Overview of electronic tongue sensing in environmental aqueous matrices: Potential for monitoring emerging organic contaminants

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Abstract

Emerging organic contaminants (EOC) are synthetic or naturally occurring chemicals that have the potential to enter the environment and cause known or suspected adverse ecological and human health effects. Despite not being commonly monitored, EOC are often detected in effluents and water bodies, because of their inefficient removal in conventional wastewater treatment plants. There is a growing concern about the presence and impact of EOC, as well as the need for reliable and effective water monitoring using sensors capable of detecting the target molecules in complex media. Due to their specificities, such as fast response times, low cost, portability and user-friendly operation, electronic tongue (e-tongue) systems present some advantages over the traditional analytical techniques (e.g. chromatographic systems) used for environmental monitoring. In this paper, e-tongue sensors are reviewed, focusing on their ability for real-time environmental monitoring. A bibliometric evaluation was carried out, along with a study of the status of the existing e-tongue systems, how they worked, and their applications in different fields. The potential of e-tongue sensors to detect organic contaminants in aqueous environmental matrices is discussed, with a particular focus on EOC.

Keywords: electronic tongue; environmental monitoring sensing; emergent organic contaminants; pharmaceuticals and personal care products

I. Background and keywords

Currently, the world faces a rising global demand for water due to an increasing population and climate change. Both water availability and quality are under stress (Pal et al. 2014). The global population is expected to exceed nine billion by 2050, and 70% of people will be living in urban areas. This growing problem is usually coupled with poor wastewater management, old wastewater infrastructure plants, and limited disposal strategies, with either minimal treatment practices or none at all (Corcoran et al. 2010). Consequently, wastewater treatment plants are releasing new classes of potential organic contaminants into water bodies, known as emerging organic contaminants (EOC), as these are not completely removed by the existing technologies (Stülten et al. 2008; Matamoros et al. 2009).

EOC are defined as "*chemical substances that have no regulation, are suspected of affecting the environment or whose effects are unknown*" (Daughton 2004; Geissen et al. 2015). Some of the EOC are included in the priority pollutant lists developed by both the European Union (EU) and the United States Environmental Protection Agency (USEPA). In 2000, an initial list of 33 priority substances was also identified under the EU Water Framework Directive (WFD) 2000/60/EC to be used as a control measure for the next 20 years (Ellis 2008). In 2007, pharmaceuticals and personal care products (PPCP) such as diclofenac, iopamidol, musks and carbamazepine were identified as future emerging priority candidates. Ibuprofen, clofibric acid, triclosan, phthalates, and bisphenol A are proposed additions to this list. Stuart and Lapworth (2013) have a clearer definition: "*Emerging organic contaminants are compounds now being found in groundwater from agricultural and urban sources that were previously not detectable, or thought to be significant. EOC include pesticides and degradates, PPCP, industrial compounds, fragrances, water treatment byproducts, flame retardants, and surfactants, as well as 'life-style' compounds such as caffeine and nicotine*".

It is necessary to find suitable sensors that allow for monitoring of EOC molecules. The development of reliable real-time sensors for environmental monitoring of EOC in wastewater treatment plants (WWTP) is challenging, as sensors must be selective for target compounds and sensitive enough to detect them at trace levels. One of the main challenges is to ensure analyte detection in environmental complex matrices that contain countless spurious molecules (potential interfering compounds), as well as microscopic life (Albareda-Sirvent et al. 2001). These matrix effects can jeopardize the analysis of a target molecule.

Sensors are an integral part of many engineered products, systems, and manufacturing processes as they provide feedback, monitoring, safety, and some other benefits (Stroble et al. 2009). The term 'sensor' started to gain currency during the 1970s. The American National Standards Institute describes a sensor as "*a device which provides a usable output in response to a specific measurand, where the output is defined as an electrical quantity, and a measurand is defined as a physical quantity, property, or condition which is measured*" (American National Standards Institute (ANSI) 1982). Sensors should be in direct contact with the object under investigation, transform non-electric information into electric signals, respond quickly, operate continuously, or at least in repeated cycles, and be small in size (Gründler 2007).

Depending on the purpose, there are different types of sensors. Ranging from very simple to complex classifications (Fraden 2010), the sensor properties (materials and detection means used, specifications, conversion phenomena, field of applications or *stimuli*) can be used to classify them. However, considering the purpose of monitor target molecules in aqueous complex matrices, the optimal sensor would detect the presence of the target molecule, determine its concentration and give general information about the complex matrix where the target molecules are inserted. Therefore, it seems that suitable sensors for providing that information are chemical sensors, taking into account the definitions given by Hulanicki et al. (1991).

Chemical sensors are complex devices optimized for a particular application. An ideal chemical sensor will respond instantaneously to a target compound (analyte) in a medium, producing a measurable signal output at a determined analyte concentration (Council 1995). However, despite significant advances in the last few decades, the way in which these devices respond to different *stimuli* in the sample is still relatively unknown. The complexity of a chemical sensor application is related to technical difficulties related with the measurements and specific nature (i.e. elemental or molecular) of the substance to be analyzed (Hulanicki et al. 1991). According to IUPAC (International Union of Pure and Applied Chemistry), chemical sensors are defined "*as devices or instruments that determine the detectable presence, concentration, or quantity of a given analyte*."

Chemical sensors are based on two functional units: a receptor part and a transducer part. In the receptor, the chemical information is transformed into a form of energy, which may be measured by the transducer. The receptor may account for different principles: (1) physical: no chemical reaction takes place; (2) chemical: where there is a chemical reaction with the analyte that gives rise to the analytical signal; (3) biochemical: in which a biochemical process is the source of the analytical signal. In some cases, it is not possible to decide whether a sensor operates in a chemical or a

physical mode, e.g. an absorption process. In the transducer section, the device transforms the energy-carrying chemical information on the sample into a useful analytical signal (Council 1995).

Regarding detection of EOC molecules in an environmental matrix, both physical and (bio)chemical principles are adequate. For physical detection, the electrical properties of a device constituted by a thin layer film, for example, prepared from molecules with affinity to the target compound and deposited on the solid support with electrical electrodes, will change as the target molecules are being adsorbed. On the other hand, electrochemical sensors are based on the current measurement resulting from the oxidation/reduction reactions of the analyte at a suitable electrode. Electrochemical sensors achieve selectivity through molecular coatings, film coatings on electrodes, or chemically modified electrodes. The design of molecular selectivity for analytes involves an accurate choice of the sensing chemistry and associated materials (Ciosek and Wró 2007). Selectivity in sensing devices is related to a preferred response to a single sample substance, where the remaining substances can be considered formally as interfering substances. In a sensor's array, each sensor must have a specific capacity to distinguish between components of the mixture, i.e. it should distinguish between sample and interferent. The sensor can respond to both analyte and interferent with a different sensitivity (Gründler 2007). Chemical reactivity can involve a wide range of chemical phenomena, including: (1) recognition of size/shape/dipolar properties of molecular analytes by molecular films, phases, or sites; (2) selective permeation of analyte in a thin-film sensor; (3) catalytic reaction cycle of the sensing materials, which results in analyte consumption (National Academy Press 1995).

The concept of electronic tongue (e-tongue) emerged through the need for the detection, classification and differentiation of complex substances. Since the first prototype in 1990 by Hayashi et al. (1990), e-tongue has become one of the most promising monitoring systems, to develop a fast, cheap, and objective method for evaluating different matrices (Śliwińska et al. 2014). Sensing tongue systems were inspired by the human tongue, which can detect five tastes: salty, sour, sweet, bitter, and *umami* (Winquist 2008). The tasting senses in a human tongue are chemical senses, as they respond to a stimulus produced by food molecules on the tongue's taste cells, thus producing the sensation of taste. The taste receptor organs are located in the taste buds. In the process of flavor detecting, a series of electrical impulses are generated with different intensities and are transmitted to the brain/transducer, where they are compared in order to identify flavors (Smith and Margolskee 2001). In a similar way, the e-tongue with an array of sensors that measure electrical signals can be interpreted by mathematical methods, leading to information about the presence of the target molecule and its concentration in the complex matrix.

Given the importance of this new way of using sensors, the focus of this review is e-tongues, due to their scientific relevance for the detection of compounds in aqueous matrices and the growing number of scientific publications using this system. There are, however, other types of tongues/noses that may be considered for the detection of organic molecules, for example using optical sensors as in the work of the Suslick group (Rakow and Suslick 2000), and the Lundstrom and D'Amico groups (Filippini et al. 2006). The number of scientific publications on EOC detection is not yet strong enough.

In order to better recognize and assess the research status on e-tongues, we performed a bibliometric study (June 2018), making use of the online version of SCOPUS. With the search word "electronic tongue" (Figure 1a), a total of 1297 scientific papers (articles and reviews) was obtained. In the 1297 papers with the subject of e-tongues, the dominant research areas are chemistry (36.3%), engineering (29.8%) and environmental sciences (6%), for which China, Spain and USA are the top 3 countries, contributing 34% of the papers. The search word "electronic tongue" was refined with the sub-subject "water" (Figure 1b) to link the subject to aqueous matrices. We also examined the connection between the search word "electronic tongue" and the sub-subject "organic contaminants" (e.g. EOC), obtaining an additional 22 papers from 2004 to 2017 (Figure 1b).

Although the number of published papers on e-tongues that focused on the detection of organic components is still small, this detection method is considered a promising monitoring tool. Since its development, it has been used for a variety of purposes, e.g. water, wastewater and food analysis (Zhuiykov 2012; Panasiuk et al. 2015; Cetó et al. 2016; Díaz-gonzález et al. 2016; Goméz-Cravaca et al. 2016; Peris and Escuder-gilabert 2016; Wei et al. 2017; Son and Hyun 2018), while fulfilling environmental monitoring needs (Di Natale et al. 1997; Krantz-Rülcker et al. 2001; Gutiérrez et al. 2008; Winquist 2008; Campos et al. 2012; Askim et al. 2013; Tahara and Toko 2013; Capelli et al. 2014; Justino et al. 2015).

Conventionally, chemical sensing of unknown substances is performed in an analytical laboratory with complex benchtop equipment, including mass spectrometry, chromatography, nuclear magnetic resonance, X-ray, and infrared technology. These methods are very accurate enabling the identification of most unidentified chemical classes with a high degree of confidence and precision (Banerjee et al. 2016), which can be used to calibrate sensors. Nonetheless, the e-tongue presents potential advantages: (i) sample pre-treatment may not be mandatory, (ii) the source of errors due to sample transport or storage may be drastically reduced or eliminated, and (iii) a fast response may be achieved in environmental emergencies (Albaladejo et al. 2010). The possibility of environmental monitoring in real-time mode and operating on long-term scales can enable data

collection that may be crucial for understanding the full range of potential contamination in all its phases and environmental compartments. Moreover, real-time tools used for environmental monitoring represent a cutting-edge technology that, with the right approval and support from government agencies, along with an increase in the quality of the produced data, will undoubtedly become a part of modern environmental monitoring laboratories (Gałuszka et al. 2015).

This review aims to present how pollutants in aqueous media can be detected using the e-tongue, and to highlight the opportunities for the detection of EOC - PPCP in these matrices. In addition, the concept of the e-tongue and examples of its successful applications are analyzed.

II. Electronic Tongue – The concept

The e-tongue is based on chemical sensors with low selectivity, displaying cross-sensitivity to multiple components in liquids (Ciosek and Wró 2007), and can be considered as "*a multisensory system, formed by an array of low-selective sensors, combined with advanced mathematical procedures for signal processing, based on pattern recognition and/or multivariate data analysis*" (Vlasov et al. 2005). The seminal work of Di Natale et al. (1997) was one of the pioneers on the subject of the e-tongue, using a chalcogenide glass sensor array with an artificial neural network analysis for the detection of heavy metal cations and inorganic anions in a complex aqueous solution. Thus, if the e-tongue is configured and properly trained (e.g. the choice of materials), it can be used to characterize complex liquid samples and recognize the qualitative and quantitative composition of multi-species solutions (Escuder-gilabert and Peris 2010).

2.1 Components

The e-tongue system with its base components is schematized in Figure 2. Typically, the electrical signals measured in an array of sensors immersed in, or covered with, liquid samples are recorded and processed by mathematical procedures to achieve a pattern. This pattern allows for a comparison of the results obtained with the data of calibrated libraries already gathered from previous complex solutions in which its composition was also carefully analyzed in conventional laboratories. This means that a library should be attained for each sensor array. In most cases, the liquid sample must be placed in a controlled temperature or at a controlled flux, if the electrical properties are dependent on the temperature or atmosphere.

Following the described order, the e-tongue's components will be explained in more detail below.

a. Methods for measuring the electrical signal

There are several types of sensors that can be applied in e-tongues. A wide variety of chemical sensors have been employed, but the ones most commonly used for detecting pollutants are electrochemical systems (e.g. potentiometric, voltammetric and amperometric) and electrochemical/physical systems (e.g. impedance) (Krantz-Rülcker et al. 2001; del Valle 2010; Zou et al. 2015). The classification is related to the primary signal after an interaction with the analyte

when a potential electrochemical current or resistivity/capacitance change is generated and measured.

Voltammetric and potentiometric sensors have several applications in environmental monitoring and the detection of pharmaceuticals in food (Gutiérrez et al. 2008; Mimendia et al. 2010; Wei and Wang 2011). While in potentiometric sensors the current is monitored without current flow, in voltammetry sensors a potential is applied, and the resulting current is measured (Winquist 2008). Voltammetric methods are more versatile and robust, as they are usually less influenced by electrical disturbances, and the potentiometric measurements are considered to be simpler (Holmin et al. 2001). From the point of view of detection, potentiometry operates in terms of the system's net charge being disadvantageous in non-electrolyte media, while cyclic voltammetry operates in complex liquids requiring compounds that can be oxidized or reduced actively onto the working electrode (Legin et al. 1999; Holmin et al. 2001; Ivarsson et al. 2001).

Amperometry is preferred for monitoring a time-dependent change with a wide dynamic range (Wang et al. 2015). Amperometric systems are directly measured in electrochemical reaction rates taking place at the electrodes, where the current derives from the oxidation or reduction of electroactive compounds at a working electrode, while a constant potential is applied (Kirsanov et al. 2004).

In the impedance system, the full scan of different alternated current frequencies, or a selected number of discrete values, may be used (conductivity or capacitance) in a simpler conceptual implementation (del Valle 2010). The impedance technique is based on the electrode perturbation caused by an external signal of small magnitude. Measurements can be performed in an equilibrium or stationary state, allowing for the characterization of aqueous environmental matrices, by analyzing the electrical impedance as a function of frequency signals applied to nanostructures adsorbed onto solid substrates (Riul et al. 2002). E-tongue systems that measure the electric impedance using conducting polymers (alone or combined with lipids) can work as sensorial unities, as they recognize the taste below the biological limit (Ferreira et al. 2003), eliminating the need for human panels.

Comparing the scientific work conducted for the four systems described above, according to SCOPUS (accessed in June 2018), the number of publications referring to the term "electronic tongue" (broken down according to the different sensors: potentiometric, voltammetric, amperometric, and impedance) has been growing steadily since the research in 1997. On

potentiometric, voltammetric and amperometric systems, the number of articles published appears to have stabilized over the last few years, whereas the number of articles published for impedance systems is increasing.

b. Array of sensors

The choice of sensors is dependent on the measuring method. In voltammetric measurements, for instance, a reference electrode (e.g. Ag/AgCl), a counter electrode (e.g. Platinum) and a working electrode are typically required. Working electrodes are made of noble and non-noble metals, such as Copper (Cu), Gold (Au), Nickel (Ni), Palladium (Pd), Platinum (Pt) and Silver (Ag), and other materials such as Glassy Carbon (GC). Working electrodes can also be covered with films, increasing the sensitivity of the sensor. The physical properties measured (e.g. capacitance and resistance) can be improved if the interdigitated electrodes (IE) are covered with thin films (Riul et al. 2002)

A thin film, deposited onto IEs, based on insulator, semiconductor or conductive materials with affinity for the target molecule, will have a different resistance and/or capacity as the analyte molecules are being adsorbed onto it, allowing for the detection of a target compound or analyte in a solution. Taylor and Macdonald (1987) have analyzed this situation and presented a simple equivalent circuit which describes the AC electrical behavior. Such impedance or conductance spectra will be dependent on both the number of molecules adsorbed onto the thin film surface and the other constituents of the solution matrix. The adsorption of target molecules could be due to both physical interactions (ionic, hydrogen bonds, van der Waals, dipolar) and chemical bonds, where the measured electrical signal will incorporate information from them in greater or lesser detail, depending on the film used. Therefore, thin films should be prepared in view of their ability to adsorb the analyte or adsorb other constituents of the aqueous matrix. Hence, several thin films should be prepared in order to develop the e-tongue, based on both physical and chemical methods of detection. Different kinds of thin molecular films could be prepared, namely Langmuir-Blodgett, or self-assembled or layer-by-layer films (Oliveira et al. 2014).

c. Mathematical treatment of measured data

Regardless of the choice of which system to use (potentiometric, voltammetric, amperometric or impedance systems) for monitoring aqueous environmental matrices, the complexity of the information extracted will involve an analysis of a large number of variables. Some of these variables are not significant in the interpretation of results, and only the relevant information is collected, thereby reducing the volume of data (Wilson and Baietto 2009). Thus, without losing any information, relevant data can be obtained using statistical methods that will reduce data volume. Some examples of the discussion on the processing methods of multivariate data in electronic

tongues and noses can be found in Richards et al. (2002), Scott et al. (2007), Palit et al. (2010) and Cetó et al. (2013).

Pattern recognition techniques (part (b) Figure 2) consist of the following sequential stages: signal pre-processing, dimensionality reduction and prediction/validation (Rodríguez Méndez et al. 2016a). The signal pre-processing prepares the feature vector for future processing. It includes compensation for sensor drift, scaling of the data, and extracting representative parameters (Raposo et al. 2016). The intrinsic complexity, richness, and cross-selectivity of the signals generated by sensor arrays provide certain advantages, as the resulting dataset contains meaningful information about the sample. The choice of method depends on the type of available input data acquired from the sensors and the type of information that is sought. The digital outputs generated by e-tongue sensors need to be analyzed and interpreted in order to provide useful information to the operator (Wilson and Baietto 2009).

There are different advanced methods based on the statistical treatment of data that can be used for feature extraction and for finding the most important parameters (Rodríguez Méndez et al. 2016a). Multivariate data analysis comprises a set of techniques that can be used for the analysis of datasets with more than one variable by reducing high dimensionality in a multivariate problem when variables are partly correlated (Wilson and Baietto 2009). The first approach for the classification of the sample typically involves graphical analysis and comparing samples or comparing the identification of unknown elements with those from known sources in libraries (Dymerski et al. 2011). This involves the development of calibrated libraries, which are required for each e-tongue. Multivariate analysis can be divided into unsupervised or supervised techniques. Unsupervised methods are used to find or confirm patterns, making comparisons between different unknown samples in order to discriminate between them, in cases where the database of known samples has not been previously constructed. Supervised methods use the response variable to discover patterns associated with the response.

Unsupervised methods include singular value decomposition and principal components analysis (PCA), which use only the matrix of features by samples, as well as clustering. Supervised methods include multiple regression and classification, as well as more recently developed techniques, such as sliced inverse regression, requiring a variable response, which is usually a phenotype, in addition to the feature by sample matrix (Rodríguez Méndez et al. 2016b). The training process for supervised methods, e.g. artificial neural networks, involves a discrete amount of known sample data to train the system and is very efficient in comparing unknown samples to known references (Hodgins 1997).

d. Conditioning of liquid samples

When electrical signals are temperature dependent, a thermostat and/or thermal bath enables continuous maintenance/monitoring of the sample temperature during analysis, providing reproducibility and repeatability of measurements (Śliwińska et al. 2014).

In some instances, flow techniques are important for e-tongue systems, providing automation of the analytical methods. The main benefits of automation of the analytical procedures are the increase in sample frequency, minimization of sample contamination, improvement of analyst security, and lower reagent/sample consumption, which implies lower personal and consumable costs (Cerdà et al. 2014). In an e-tongue system, there are two main flow mechanisms that are commonly used for water analysis (Mesquita and Rangel 2009): flow injection analysis (FIA), operated exclusively by hand, and sequential injection analysis (SIA) based on multi-commutation operation. Comparing the two techniques, SIA presents advantages over FIA, as it uses fewer reagents and results in less waste production, being an environmentally friendly methodology that can perform the largest number of analyses. SIA systems have been successfully used with potentiometric e-tongues (Cortina et al. 2005). When these techniques are used, FIA and SIA have the potential to decrease analysis time and increase repeatability (Śliwińska et al. 2014). Nonetheless, there is no solid argument in favor of using a particular flow technique separately, but the advantages increase if they are combined or developed specifically for the purpose, e.g. Richards et al. (2003).

2.2 Applications

Because of the ease with which the e-tongue can be operated, research efforts have been dedicated to the development and use of a wide range of applications, e.g. (a) carcinogenic trihalomethanes in public water supply systems (Carvalho et al. 2007), (b) detection of phenolic compounds (Olivati et al. 2009), (c) detection and monitoring of ammonium, nitrite and nitrate ions in waters (Nuñez et al. 2013) and (d) quantification of ammonium and phosphate ions in wastewaters (Campos et al. 2014). Di Natale et al. (2000) combined e-nose and e-tongue sensors to classify urine, merging data obtained from each of the sensor arrays. Also, e-tongue coupled with e-nose was used for analyzing different types of Moroccan waters (Haddi et al. 2014). Table 1 presents a summary of some e-tongue and hybrid systems in different fields: aqueous environmental matrices and complex liquid matrices. Published manuscripts were chosen based on either their importance for improving the sensing field or the complexity of the matrices, which can actively contribute to the development of a new e-tongue system. The results from all these papers can serve to contribute to an upgraded e-tongue system for detecting EOC in aqueous environmental matrices.

Portable environmental sensing technology is particularly appealing for pollution monitoring, but it is more limiting than its non-portable counterparts. However, e-tongue systems have great potential and are highly relevant for continuous environmental pollutant monitoring (Kim et al. 2012). It is important to stress that environmental portable sensing technology meets the criteria of green analysis: (a) automation, (b) low power consumption, (c) avoidance of reagent use and (d) no waste generation (Tobiszewski et al. 2010). Traditional analytical instruments can be less attractive, as they are not able to provide continuous monitoring or work as remote sensing, and have high operating costs.

III. Opportunities in sensing technology applied to aqueous matrices

Environmental samples can be extremely complex. Therefore the main obstacles when dealing with liquid samples are the low concentrations of EOC occurrence in water media (Bourgeois et al. 2003; Justino et al. 2015).

Either e-tongue systems or chromatography methods can be used to detect and determine such pollutants at low concentrations (ng/L or pg/L) levels. Consequently, to validate e-tongue data, chromatography methods are often used to confirm the concentration levels of the target compound. Tahri et al. (2018) showed that Headspace GC-MS Gas Chromatography-Mass Spectrometry (HS-GC–MS) could contribute to the validation results obtained from a voltammetric e-tongue system. Some examples of studies that can be coupled with an e-tongue system: (a) Gas chromatography, coupled with tandem mass spectrometry (GC–MS/MS), and liquid chromatography-tandem mass spectrometry (LC-MS/MS) were used to determine the contaminants of emerging concern (e.g. nonlyphenol - PPCP) in municipal wastewater effluents and marine receiving water (Vidal-Dorsch et al. 2012); (b) Ronan and Mchugh (2013) used liquid chromatography coupled with tandem mass spectrometry with electrospray ionization in negative mode (LC/ESI-MS/MS) to determine natural and synthetic steroid estrogens in seawater and marine biota; (c) Li et al. (2016) also used the LC-MS/MS method to determine 45 commonly used PPCP in sludge. To achieve equal ranges of accuracy in detection and analysis when compared with chromatography methods, many electronic sensing investigations have focused their efforts on the detection of contaminants in real environmental matrices.

411 A SWOT (Strengths, Weaknesses, Opportunities, Threats) analysis was carried out, Figure 3
412 highlights some of advantages and limitations of e-tongue sensing, as well emphasizing the positive
413 external aspects that would enhance the benefits of this system and pointing out some of the
414 negative aspects that can jeopardize the competitive advantages of e-tongue sensing. One of the
415 main advantages of this technology is that it enables quick access to information in simple or
416 complex liquid, which, combined with its relatively easy production, will soon allow the e-tongue
417 to be used on a global scale. Moreover, e-tongue systems are embodied in the trend of Industry 4.0,
418 allowing for the use of portable instruments in environmental site assessments, automation, and
419 online detection (the internet of things). Environmental samples represent a composite mixture of
420 various compounds in gaseous, liquid, or solid states. This complexity can result in analytical
421 problems, such as interferences, which usually pose a challenge for field analysts. From a global
422 point of view, traditional environmental assessment techniques using off-side analysis provide
423 better data quality, but the trade-off is a poorer understanding of the pollution distribution and a
424 lower information value of the data set, compared with on-site analysis.

425 The fast progress in e-tongue technology in recent years has increased the number of applications
426 for environmental sample analysis. An example of a successful e-tongue system used in aqueous
427 environment media is the work of Campos et al. (2013), who developed an e-tongue to monitor the
428 presence of ammonium nitrate in water, based on pulse voltammetry. It consisted of an array of
429 eight working electrodes (Au, Pt, Rh, Ir, Cu, Co, Ag and Ni) encapsulated in a stainless steel
430 cylinder. The electrochemical response of these different electrodes was studied in the presence of
431 ammonium nitrate in water, to further improve the design of the wave form used in the
432 voltammetric tongue. Afterwards, the response was tested with a set of 15 common inorganic salts
433 (NH_4NO_3, $MgSO_4$, NH_4Cl, NaCl. Na_2CO_3, $(NH_4)_2SO_4$, $MgCl_2$, Na_3PO_4, K_2SO_4, K_2CO_3, $CaCl_2$,
434 NaH_2PO_4, KCl, $NaNO_3$, K_2HPO_4). PCA showed good discrimination between ammonium nitrate
435 and the remaining studied salts. One year later, the same research team used a voltammetric e-
436 tongue to evaluate the concentration of ammonia and orthophosphate in influent and effluent
437 wastewater, since the quantification of these components in WWTP has further implications in the
438 eutrophication process (Campos et al. 2014).

439 Regarding detection of EOC, e.g. PPCP, and excluding the cases of pharmaceutical applications, the
440 publications mentioning e-tongues are practically non-existent in the literature (Raposo et al. 2016
441 and the references therein). PPCP are of increasing concern due to their environmental persistence,
442 accumulation in the environment at a global scale, and their steady detection in all environmental
443 water compartments. Pharmaceutical products, for instance, are additionally designed to maintain

444 their active forms and chemical properties long enough to perform their therapeutic purposes, and
445 thus at least 50% of a dose may be potentially excreted unchanged into the environment, where
446 these products will then remain (Bila and Dezotti 2003). Consequently, PPCP have been widely
447 detected in the effluents of WWTP, due to their incomplete removal treatment rates, and in their
448 receiving water bodies (Matamoros et al. 2009; Zhang et al. 2014). PPCP and their metabolites
449 (generated by metabolization and abiotic processes, such as hydrolysis or photolysis) are usually
450 detected in trace concentrations, and many of them have raised considerable ecotoxicological
451 concerns (Stülten et al. 2008).

452 detection of these micro-pollutants, attempts have been made to develop sensors that can work on
453 their continuous monitoring in aqueous complex matrices.

454 Arvand et al. (2012) developed a voltammetric sensor based on glassy carbon electrodes modified
455 with carbon nanotubes for the detection of diclofenac (anti-inflammatory) in blood serum and
456 seawater. The aim of the study was to develop a new technology that: (a) was simple, (b) has a
457 reduced-cost nanocomposition, (c) has multifunctional properties benefitting from multi-walled
458 carbon tubes - MWCNTs/ $Cu(OH)_2$ - nanoparticles and hydrophobic ionic liquid 1-ethyl-3-
459 methylimidazolium hexafluorophosphate (EMIMPF6) and (d) has good electrocatalytic activity for
460 the electro-oxidation of diclofenac. The authors achieved a new voltammetric sensor sensitive in the
461 range of 0.18-119 mM, with a detection limit of 0.04 mM (Arvand et al. 2012). Liu et al. (2011)
462 developed an impedance Ni(II)tetrakis(4-sulfonatophenyl) porphyrin (NiTPPS) carbon nanotube
463 composite electrode for the detection of three endocrine disrupting compounds - bisphenol A,
464 nonylphenol and ethynylestradiol in underground, tap and lake water. The authors optimized
465 experimental parameters: hydrodynamic potential of 0.7 V for flow injection analysis (FIA) and
466 NiTPPS surface coverage of 2.2 nmol cm^{-2}. The final results showed an improvement in the
467 sensitivity, stability and detection limit (from 15 nmol/L to 260 nmol/L).

468 To detect 4-n-octylphenol (OP) in solutions with a concentration range of 5×10^{-8} to 1×10^{-5}
469 mol/L, Zheng et al. (2012) developed a multi-walled carbon nanotube (MWCNTs) modified glassy
470 carbon electrode (GCE). The oxidation peak of OP (oxidized directly on the MWCNTs/GCE)
471 showed an improvement with the use of MWCNTs/GCE, compared with those using a bare glassy
472 carbon electrode. The detection limit achieved was 1.5×10^{-8} mol/L. Wan et al. (2013) conducted
473 studies in the detection of 4-tert-octylphenol in lake and river waters with a polymer/carbon
474 nanotube (CNT) film-coated electrode. The electrode was prepared by coating a polished and clean
475 glassy carbon electrode with a CNT film and then covering it with a conducting film from L-lysine.

476 The detection limit achieved was 0.5 nM, and the method could be applied for low concentration,
477 in-site and online monitoring of 4-tertoctylphenol in water (Wan et al. 2013).

478 A sensing layer, based on layer-by-layer films prepared with the common polyelectrolyte poly
479 (allylamine hydrochloride) (PAH) and pazo-polyectrolyte poly[1-[4-(3-carboxy-4-hydroxyphenyl-
480 azo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) was used for the detection of
481 deltamethrin, a pesticide, where the sensor response was obtained from impedance spectroscopy
482 measurements (100 Hz) (Abegão et al. 2013). Sensor sensitivity was 41.1 ± 0.7 kΩ per decade of
483 concentration and had a reproducibility of approximately 2% in a binary solution of ethanol and
484 deltamethrin. The sensor was able to detect concentrations below 0.1 nM. One year later, Pimentel
485 (2014) also worked with an e-tongue system based on impedance spectroscopy, which attempted to
486 detect a low concentration (nM and pM) of ibuprofen in an aqueous medium. The same working
487 group developed a nano-sensor that can detect picomolar concentrations of triclosan in an aqueous
488 medium (Marques et al. 2017). Also seeking to detect triclosan, Gao et al. (2010) synthesized
489 molecularly imprinted core-shell carbon nanotubes and detected PPCP in aqueous matrices in
490 concentration ranges from 0.01 to 40 μg/mL.

491 For sensitive and selective detection, the pigment Carmine in liquid samples, Zhao et al. (2018)
492 developed a PEDOT:PSS/AuNPs/CA - Poly(3,4 ethylenedioxythiophene):
493 Polystyrene sulfonate/gold nanoparticles/βMercaptoethylamine - modified screen-printed carbon-
494 based disposable electrochemical sensor. The sensor response was obtained by cyclic voltammetry,
495 differential pulse stripping voltammetry, and impedance spectroscopy, in a range of concentration
496 between 9.0×10^{-9} to 3.9×10^{-6} mol/L, with a detection limit of 6.05×10^{-9} mol/L, showing good
497 stability and reproducibility.

498 The full implementation of the e-tongue system will require a high-sensitivity EOC concentration in
499 the environment ≤ ng/L ≥ and long-term stability, together with amenability to being incorporated
500 into automatic systems and therefore be applied in the field. In contrast to the inorganic compound
501 e-tongue applications (e.g. heavy metals that will potentially be deployable in the near future), e-
502 tongue systems designed to detect organic molecules in complex aqueous matrices will require
503 further development, especially regarding selectivity and stability (Díaz-González et al. 2016).

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IV. Conclusions

Since 1989, there has been an ever greater number of scientific publications regarding the applications of e-tongue systems for environmental monitoring. E-tongue prototypes can have different types of measuring methods (e.g. potentiometric, voltammetric, amperometric, or impedance), and several applications have been developed and studied over the years, resulting in a deeper understanding of these devices.

The choice of e-tongue methods is highly dependent on the composition and complexity of the solution to be examined. In real-time monitoring of EOC contaminants, such as PPCP, e-tongue sensing technologies are still under development. To the best of the authors' knowledge, there are a few works concerning both environmental aqueous matrices and EOC. Nevertheless, the efforts to properly train these devices to characterize complex liquid samples and detect contaminants in aqueous media have increased the possibility of constructing a device that is sensitive enough to be comparable with conventional techniques. However, despite the high sensitivity, low-cost, easy operation and rapid response that will enhance its commercial value, there remains a lack of selectivity as far as e-tongue data are concerned.

E-tongue technology will undoubtedly find important applications in environmental monitoring. With continuing strides being made in scientific research, the e-tongue approach employed without sample pre-conditioning and using a simple analysis can address the problem of EOC in aqueous

matrices. The hybrid systems that reap the advantages of different sensing devices, or the e-tongue system working with the impedance spectroscopy response and nanofilms produced, for example, with the layer-by-layer technique, may present possible solutions that are of interest for the further development of real-time sensors.

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Figures Caption

Figure 1. a) Annual distribution of published scientific papers on e-tongues from 1989 to 2017; b) number of scientific papers published on e-tongues applied to water and organic contaminants (data adapted from SCOPUS, accessed in June 2018).

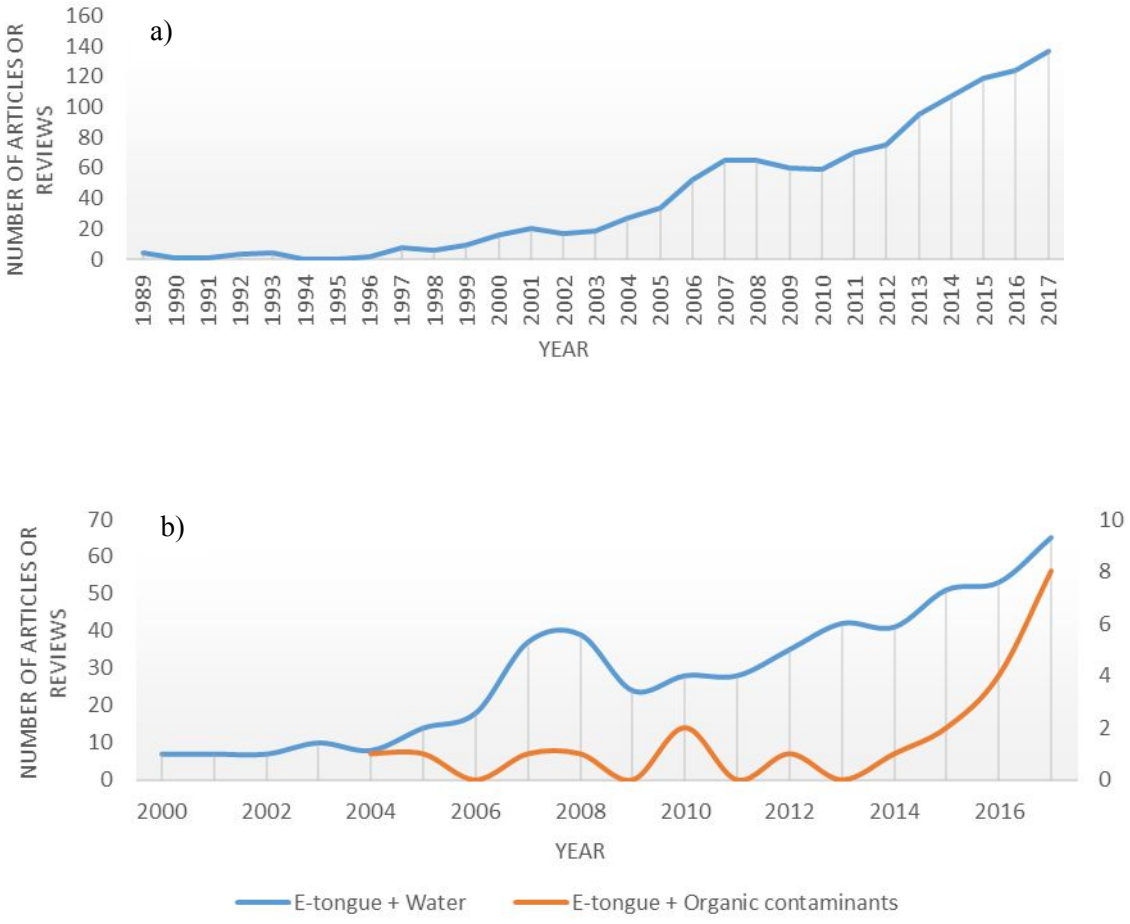
Figure 2. Schematic components of an electronic tongue.

Figure 3. Electronic tongue SWOT analysis.

Table Title

Table 1. Applications of e-tongue and hybrid sensing systems. (abbreviations or acronym presented below)

(Di Natale et al. 1997); (Moreno et al. 2006); (Sun et al. 2008); (Liu et al. 2011); (Wan et al. 2013); (Kirsanov et al. 2014); (Haddi et al. 2014); (Atar et al. 2015); (Guanais Goncalves et al. 2016); (Lvova et al. 2016); (Cetó et al. 2017); (Facure et al. 2017) ; (Di Natale et al. 2000); (Wei and Wang 2011); (Woertz et al. 2011); (Zheng et al. 2012); (Nuñez et al. 2013); (Abegão et al. 2013); (Wesoły et al. 2016); (Shehata et al. 2017); (González-Calabuig et al. 2018)



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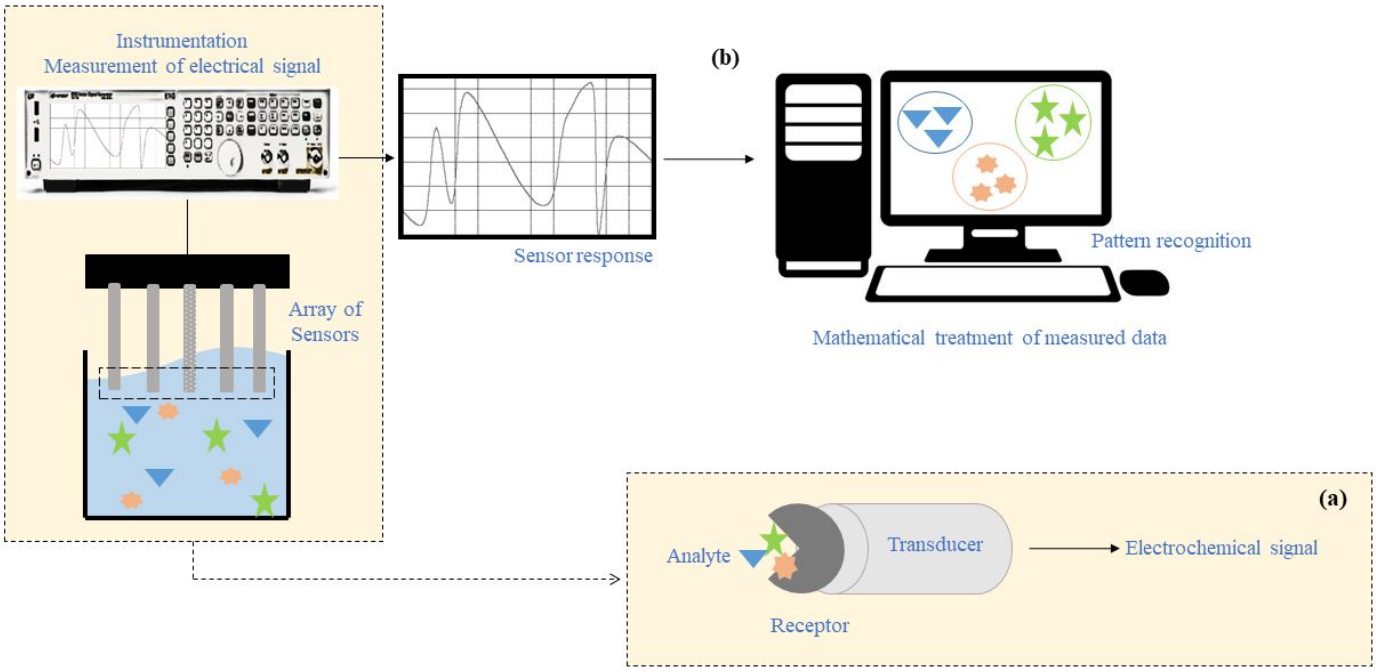

Figure 2. Schematic components of an electronic tongue.

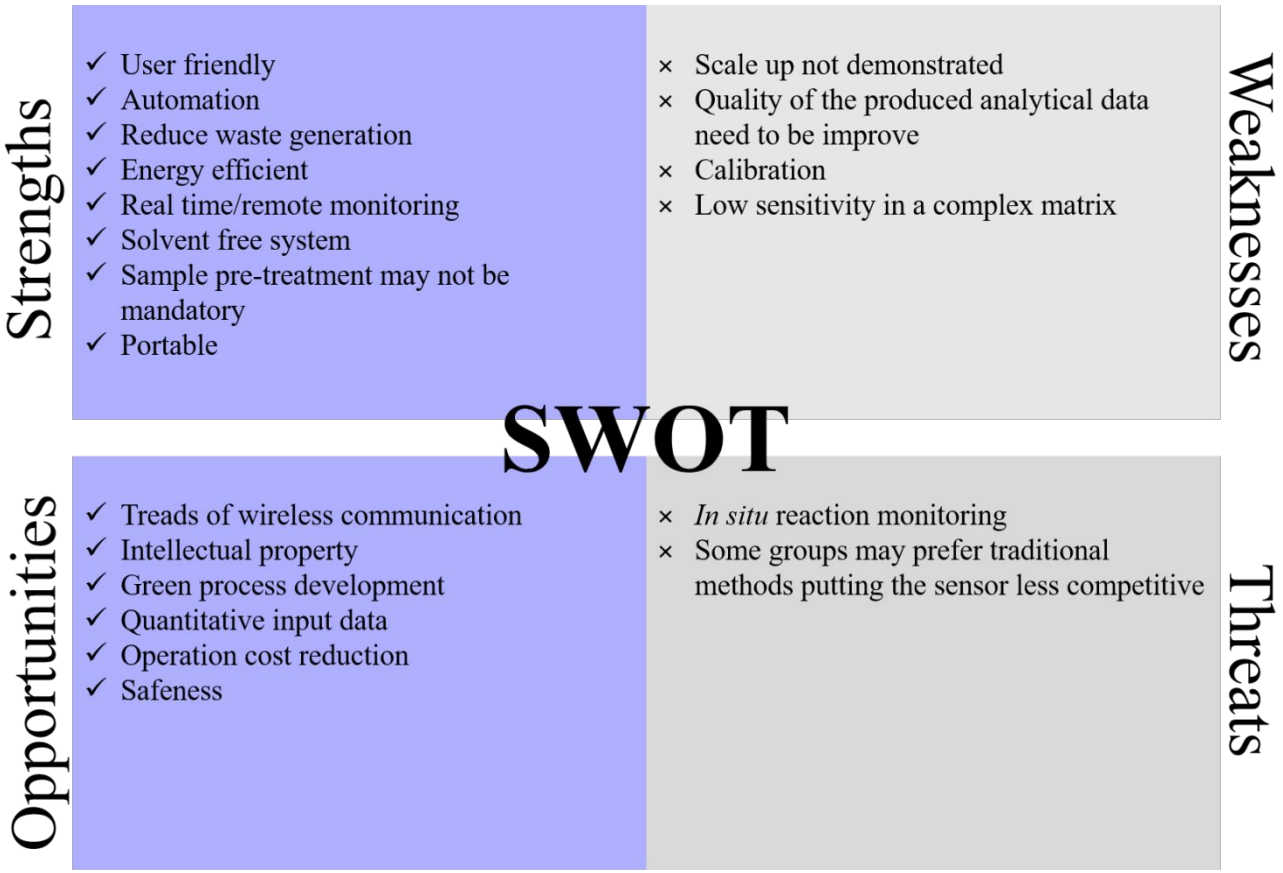

Figure 3. Electronic tongue SWOT analysis.

Table 1. Applications of e-tongue and hybrid sensing systems

Sensing Type	Sensor specifications	Matrices	Measured Parameters	Methods of data analysis	Concentrations	Detection limit	Main Conclusions	Refs.
Environmental Matrices								
E-tongue	22 electrodes based on chalcogenide glasses variously spike and conventional electrodes	Polluted water – river	Cu, Cd, Fe, Cr, Zn, Cl, SO_4 and H	MLR, PLS, NLLS and BP-NN	[Cu (6-8), Cd (6-7), Zn (3-5), Cr (4-7), Fe (4-7), Cl (3-5.3), SO_4 (3-3.9), H (2.6-8)] –log[C]	-	PLS, NLLS and BP–NN were similar in qualitative information.	(Di Natale et al. 1997)
E-tongue	Monolithically integrated array of chemical sensors, composed by six ISFETs, IDS and silicon diode	Mineral water	Na^+, K^+, Ca^{2+}, Cl^-, conductivity and potencial redox	HCA and PCA	-	-	The device responded with good reproducibility to different kinds of mineral water by using pattern recognition methods.	(Moreno et al. 2006)
E-tongue	PQC sensor array based on MIP coating	Tonic water	Quinine and saccharine	-	Quinine (10-1080) mg/L and saccharine (51-3420) mg/L	Quinine 2.04 mg/L and saccharine 32.8 mg/L	The sensor provided a satisfactory response detecting the change in bitter taste of drinks and beverages at practical concentrations, comparable to the taste assessment from a human taste panel.	(Sun et al. 2008)
E-tongue	Impedance response - NiTPPS compound on a carbon nanotube-coated glassy carbon electrode	Underground, tap water and lake water	Bisphenol A, nonylphenol, and ethynylestradiol	-	1 µmol/L	15 nmol /L - 260 nmol /L	The results showed that the sensitivity, stability and detection limit of the composite electrode were significantly improved, compared with those obtained at electrodes coated with carbon nanotubes or other materials.	(Liu et al. 2011)
Others	Voltammetric response and electrochemical detection - polymer/CNT film coated electrode	Lake and river water	4-tert-Octylphenol	-	6.5–20 nM	0.5 nM	This method avoids a tedious extraction process, it is time-saving and cost-effective. This method therefore can be applied for the detection of 4-tert-octylphenol at low concentration levels and for in-site and on-line monitoring of 4-tertoctylphenol in water.	(Wan et al. 2013)
E-tongue	Potentiometric	Urban water reservoirs	*Daphnia magna* bioassay	PCA, CCA, PLSR and PRM	-	-	It was found that root mean square prediction errors, given by PRM and PLS, did not exceed 20%.	(Kirsanov et al. 2014)

Sensing Type	Sensor specifications	Matrices	Measured Parameters	Methods of data analysis	Concentrations	Detection limit	Main Conclusions	Refs.
Hybrid	*E-nose coupled with E-nose* E-nose: metal oxide semiconductor (MOS home-fabricated) E-tongue: potentiometric	Natural, sparkling, river and tap water and wastewater	E-nose: CH_4 and combustibles gases, alcohols, xylene, toluene, NH_3, hydrogen, sulfide, methane E-tongue: Ca^{2+}, K^+, Cd^{2+}, F^-, Na^+, Cl^-, NO_3^- and H^+	PCA and LDA	-	-	The metal oxide sensors together with PCA, allows to distinguish amongst the potable and non-potable water samples with a total variance of 86.98 %. The potentiometric sensor showed an accuracy of 100% success rate in the recognition of the eight Moroccan water sources with LCA coupled with leave-one-out-cross validation method.	(Haddi et al. 2014)
Others	Allylmercaptane modified gold surface plasmon resonance chip and imprinted poly(2-hydroxyethyl methacrylate methacryloylamidogluta mic acid) [p(HEMAGA)] nanofilm	Wastewater	Triclosan	-	0.10, 0.20 and 0.30 ng/mL	0.017 ng/mL	Recovery rates were 98–102%; Compared with other complex analytic techniques, TCS-imprinted SPR nanosensor demonstrated comparable or better performance.	(Atar et al. 2015)
E-tongue	Potentiometric	Commercial mineral water, tap water and two types of surface water	Cyanobacterial microcystin toxins	PLS and PLS-DA	0.1 to 10 µg/L	10^{-6} mol/L	The experiments demonstrate the success of the E-tongue in the microcystin toxins concentration prediction comparing to standard chromatographic technique UHPLC-DAD and colorimetric enzymatic analysis.	(Lvova et al. 2016)
E-Tongue	Optical - colorimetric sensor array	Mineral water	Cyclohexanone, dimethylmethylphosphonate, piperazine, imidacloprid, 5-fluorouracil and paraoxon.	PCA	1 10^{-6} mol/L - 3.9 10^{-4} mol/L	Below 3.9 10^{-4} mol/L	Results show that the sensors are sensitive, but with low selectivity, in the interval from 10^{-7} mol/L to 10^{-4} mol /L. The sensor signals show a linear correlation with the logarithm of the concentration. Although the limited selectivity of individual sensors, the different sensitivity patterns allow for a clear identification of the compounds, independent of their concentration.	(Guanais Goncalves et al. 2016)

Sensing Type	Sensor specifications	Matrices	Measured Parameters	Methods of data analysis	Concentrations	Detection limit	Main Conclusions	Refs.
E-tongue	Voltammetric - gold electrode	Spiked tap water	Brominated trihaloacetic acids	PCA and ANN	0- 1200 µg/L	-	Satisfactory recovery values were obtained in the analysis of spiked water samples, as demonstrated from the lack of matrix effects.	(Cetó et al. 2017)
E-tongue	Impedance - reduction of graphene oxide in the presence of conducting polymers (PEDOT:PSS and polypyrrole) and AuNPs	Mineral and Tap water	Organophosphate pesticides	PCA	0.1 nmol L^{-1}- 5 nmol L^{-1}	0.1 nmol L−1	The graphene oxide associated with conductive polymers and gold nanoparticles granted good stability, high reproducibility and high sensitivity to the developed e-tongue. With PCA analysis, the e-tongue was able to classify solutions of different pesticides at distinct nanomolar concentrations, and discriminate real samples from the samples prepared in buffer solutions, presenting a correlation with the concentration and the value of the PC component.	(Facure et al. 2017)
Complex Matrices								
E-tongue	Voltammetric	Bovine milk	Chloramphenicol, erythromycin, kanamycin sulfate, neomycin sulfate, streptomycin sulfate, tetracycline and dimethyl sulfoxide	PCA, DFA, PCR, PLSR and LS-SVM	0.5, 1.0, 1.5 and 2.0 µg/kg	-	The six antibiotics at the maximum residual levels could not be separated from bovine milk completely by PCA; all the samples were demarcated clearly by DFA; PCR had the most stable results in regression models.	(Wei and Wang 2011)
Hybrid	*E-tongue coupled with E-nose* E-tongue: potentiometric electrode sensors E-nose: Porphyrin-based quartz microbalance gas sensor array	Urine and milk	Urine: protein, glucose, ketones, urobilinogen, bilirubin, blood, pH, specific weight. Milk: pasteurised and ultrahigh temperature (UHT) distinction	PCA	-	-	High abstraction level (pre-analysis of each system and successive merging of the most prominent features) appears to be the most significant way to preserve the best knowledge content from each separate analysis.	(Di Natale et al. 2000)

Sensing Type	Sensor specifications	Matrices	Measured Parameters	Methods of data analysis	Concentrations	Detection limit	Main Conclusions	Refs.
E-tongue	Insent TS-5000Z and Astree2	Sodium saccharin, ibuprofen lysinate, ibuprofen, acetaminophen, caffeine, caffeine citrate, quinine hydrochloride	Identification	PCA	[Sodium saccharin (8 concentrations between 1 and 500), ibuprofen lysinate (10 concentrations between 0.01 and 30), ibuprofen (10 concentrations between 0.013 and 0.13), acetaminophen (10 concentrations between 0.13 and 66), caffeine (10 concentrations between 0.05 and 90), caffeine citrate (10 concentrations between 0.03 and 45), quinine hydrochloride (9 concentrations between 0.02 and)] mmol/l	-	Ionic substances are easier to detect than neutral ones; qualification could only be performed for the TS-5000Z; Insent taste provide more reliable (in vitro/in vivo correlation) and precise (reproducibility and repeatability).	(Woertz et al. 2011)
Others	Multi-walled carbon nanotubes modified glassy carbon electrode	Ethanol	4-n-octylphenol	-	5×10^{-8} to 1×10^{-5} mol/L	1.5×10^{-8} mol/L	The modified electrode showed good selectivity, sensitivity, reproducibility and high stability.	(Zheng et al. 2012)
E-tongue	15 potentiometric poly(vinyl chloride) membrane sensors sensitive to cations and anions	Milli-Q distilled water	NO^-_3, NO^-_2, Cl^-, NH^+_4, K^+ and Na^+	ANN	[NO^-_3 (0.01-1), NO^-_2 (0.05-5), Cl^- (0.2-20), NH^+_4 (0.01-1), K^+ (0.01-1) and Na^+ (0.2-20)] mM	[NO^-_3 (4.6×10^{-6}), NO^-_2 (3.4×10^{-5}), Cl^- (7.9×10^{-5}), NH^+_4 (1.0×10^{-7}), K^+ (7.3×10^{-8}) and Na^+ (6.4×10^{-7})] mol/L	E-tongue system allowed the quantification of nitrate, nitrite, and ammonium in an aqueous medium in the presence of interfering species such as sodium, potassium and chloride ions. It was possible to distinguish between nitrate and nitrite species with some deviations for ammonium.	(Nuñez et al. 2013)
Others	Electrical impedance of PAH/PAZO nanofilm	Ethanol	Deltamethrin	-	10^{-10} M to 10^{-6} M.	Below 0.1 nM	Electrical resistance measurement at 100 Hz, revealed to be an adequate variable for deltamethrin concentration transduction.	(Abegão et al. 2013)

Sensing Type	Sensor specifications	Matrices	Measured Parameters	Methods of data analysis	Concentrations	Detection limit	Main Conclusions	Refs.
E-tongue	Potentiometric – 8 miniaturized electrodes based on PVC membranes (plasticized using DOS or o-NPOE), containing an appropriate lipophilic salt, exhibiting generic anion (TDMAC, TBHDPB, IL) or cation (KTFBB) response.	Active Pharmaceutical Ingredients	acetaminophen, ascorbic acid, acetylsalicylic acid and Caffeine as an interferent	PLS and ANN	acetaminophen (1–20 mmol/L), ascorbic acid (0.3–7 mmol/L), acetylsalicylic acid (1.4–8 mmol/L), Caffeine (0.13-1.3 mmol/L)	-	The extraction of dynamic components of the transient response employing the Wavelet transforms the removal of the less significant inputs by means of Causal Index pruning and training of an ANN with the selected coefficients allowed the simultaneous determination of the 3APIs counterbalancing any interference caused by caffeine.	(Wesoły et al. 2016)
Others	Potentiometric	Pharmaceuticals	Dissolution identification: Naproxen Sodium and Diphenhydramine Hydrochloride	-	220 mg of naproxen sodium and 25 mg of diphenhydramine hydrochloride per a tablet.	Naproxen Sodium: 8.28×10^{-5}M Diphenhydramine Hydrochloride: 7.94×10^{-6}M	In-line potentiometry in the simultaneous assay and dissolution monitoring of binary formulated oral solid dosage forms	(Shehata et al. 2017)
E-tongue	Voltammetric - array of 4 sensors, reference Ag/AgCl and Pt counter electrode	Aqueous complex solution	2,4-dinitrophenol, 4-nitrophenol and picric acid	ANN	0-300 µg/L	-	The model successfully predicted the concentration of the three considered phenols with a normalized root mean square error of 0.030 and 0.076 for the training and test subsets, respectively, and $r \geq 0.95$.	(González-Calabuig et al. 2018)

Notes:

AuNPs - gold nanoparticles; ANN- artificial neural network; BP–NN - back-propagation– neural network ; CCA - canonical correlation analysis; DFA - discriminant function analysis; DOS - poly(vinyl chloride); HCA - hierarchical clustering analysis; IDS - interdigitated platinum electrode; independent; IL- ionic liquid; ISFET - ion selective field effect transistors; LDA - linear discriminant analysis; KTFPB - potassiumtetrakis [3,5-bis(tri- fluoromethyl)phenyl] borate; LS-SVM - least squares-support vector machines; MIP - molecularly imprinted polymer; MLR - multiple linear regression; NiTPPS - Ni(II)tetrakis(4-sulfonatophenyl) porphyri; NLLS - non-linear least squares; p(HEMAGA - poly(2-hydroxyethylmethacrylate–methacryloylamidoglutamic acid); o-NPOE -plasticizers:o-nitro- phenyl octyl ether; PCA - principal component analysis; PCR- principal component regression; PLS - partial least squares; PLS-DA - partial least squares-discriminant analysis; PLSR - partial least squares regression; PQC- piezoelectric quartz crystal; PRM - partial robust M-regression; PVC - poly(vinyl chloride); SPR - surface plasmon resonance; TDMAC - tridodecylmethy- lammonium chloride ; TBHDPB - tributylhexadecylphos-phoniumbromide