injection analysis (FIA) but also sequential injection analysis (SIA) – as sample or standard-handling systems has increased in the last 3 years. Manual analysis is, sometimes, a hindrance in using the e-tongues as fast analytical techniques due to the high number of standards or samples required in the calibration process to generate reliable multivariate models. Mechanization can simplify their operation providing benefits such as reduction of the analysis time and reagents consumption, improvement of the reproducibility and reduction of drifts in measurement. A complete review of the literature reporting the use of e-tongues along with flow analysis principles has been presented by Gutés et al. [11].

Regarding the sensor array used in the design of e-tongues, a wide variety of chemical sensors have been employed: electrochemical (potentiometric, voltammetric, amperometric, impedimetric, conductimetric), optical, mass, and enzymatic sensors (biosensors) [12–17]. A full discussion about the different architectures of such devices has been reported [13]. The main features about these systems are summarized here.

Potentiometric sensors were used in the first studies on the application of sensor arrays for multicomponent analysis of liquids [18–20] and they still remain the most widely used type in e-tongue systems, especially ion-selective electrodes (ISEs). The first e-tongue system (called 'taste sensor') was introduced by Toko and co-workers [19] and consisted of eight potentiometric electrodes with lipid-polymeric membranes (PVC membranes with lipid derivatives). Later, Legin et al. [20] presented an e-tongue comprising solid-state crystalline ISEs based on chalcogenide glass. Both systems have been used in a wide variety of analytical problems and in some applications they have been coupled.

The main disadvantages of potentiometric sensors are their temperature dependence and the adsorption of solution components that affect the membrane potential. These factors can be minimized by controlling the temperature and washing the electrodes. On the other hand, the advantages of ISEs are their well-known operation principle, low cost, simple set-up, easy fabrication and, the possibility of obtaining sensors selective to many various species [12,13].

Voltammetric sensors are also widely used in e-tongue systems. These devices are advantageous for multicomponent measurements because of their high selectivity, high signal-to-noise ratio, low detection limits and various modes of measurement. Furthermore, the surface of the electrodes can be modified with various chemosensitive materials obtaining sensors of various sensitivity and selectivity towards a variety of species. However, their applicability is limited to redox-active substances [12–14]. On the other hand, temperature dependence and large surface alteration causing drifts in sensor response have also been found. To overcome this last problem, electrodes electrochemical cleaning steps or mechanical polishing are used. Recently, a shelf-polishing device has been proposed [21].

Impedimetric e-tongues were introduced by Riul et al. and consist of a bare interdigitated electrode, and interdigitated electrodes coated with various chemosensitive materials deposited by

Table 1
Applications of e-tongues in food process monitoring.

Sample	Type of study	Chemical sensors	Data processing algorithm	Ref.
Starting culture for light cheese production	Fermentation monitoring	Potentiometric sensors (30 chalcogenide glass and solvent polymeric working electrodes; Ag/AgCl reference electrode)	PLS	[50]
	Discrimination of samples from fermentation batches			
Milk	On-line monitoring of sources of raw milk	Voltammetric working electrodes (Au, Pt and Rh) embedded in a dental material	PCA	[51]
	On-line monitoring of the cleaning process of the pasteurization unit	Voltammetric working electrodes (Au, Pt, Rh and stainless steel) embedded in PEEK™		
Red wine	Monitoring of the ageing process	Voltammetric sensors (7 polypirrole-based sensors, 4 CPEs based on phthalocyanines and 2 CPEs based on perylenes; Ag|AgCl/KCl saturated reference electrode; Pt wire counter electrode)	PCA, SIMCA	[52]
	Discrimination of samples aged in oak barrels of different wood origin and toasting level			
Wine	Analysis of the effects of several treatments on wine phenolic compounds composition	Potentiometric sensors (14 plasticized PVC sensors, 11 chalcogenide glass sensors,1 glass pH electrode; Ag/AgCl reference electrode)	PCA, ANOVA, ASCA, PLS	[53]
	Prediction of chemical parameters			

PLS, partial least squares; PCA, principal component analysis; CPE, carbon paste electrode; SIMCA, soft independent modeling of class analogy; ANOVA, analysis of variance; ASCA, ANOVA-simultaneous component analysis.

means of the Langmuir–Blodgett technique [22–25]. This type of e-tongues is based on the measurement of impedance either at one fixed frequency or a broader spectrum using impedance spectroscopy. They have been applied to the recognition of basic taste substances, beverages, and mineral waters showing excellent sensitivity [16,26–33]. Moreover, there is no requirement of active species in the measuring system and – unlike the case of the other electrochemical methods – no need of a standard reference electrode (which might be troublesome in many practical applications because a reliable reference is a critical issue in miniaturized sensor arrays).

Although to a lesser extent than electrochemical sensors, optical sensors are also used in e-tongues technology. These devices offer several modes of operation such as fluorescence, absorbance, reflectance, etc. Additionally, analytes difficult to detect electrochemically (e.g. uncharged and/or non-electroactive) can often be studied with optical sensors. However, some drawbacks such as sensor preparation, durability, and signal interferences limit their application [12,13]. Optical e-tongues have been mainly used in biomedical analysis and few applications can be found in the literature devoted to food analysis [34,35].

Mass sensors are miniaturized solid-state devices based on the piezoelectric effect. Although mass sensors are frequently used in electronic nose systems, these devices are hardly used in e-tongues [13]. Nevertheless, their high sensitivity, detection principle based on universal weight changes, capability of real-time electronic read-out, small size, robustness, and low unit cost make mass sensors applications to be promising [36].

The architecture of an e-tongue system is intrinsically open, thus several kinds of sensors have been coupled and even other techniques (i.e., electronic noses) have been used together with the e-tongue to produce wider complementary information about analytes. In humans, the senses of olfaction and taste always cooperate and influence each other, especially in food flavor evaluation. Therefore, the idea of using an integrated sensor system, which would comprise both an electronic nose and an electronic tongue, sounds natural and has been explored by several researchers for the analysis of foodstuffs [37–44]. It was found that each system was able to distinguish different samples alone, but the data fusion improved classification. Thus, the combination of an electronic tongue with an electronic nose can provide a higher recognition power of the combined system. This feature may be of significant practical impact when very similar samples are analyzed and reliable identification is crucial.

Finally, it must be remarked that the sensor array should be selected taken into account the chemical nature of the samples studied. However, similar sensors are applied sometimes to absolutely different samples, which can produce artifact results.

Other important aspect of multisensor analysis is the signal processing. To deal with the data from sensor arrays different pattern recognition methods are used – mainly principal component analysis (PCA) and artificial neural networks (ANN) – and multivariate calibration methods – mainly ANN and partial least square regression (PLS) – which allow fitting the multidimensional output of the sensor set. It should be taken into account that adequate data processing is an essential step of the e-tongue approach but even advanced math methods cannot improve the results. The data produced by the sensor array must be reproducible and reliable. This is ensured by the responsible design of the sensor array and thoroughly elaborated measuring procedure. A more detailed description of data processing methods in sensor analysis is beyond the scope of this review. Theoretical discussions of available methods can be found in many books and papers [45–49].

4. Applications of electronic tongues in food analysis

A search of the recent, relevant literature shows that six major categories of use for e-tongues in food analysis can be considered: (i) process monitoring, (ii) freshness evaluation and shelf-life investigation, (iii) authenticity assessment, (iv) foodstuff recognition, (v) quantitative analysis, and (vi) other quality control studies. The most important contributions to each of these in the present decade/century will be described (Tables 1–6).

Table 2
Applications of e-tongues in food freshness evaluation and shelf-life investigation.

Sample	Type of study	Chemical sensors	Data processing algorithm	Ref.
Fish (cultured sea bream *Sparus auratus* fillets)	Discrimination between storage times	Potentiometric sensors (2 Ag/Pt, 2 Au, 2 Ag, 2 C (graphite), 2 Ag/Pd, 2 Ag/AgCl, 2 Cu, 2 RuO_2 thick-film pastes; calomel reference electrode)	PCA, ANN, PLS	[55]
	Prediction of chemical and biochemical degradation parameters			
Fish (cultured sea bream *Sparus auratus* fillets)	Discrimination between storage times	Potentiometric sensors (5–12 Au, Ag, Cu, Ni and C (graphite) working electrodes; Ag/AgCl reference electrode)	PCA, ANN, MLR	[56]
	Prediction of biochemical degradation parameters			
Fish (tench (*Tinca tinca*))	Discrimination between storage times	Voltammetric sensors (CPEs or SPEs based on phthalocyanines; Ag|AgCl/KCl reference electrode; Pt wire counter electrode)	PCA, PLS–DA	[57]
	Prediction of fish degradation degree			
Apricots (*Prunus armeniaca* L.)	Discrimination between post-harvest storage treatments	Potentiometric sensors (7 ISFETs based on polymer membranes working electrodes; Ag/AgCl reference electrode)	CDA, PLS	[58]
	Discrimination between apricot varieties			
	Discrimination between storage times			
	Correlation with chemical and sensory panel parameters			

PCA, principal component analysis; ANN, artificial neural network; PLS, partial least squares; MLR, multiple linear regression; CPE, carbon paste electrode; SPE, screen-printed electrodes; PLS–DA, partial least squares–discriminant analysis; ISFET, ion-selective field effect transistor; CDA, canonical discriminant analysis.

Table 3
Applications of e-tongues in food authenticity assessment.

Sample	Type of study	Chemical sensors	Data processing algorithm	Ref.
Honeys	Discrimination between samples accordingly to the most predominant pollen type	Potentiometric sensors (20 all-solid-state electrodes with PVC polymeric membranes applied on solid conducting silver-epoxy supports; Ag/AgCl reference electrode)	PCA, LDA	[59]
Goat milk	Detection of adulteration of samples with cow milk	Potentiometric sensors (2 units of 20 all-solid-state electrodes with PVC polymeric membranes each, applied on solid conducting silver-epoxy supports, working in parallel; Ag/AgCl reference electrode)	LDA	[60]
Red wines	Correlation with chemical parameters	Voltammetric sensors (3 CPEs modified with phthalocyanines, 6 polypyrrole conducting polymers, 1 bare CPE and 1 unmodified Au disk electrode as sensor references)	PLS, PCA	[61]
	Discrimination between chemical adulterants			
White wines	Discrimination between grape varieties	Voltammetric sensors (CPEs modified with 3 rare-earth bisphthalocyanines and 3 perylenes; Ag|AgCl/KCl saturated reference electrode; Pt wire counter electrode)	PCA	[62]
White wines	Discrimination of grape varieties and geographical origins	Amperometric sensors (1 PEDOT conducting polymer, composite materials of Au and Pt nanoparticles embedded in a PEDOT layer; Ag/AgCl reference electrode; glassy carbon rod counter electrode)	PCA, PLS–DA	[63]
Vegetable oils	Discrimination between olive oils of different qualities and discrimination between different vegetable oils	Voltammetric sensors (CPEs modified with 6 plant oils; Ag|AgCl/KCl saturated reference electrode; Pt wire counter electrode)	PCA	[64]
Extra virgin olive oils	Discrimination between geographical origins	Amperometric sensors (a dual and a single glassy carbon electrode; Ag/AgCl saturated reference electrode; platinum counter electrode)	PCA, ANN	[65]

PCA, principal component analysis; LDA, linear discriminant analysis; CPE, carbon paste electrode; PLS, partial least square regression; PEDOT, poly(3,4-ethylenedioxythiophene); PLS–DA, partial least squares–discriminant analysis; ANN, artificial neural network.

Table 4
Applications of e-tongues in foodstuff recognition.

Sample	Type of study	Chemical sensors	Data processing algorithm	Ref.
Fermented milk	Discrimination between different types of samples	Hybrid e-tongue comprising conductimetric, potentiometric (pH, CO_2 and Cl^- ISEs) and voltammetric (Au, Ir, Pd, Pt, Re and Rh wires; Ag/AgCl reference electrode; stainless steel auxiliary electrode) sensors	PCA, ANN	[67]
Mineral waters and apple juices	Discrimination between different brands of samples	Potentiometric sensors (17 PVC membrane ISEs; Ag/AgCl reference electrode)	PCA, ANN	[68]
Orange juices, tonic, and milk	Discrimination between different brands of samples	Potentiometric sensors (15 PVC membrane ISEs, 2 PVC membrane partially selective electrodes; Ag/AgCl reference electrode)	PCA, ANN	[69]
Milk	Discrimination between different brands of samples	Potentiometric sensors (8 Au electrodes with PVC membranes modified with various additives; Ag/AgCl or IL reference electrodes)	PLS–DA	[70]
Commercial waters, orange-based drinks and tea samples	Discrimination between different kinds of water samples	Potentiometric sensors (9 PVC membrane ISEs; Ag/AgCl reference electrode)	PCA	[71]
	Ranking of orange drinks samples according their natural juice content			
	Discrimination between different kinds of tea samples			
Orange, pear, peach and appricot juices	Discrimination between different kinds of juices	Amperometric sensors (Pt, Au and Pt/PEDOT working electrodes; Ag/AgCl reference electrode; glassy carbon rod counter electrode)	PCA, PLS–DA	[72]
	Discrimination between orange juices from different brands			
Apples	Discrimination between varieties	Potentiometric sensors (15 PVC membranes based electrodes; Ag/AgCl reference electrode)	PCA, PLS	[73]
	Determination of organic acids			

ISE, ion-selective electrode, PCA, principal component analysis; ANN, artificial neural network; MLR, multiple linear regression; IL, ionic liquid (1-dodecyl-3-methyl-imidazolium chloride); PLS–DA, partial least squares–discriminant analysis; PEDOT, poly(3,4-ethylenedioxythiophene); PLS, partial least square regression.

4.1. Process monitoring

Several successful applications of e-tongues to the monitoring of taste components along a food production process have been published. The main features of such applications are summarized in Table 1.

An e-tongue based on 30 non-specific potentiometric sensors has been applied to the monitoring of a batch fermentation process of starting culture for cheese production [50]. PLS control charts allowed detection of fermentations running under 'normal' and 'abnormal' operating conditions at an early stage. Moreover, the capability of the e-tongue to quantify organic acids (such as citric, lactic, and orotic) in the fermentation media was demonstrated with average prediction errors in the 5–13% range. This e-tongue can thus be considered a promising tool for fermentation process monitoring.

In the dairy industry, the demands of the sensors are considerable. It should be able to withstand extreme conditions (hot base and acid solutions), be hygienic and able to be sterilized. Also, no reference electrode is allowed. In the work by Winquist et al. [51], these demands were fulfilled by specially designed voltammetric e-tongues. These devices were inserted in the process line of a dairy industry for direct in-line measurements and they were in operation for 8 months without malfunction and maintenance. The e-tongues were used to follow the different sources of raw milk coming into the process and to monitor the cleaning process of the pasteurization unit.

Parra et al. [52] designed an e-tongue to monitor the ageing of red wines and to discriminate wine samples aged in oak barrels of different characteristics. This e-tongue comprised 13 voltammetric electrodes chemically modified with different sensitive materials (polypyrrole, metallophthalocyanine derivatives and perylene derivatives). The diversity of the sensing materials allowed obtaining a high cross-selectivity in the responses of the sensors forming the array. Multivariate inspection of voltammetric data showed the high capability of discrimination and classification of this e-tongue.

The purpose of the paper by Rudnitskaya et al. [53] was the assessment of the influence of micro-oxygenation and maceration with oak chips on wine composition and specifically on wine phenolic compounds. Effects of these treatments on wines from different vintages were studied using a set of conventional physicochemical measurements and a potentiometric e-tongue. Furthermore, the e-tongue was capable of predicting total phenolic content, color density and hue and chemical ages of wine with prediction errors lower than 15%.

4.2. Freshness evaluation and shelf-life investigation

Improved methods for the assessment of food freshness and shelf-life time have been high on the priority list of food manufacturers for many years. In this field, e-tongues have proved their potential in predicting freshness or spoilage of different food raw material and products [4,54–57] (Table 2).

Ahlers discusses the use of e-tongues for assessment of meat quality, special emphasis being put on the evaluation of freshness [54]. Several experiences have been carried out with pork and veal, with highly satisfactory results.

Applications of e-tongues to evaluate fish freshness have also been reported [55–57]. Results obtained point out the usefulness of e-tongues for *in situ* and *at site* freshness evaluation and as

Table 5
Applications of e-tongues in food quantitative analysis.

Sample	Type of study	Chemical sensors	Data processing algorithm	Ref.
Synthetic taste solutions and wines	Determination of NaCl and citric acid in taste solutions	Potentiometric sensors (5 PVC polymeric membranes; Ag/AgCl reference electrode)	PCA	[74]
	Discrimination between red and white wines			
Wines	Discrimination of wines from different geographical areas	Potentiometric sensors (14 with chalcogenide glass and crystalline membranes, 2 metallic, 6 with plasticized polymer membranes and pH glass electrode as working electrodes; Ag/AgCl reference electrode)	PCA, ANN, PLS, SIMCA	[75]
	Discrimination of wines of the same vintage and denomination and different vineyards			
	Determination of different components and parameters			
	Prediction of sensory parameters			
Wines	Correlation with sensorial descriptors and chemical parameters	Potentiometric sensors (5 electropolymerised metalloporphyrins working electrodes; Ag/AgCl reference electrode)	PCA, PLS, PLS–DA	[42]
Grapes juices and wines	Discrimination between grape varieties	Potentiomertric sensors (6 ISFETs based on polymeric membranes and chalcogenide glass membranes working electrodes; Ag/AgCl reference electrode)	PCA, SIMCA, PLS	[76]
	Discrimination between vintages			
	Determination of different parameters and components			
Extra virgin olive oils	Discrimination of samples according to their phenolic content and bitterness index	Voltammetric sensors (5 CPEs modified with lanthanide bisphthalocyanines, 6 polypirroles conducting polymers and 1 unmodified CPE; Ag|AgCl/KCl saturated reference electrode; Pt gauze counter electrode)	PCA, PLS–DA, PLS	[77]
	Correlation with the polyphenol content, the bitterness index (analyzed by chemical methods) and the bitterness degree (determined by a panel of experts)			
Synthetic taste solutions and tonic waters	Determination of quinine and saccharine	Piezoelectric quartz crystal sensor array based on molecularly imprinted polymers	Simple linear regression	[36]
	Comparison with bitterness intensity determined by a human taste panel			
Tomatoes (*Lycopersicon esculentum* Mill.)	Discrimination between cultivars	2 e-tongues: a home-made e-tongue based on 18 potentiometric sensors and the Astree commercial e-tongue (7 ISFETs based on polymer membranes working electrodes; Ag/AgCl reference electrode)	PCA, CDA, PLS	[78]
	Determination of taste compounds			
	Correlation with sensory panel evaluation			

PCA, principal component analysis; ANN, artificial neural network; PLS, partial least squares; SIMCA, soft independent modeling of class analogy; PLS–DA, partial least squares–discriminant analysis; ISFET, ion-selective field effect transistor; CPE, carbon paste electrode; CDA, canonical discriminant analysis.

an alternative to other destructive, high-cost and time-consuming methodologies.

Gil et al. [55] studied the evolution with time on fillets of cultured sea bream (*Sparus auratus*) by means of a potentiometric e-tongue containing 16 electrodes. Fish freshness indicators such as texture, pH, color, microbial analysis, total volatile basic nitrogen and biogenic amines were also determined versus time. Multivariate analysis of e-tongue data allowed the assessment of the storage time of fish fillets with a rate of success of 100%. On the other hand, good correlations were found between potentiometric data and fish freshness indicators with correlation coefficients higher than 0.90. The same authors in other work [56], using data obtained only from Au and Ag wires were able to classify *Sparus auratus* fillets according to their storage time. Moreover, a correlation coefficient of 0.96 was observed between K_1 index (fish freshness parameter) and potentiometric data.

In the paper by Rodríguez-Méndez et al. [57] two voltammetric e-tongues based on carbon paste or screen-printed electrodes modified with phthalocyanines were developed and applied to monitor fish spoilage. The discrimination ability demonstrated by PCA and the capability of prediction of fish freshness calculated by partial least squares–discriminant analysis (PLS–DA) was similar in both cases. Signals provided by carbon paste electrodes showed better sensor-to-sensor reproducibility than screen-printed elec-

Table 6
Applications of e-tongues in other food quality control studies.

Sample	Type of study	Chemical sensors	Data processing algorithm	Ref.
Beer	Batch-to-batch variation following the brewing process	Potentiometric sensors (7 ISFETs based on polymer membranes working electrodes; Ag/AgCl reference electrode)	PCA	[79]
	Detection of off-flavor		SIMCA	
	Quantitation of bitterness		PLS	
Soft drinks	Quality of high-fructose corn syrup		SIMCA	
Green tea infusions	Discrimination between quality grades	Potentiometric sensors (7 ISFETs based on polymer membranes working electrodes; Ag/AgCl reference electrode)	PCA, ANN	[80]
Rice	Correlation with human taste panel scores	Potentiometric sensors (10 working electrodes made from lipid membranes; Ag/AgCl reference electrode)	MLR	[81]
	Correlation with chemical analysis			
	Discrimination between milling yields		PCA	
Mineral waters	Discrimination between high and low mineralized waters	Potentiometric sensors (6 ISFETs with different urethane polymer membranes, 2 interdigitated Pt electrodes, 1 temperature diode)	PCA	[82]
Beer	Correlation with human taste panel scores	29 potentiometric sensors (plasticized PVC sensors, chalcogenide glass sensors, glass pH electrode; Ag/AgCl reference electrode)	PCA, CCA, PLS	[83]
Orange juices	Discrimination between different brands of samples	Potentiometric sensors (16 PVC-based microelectrodes, 1 pH electrode; Ag/AgCl reference electrode)	PLS	[84]
Tea and herbal products infusions	Discimination between beverages	Potentiometric sensors (16 polyuretane-based microelectrodes; Ag/AgCl reference electrode)	PCA, PCR	[85]
	Discrimination between tea brands			
Milk	Discrimination of samples adulterated with hydrogen peroxide	Voltammetric sensors (Au and Prussian Blue-modified gold electrodes; silver-epoxy pseudo-reference electrode; Au counter electrode)	PCA	[86]
	Discrimination between samples with different pasteurization process			
Wine	Discrimination between ageing methods	6 voltammetric sensors (Pt, CPE and CPEs based on phthalocyanines; Ag|AgCl/KCl saturated reference electrode; Pt wire counter electrode)	PCA, PLS–DA, PLS	[87]
	Prediction of chemical parameters			
Wine	Prediction of wine age	28 potentiometric sensors (plasticized PVC sensors, chalcogenide glass sensors, glass pH electrode; Ag/AgCl reference electrode)	PCA, OSC, PLS	[88]
Wine	Prediction of wine age	26 potentiometric sensors (plasticized PVC sensors, chalcogenide glass sensors, glass pH electrode; Ag/AgCl reference electrode)	PCA, PLS, ASCA	[89]
	Determination of organic acids and phenolic compounds			

ISFET, ion-sensitive field effect transistor; PCA, principal component analysis; SIMCA, soft independent modeling of class analogy; PLS, Partial least squares; ANN, artificial neural network; CCA, canonical correlation analysis; PCR, principal component regression; CPE, carbon paste electrode; PLS–DA, partial least squares–discriminant analysis; OSC, orthogonal signal correction; ASCA, ANOVA-Simultaneous component analysis.

trodes. However, the screen-printing technology allowed for the preparation of miniaturized electrodes, which are promising for the fabrication of low-cost sensors with higher sensibility compared to the corresponding modified carbon paste electrodes.

An example of e-tongues application in shelf-life investigation is reported by Kantor et al. [58]. In this paper, a commercial potentiometric e-tongue was used (Astree, Alpha-MOS, Toulouse, France). This device comprises a 16-position autosampler, an array of 7 liquid sensors (ion-selective field effect transistors, ISFETs), and an advanced chemometric software package containing various pattern recognition analysis modules. The autosampler includes fluidic pumps for cleaning out the beaker for sensor rinsing when needed. The instrument also has an option of sample temperature control to ensure analytical reproducibility of measurements. The detectors consist of an array of seven silicon transistors coated with different polymer membranes displaying sensitivity to acids, salts, mono- and disaccharides. Furthermore, sensors have cross-sensitivity for taste chemicals which are typically found in foodstuffs and beverages. Up to 25 different sensors are commercially available. Finally, the chemometric package includes PCA, PLS, discrimination function analysis (DFA) and soft independent modelling of class analogy (SIMCA) modules for sensors data evaluation.

This e-tongue was used for the recognition of different apricot varieties and detecting taste changes during storage period and the effect of different storage treatments [58]. Furthermore, moderate correlations between e-tongue data and degree Brix ($r > 0.80$) and pH measurements ($r > 0.60$) were obtained. It was demonstrated to be a valuable tool for monitoring the effects of post-harvest techniques on fruit ripening process.

4.3. Authenticity assessment

The authenticity of foods is currently of great concern for researchers, consumers, industries, and policymakers. An authentic raw material or finished product has to comply with labelling in terms of ingredients, production technology, genetic identity, origin, etc. E-tongues have proven their potential in authenticity assessment of different kinds of foods (Table 3) due to their simplicity, efficiency, speed and low cost of the determinations [59–64].

In the paper by Dias et al. [59] an array with 20 all-solid-state potentiometric electrodes with polymeric membranes, was constructed and evaluated for differentiation of commercial honeys with different pollen profiles. The chemometric tools used were PCA and linear discriminant analysis (LDA). It was found that the e-tongue had a reasonable efficiency (84% and 72% of success in calibration and cross-validation, respectively) for classification of honey samples accordingly to the most predominant pollen type. The present e-tongue showed promising behavior for monofloral honey assortment.

Another topic of adulterations is milk and dairy products. Dias et al. [60] proposed an all-solid-state potentiometric e-tongue with two units of polymeric membranes to detect raw goat milk adulterations with raw cow milk. LDA results showed a satisfactory capability (97% and 87% for original and cross-validation classifications, respectively) of this methodology to evaluate the possible adulterations. However, in order to use this e-tongue as a routine methodology it is needed to improve the multisensor system by testing and including more sensible sensors to milk composition variations.

Fraudulent performances are increasingly carried out in different alcoholic beverages among them wines are an important target. In this framework, e-tongues have been used for the identification or authentication of wines according to elaboration features (grape variety or their geographical origin) and for the detection of fraudulent samples derived from deliberated addition of chemicals to wine to correct or enhance its organoleptic properties.

In this context, a hybrid array of voltammetric sensors formed by different families of sensitive materials (phthalocyanines and conducting polypyrrole polymers) was used by Parra et al. [61] to detect and identify some chemical adulterations commonly carried out in red wines. Good correlations between the sensor responses and chemical parameters measured by traditional methods were obtained. The predicting ability of the alcoholic degree and acid related parameters were particularly remarkable with predicting errors lower than 3%. Moreover, the array was able to distinguish among the different kinds of adulterations. The use of different families of sensitive materials enhanced the cross-selectivity and improved the capability of discrimination of the array.

Rodríguez-Méndez et al. [62] constructed an array formed by carbon paste electrodes modified with rare-earth bisphthalocyanines and perylenes. This array provided a rich variety of voltammetric responses towards acids, bases, ionic solutions and antioxidants. Moreover, PCA analysis of data obtained from wine samples allowed their classification according to the grape varieties used for their elaboration.

In the work by Pigani et al. [63] the voltammetric responses on white wines of different grape varieties and geographical origins were collected by three different poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymer modified electrodes. The subsequent chemometric analysis was carried out both separately on the signals of each sensor, and on the signals of two or even three sensors. All the modified electrodes showed good classification capabilities (92–100%) of the wine samples.

Another application area of e-tongues is the authenticity assessment of vegetable oils [64–66]. In the work by Apetrei et al. [64] a novel method to analyze vegetable oils was developed. The method consisted of using modified carbon paste electrodes where the oils to be analyzed were used as a binder. PCA analysis of the voltammetric signals obtained after immersing the oil-based electrodes in different electrolytic solutions allowed for a clear discrimination between olive oils and seed oils (corn and sun-flower oils) and between olive oils of different qualities (virgin extra, virgin ordinary, virgin lampante and refined olive oils).

There are examples in which electronic noses have provided better results than e-tongues for the analysis of extra virgin olive oils [65,66]. An electronic nose and an electronic tongue were used by Cosio et al. [65] to verify the geographical origin of extra virgin olive oils. Analyses were conducted with a commercial electronic nose (model 3320 Applied Sensor Lab Emission Analyzer) comprising an array of 22 sensors. The e-tongue device included a FIA system and three carbon electrode detectors. In order to obtain a complete description of oil samples, free acidity, peroxide value, ultraviolet indices, and phenol content were also determined. The dataset included 36 Garda oils (distinguished with a European Protected Denomination of Origin trademark) and 17 oils from other regions. Classification models to separate Garda and not-Garda oils were built by means of ANN using all the chemical variables and sensor signals, using only e-tongue sensors and using four selected electronic noses. ANNs yielded very satisfactory results (mean rate in prediction comprised in the 0.2–4.2% range) in all cases and indicated the electronic nose as the most appropriate tool for the characterization of the analyzed oils. In a further work [66], the authors applied the same e-systems to the evaluation of different storage conditions of extra virgin olive oils. Again, results showed how the electronic nose was enough to correctly classify samples stored in different conditions, while classical chemical parameters and the electronic tongue were not relevant.

4.4. Foodstuff recognition/characterization

Table 4 summarizes the main features of some applications of e-tongues in foodstuff recognition [67–73].

A hybrid e-tongue based on a combination of potentiometry, voltammetry and conductivity measurements was proposed for classification of six different types of fermented milk by Winquist et al. [67]. Using data from the voltammetric, potentiometric and conductivity measurements independently a partial overlapping between sample classes was observed. However, the combination from all information sources could separate all six samples.

An e-tongue comprising 17 ion-selective electrodes was applied to discriminate between different brands of mineral waters and apple juices by Ciosek et al. [68]. Since the main components of mineral water are ionic, high-selective sensors were able to easily differentiate the water samples. However, in the case of juice samples lower recognition accuracy was obtained due to ionic inorganic but also organic species characterizing juice taste. To solve this problem, a system based on selective and partially selective sensors was developed to discriminate between different brands of orange juice, tonic, and milk with an accuracy of 90–100% [69]. In this way, the combination of two types of sensors provides a versatile device for qualitative analysis of various types of beverages. In other paper [70], the classification of milk samples originating from various producers was successfully accomplished using a miniaturized potentiometric e-tongue (also with selective and partially selective sensors) and PLS–DA. Moreover, the application of miniaturized reference electrode, integrated on the same substrate provided satisfactory results (100% of correct classifications), which can be helpful in future hand-held e-tongue systems.

Gallardo et al. [71] used an e-tongue based on a set of ion-selective sensors in combination with PCA for the classification of food samples in batch and in flow injection mode. First attempt was to classify synthetic samples prepared with controlled variability. Once this ability was proven, satisfactory classification results were obtained for commercial waters, orange-based drinks. In the case of tea samples, only a gross classification of these beverages was accomplished.

Different electrodes were tested for use as non-specific amperometric sensors for analysis of different fruit juices from different fruits or different brands [72]. The sensors were traditional Pt and Au electrodes and Pt/PEDOT. The PEDOT electrode demonstrated the most discriminating ability, and it was the only system capable of satisfactorily discriminating between juices from the same fruit but from different brands (100% of correct classifications by means of PLS–DA). Moreover, the electrode cleaning procedure was much simpler and less time-consuming for the PEDOT electrode than for the others.

In the work by Rudnitskaya et al. [73] a potentiometric e-tongue and Fourier transform infrared spectroscopy (FTIR) were evaluated and compared with respect to apple quality measurements. The study was carried out using data obtained from each analytical instrument independently but also merging both data sources by means of several approaches for data fusion. Both, e-tongue and FTIR proved to be promising tools for discrimination of apple varieties and determination of organic acids contents in apples. Fusion of the data from these two instruments allowed for improving the classification of apple cultivars. However, no significant difference was found using the merged data from the two devices for quantitative data processing. The authors attributed this result to the fact that outputs of both instruments contain similar chemical information.

4.5. Quantitative analysis

Some applications to quantitative analysis of several quality parameters as well as inorganic and organic components of wines have been reported [42,74–76] (Table 5).

An e-tongue composed of a polymer membrane sensor array and data processing routines was introduced as an analytical tool for quantification of saltiness (NaCl) and sourness (citric acid) in synthetic taste solutions as well as for discrimination between wines from different grapes [74].

Another attempt of using e-tongues for wine analysis is reported by Legin et al. [75]. The e-tongue, based on 23 potentiometric cross-sensitive chemical sensors, allowed the measurement of several quantitative parameters of the wines (total and volatile acidity, pH, contents of several wine components) with precision within 5–12%. In addition, the system was capable of predicting human sensory scores with precision errors within the 4–27% range.

In the paper by Di Natale et al. [42], electronic nose and tongue data were used to build predictive models of both chemical and sensorial parameters of wine samples. The electronic nose consisted of a porphyrin based quartz piezoelectric microbalance gas sensor array. The e-tongue was composed of potentiometric electrodes modified by metalloporphyrins. Chemometric analysis of data showed that simultaneous use of both devices increased the prediction accuracy of estimates. A better accuracy was obtained for sensorial descriptors with respect to the chemical parameters (0.1–52% and 4.7–12.5% mean relative errors obtained from PLS models for chemical and sensorial parameters, respectively).

An integrated multisensor composed by ISFETs devices combined with a FIA system has been applied as an e-tongue to grape juice and wine sample analysis [76]. Multivariate analysis of data demonstrated the potential of using those multisensors for quantitative prediction of several sample parameters and concentration components (PLS relative errors lower than 10%) in good agreement with standard methods (regression coefficients higher than 0.99). The novelty of this system relies on the use of an integrated multisensor fabricated with microelectronic technology, thus allowing the miniaturization of the flow cell.

Apart from wine and grape juice samples, e-tongues have been used for the determination of taste compounds in other kinds of foodstuffs. An e-tongue comprising voltammetric electrodes modified by different sensitive materials was proposed by Rodríguez-Méndez et al. [77] to evaluate the phenolic content of extra virgin olive oils. Good correlations (PLS correlation coefficients higher than 0.99) between the e-tongue data and the polyphenol content, the bitterness index and the bitterness degree were obtained.

Other application of e-tongues in determining taste-causing compounds in beverages is reported by Sun et al. [36]. In this paper, piezoelectric quartz crystal (PQC) sensor array based on molecularly imprinted polymer (MIP) coating was developed for determination of quinine and saccharine in bitter drinks. The MIP-PQC was applied for sensing commercially available tonic waters showing higher sensitivity than a human taste panel to detect the change in the bitter taste of samples.

In the work of Beullens et al. [78] the potential of two e-tongues to analyze tomatoes taste is evaluated. One of them comprised 18 potentiometric sensors and was lab-made, and the other device was the Astree e-tongue (previously commented in Section 4.2). The lab-made system was highly appropriate to quantify individual sugars, acids and minerals contents in tomatoes (correlation coefficients of PLS models higher than 0.97 and 0.87 in calibration and validation, respectively), but it could not predict some taste parameters evaluated by a sensory panel. Conversely, the Astree e-tongue was not suitable to quantify most of the tomatoes components, but the sensor readings were correlated to the panel taste parameters (correlation coefficients of PLS models higher than 0.92 and 0.70 in calibration and validation, respectively).

4.6. Other quality control studies

In this section, other miscellaneous quality aspects non-included in the preceding sections are considered (Table 6).

Tan et al. [79] point out several applications of the Astree e-tongue in the quality control of beverages. In the work by Chen et al. [80] the Astree e-tongue was successfully used to identify tea grade levels.

Tran et al. [81] distinguished the tastes of brown rice and milled rice with different milling yields by means of an e-tongue based on potentiometric sensors made from lipid membranes. Moreover, good correlations (determination coefficients higher than 0.99) between e-tongue response and sensory taste scores and chemical taste components (free amino acids and free sugars content) of raw and cooked rice were obtained.

Moreno-Codinachs et al. [82] designed an integrated multisensor for FIA-based e-tongue applications. The multisensor chip included six independent ISFETs, a pair of interdigitated platinum electrodes, and a diode temperature sensor. Discrimination of commercial mineral drinking water samples according their mineralization degree by means of PCA was achieved.

The aim of the study by Rudnitskaya et al. [83] was the evaluation of a potentiometric e-tongue as an analytical tool for measuring beer taste attributes. This device was capable to predict 20 attributes of the beer taste obtained from a trained sensory panel (PLS correlation coefficients ranged between 0.64 and 0.97). Some PLS models obtained only allowed a rough estimate or a semi-quantitative prediction of taste attributes but good prediction accuracy was obtained for the attributes intensity and sweet flavor. It must be remarked that this paper represents one of the most complete studies reported up till now due to the extensive set of taste attributes examined and the relative complexity of the sample.

The research group of Ciosek and co-workers have published several papers dealing with the manufacture of miniaturized e-tongues that can be used as portable systems for food analysis [70,84,85]. An integrated array of solid-state ion-selective and partially selective microelectrodes based on PVC membranes was successfully applied to the recognition of different brands of orange juice [84]. In a further work [85] polyurethane membranes dopped with various chemosensitive materials in a miniaturized e-tongue system was developed and proposed for the classification and recognition of various tea and herbal product types. Polyurethane membranes exhibit better adhesion to the epoxy glass support of the electrode array, which is helpful in obtaining repeatable sensor responses and to improve the long term stability of the device.

Disposable integrated voltammetric e-tongues have been developed by Paixão and Bertotti [86]. Sensors comprising bare and Prussian Blue-modified electrodes were manufactured. These devices were efficient to differentiate between different taste substances (Cu and Prussian Blue-modified gold electrodes), to distinguish milk samples adulterated with hydrogen peroxide and to discriminate between milk samples with different pasteurization processes (Au and Prussian Blue-modified gold electrodes). In the particular case of milk analysis, the development of disposable sensors is especially important because the high content of organic materials which adsorb onto the electrode surface may change the voltammetric response.

In the literature there are some applications of e-tongues related to wine ageing assessment [87–89]. A voltammetric e-tongue has been used to discriminate between red wines aged in oak barrels and red wines matured in steel tanks in contact with oak wood chips or staves [87]. Chemical parameters of wines were also determined by means of conventional analytical techniques. PCA demonstrated that both methods permit to discriminate wines according to the type of ageing. Moreover, PLS–DA on e-tongue data allowed for establishing prediction models of the methodology used to age wines. Finally, good PLS correlations (0.99–0.83) were found between the signals obtained with the e-tongue and 8 chemical parameters (tannins, tartaric acid, glycerol, alcoholic grade, dry extract, total acidity, volatile acidity and reducing sugars).

In the paper by Rutnitskaya et al. [88] a potentiometric e-tongue was applied to the analysis of 147 samples of Port wines of different ages and of different types. Samples were also analyzed by means of conventional analytical techniques. Multivariate calibration for the prediction of the wine age was made by applying PLS regression and orthogonal signal correction (OSC) was evaluated as data pre-processing method. The age of the Port wine was predicted with similar accuracy (about 1.5 or 5 years, depending on the sample dataset used in the calibration step) using both e-tongues and chemical analysis data. E-tongue response showed a temporary drift in the Port wines, especially significant along the first days of measuring sessions. Data pre-treatment using OSC was favorable for e-tongue data since this procedure successfully removed time dependence of the response and produced improved calibration models. Recently, a similar e-tongue has been used for Madeira wine age prediction and quantification of the organic acids and phenolic compounds [89].

Finally, another recent, important application of e-tongues is the evaluation of the quality of ham as well as its evolution along the production process, proposed in a joint work of two Spanish research groups of the Institute of Agrochemistry and Food Technology and the Polytechnic University of Valencia (Spain). The corresponding results will probably be published at the end of this year.

5. Conclusions and future trends

E-tongues analytical systems are still being developed but the advantages are already clear. Strengths of the e-tongue include a fast determination of several compounds in foodstuffs as well as a sample classification with a direct measuring stage. Nevertheless, a disadvantage of these systems is the huge amount of previous measurements required for the modelling, calibration or learning steps. These are essential steps for e-tongues performance that cannot be neglected and must be carefully performed. On the other hand, there are several problems associated with the sensors manufacturing (i.e., reproducibility, drift, the transfer of properties from one lot of sensors to another, etc.) to be solved.

Regardless of these concerns, the future for the e-tongue appears to be promising as it can fulfil niche analyses. This is because research and development activities are continuing apace in several laboratories around the world. Even the early instruments have performed well for some applications and it is believed that the newer prototypes will advance the field further. Some of these major highlights include:

- The development of new measurement methods, the search for new chemosensitive materials and new techniques for the preparation of chemosensitive layers.
- The coupling of e-tongues with distributed expert systems for the advanced in-line monitoring of food production processes, especially alcoholic (grape must, wort) fermentations, e-tongues being the corresponding measuring devices.
- The application of e-tongues as a detection scheme in flow-based analytical systems. It is remarkable the increasing number of publications that flow-based e-tongues are currently experimenting, which confirms them as a trend in modern analytical chemistry. There is no doubt that these systems may be used for the resolution of more complex analytical problems, increasing the number of analytes to be determined, and also the identification/classification of even more similar samples.

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