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Potential use of electronic noses, electronic tongues and biosensors as multisensor systems for spoilage examination in foods

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Abstract

Development and use of reliable and precise detecting systems in the food supply chain must be taken into account to ensure the maximum level of food safety and quality for consumers. Spoilage is a challenging concern in food safety considerations as it is a threat to public health and is seriously considered in food hygiene issues accordingly. Although some procedures and detection methods are already available for the determination of spoilage in food products, these traditional methods have some limitations and drawbacks as they are time-consuming, labour intensive and relatively expensive. Therefore, there is an urgent need for the development of rapid, reliable, precise and non-expensive systems to be used in the food supply and production chain as monitoring devices to detect metabolic alterations in foodstuff. Attention to instrumental detection systems such as electronic noses, electronic tongues and biosensors coupled with chemometric approaches has greatly increased because they have been demonstrated as a promising alternative for the purpose of detecting and monitoring food spoilage. This paper mainly focuses on the recent developments and the application of such multisensor systems in the food industry. Furthermore, the most traditionally methods for food spoilage detection are introduced in this context as well. The challenges and future trends of the potential use of the systems are also discussed. Based on the published literature, encouraging reports demonstrate that such systems are indeed the most promising candidates for the detection and monitoring of spoilage microorganisms in different foodstuff.

Keywords: Spoilage; Multisensors; Electronic noses; Biosensors; Electronic tongues

1. Introduction

Nowadays food safety is a worldwide public health issue that considers different aspects which could promote hygiene and society health. The presence of foodborne pathogens is a major global threat to public health and is one of the substantial concerns from the production to consumption chain. Many death or illness cases associated with unsaftey food as a plethora of diseases including diarrhoea, dysentery due to some food pathogens (e.g, *Salmonella* spp., *Shigella* spp., *Listeria monocytogenes)* being reported around the world. Furthermore, some spoilage microorganisms (e.g. *Botrytis* spp., *Pseudomonas* spp., *Acinetobacter* spp.) can significantly cause economic losses to the food manufactures by providing suitable conditions for spoiling remaining food materials (Pinu, 2016).

Microbiological quality and safety of foodstuff should be monitored and checked to ensure the consumption security of foods to human beings. Therefore, the originating factors and detection of spoilage in any microbiological stage across the entire food supply chain is of particular importance. The identification of microbial species in foodstuff are still routinely carried out by conventional methods such as biochemical and culturing approaches which have the disadvantages of being labour-intensive and time-consuming. Additionally, some analytical techniques enabling identification of spoilage indicators have been reported in the literature. They include purge and trap (PT), Proton transfer reaction mass Spectrometry (PRT-MS), Secondary Electrospray Ionization Mass Spectrometry (SESI-MS), Solid Phase Microextraction (SPME), Selected Ion Flow Tube Mass Spectrometry (SIFT-MS), Gas Chromatography Mass Spectrometry (GC-MS), Gas Chromatography Time of Flight Mass Spectrometry (GC-TOFMS). Apart from the fact that most of these methods require specific analytical skills and the cost of the sample preparation is relatively expensive, they are also not appropriate for continuous monitoring in food industry (Ghasemi-Varnamkhasti et al., 2012). Moreover some techniques mentioned above, for instance PTR-MS, are not readily available to be used in the food industry. Hence, there is a necessity for the development and use of innovative instrumental techniques as fast, reliable, non-expensive devices for the purpose of food spoilage characterization.

Spoilage can occurs in either stages of slaughtering or harvesting, cleaning, blanching, processing, packaging and storage, handling and distribution (Wang, Li, Yang, Ruan, & Sun, 2016). It is worth mentioning the nature of spoilage and the constituents produced during this phenomenon are enormously complicated because the food matrix including fat, carbohydrate, and protein can support microbial growth and the exponential acceleration of spoilage. Awareness of such issues is necessary while developing and using instrumental systems. Since the changes are created either in aroma profile or food body, therefore more efficient monitoring of both mediums could result in better judgment of spoilage (Kiani, Minaei, & Ghasemi-Varnamkhasti, 2016).

In recent decades, some diagnostic tools such as electronic noses, electronic tongues and biosensors have attracted much interest in food spoilage detection and could be considered as potential alternatives for detection of food spoilage. The development of such multisensor systems is currently an on-going activity. In recent years computerized techniques called chemometric tools have been coupled with such instruments and the capability promotion has been reported in the literature accordingly (Ghasemi-Varnamkhasti & Aghbashlo, 2014). However, the industrial use of such instruments in detecting food spoilage is still in its early stages. In particular for the case of biosensors and electronic tongue, some technical problems still need to be solved before they can be used in the food industry.

In this paper, different aspects of food spoilage along with conventional detection methods are reviewed. In addition, the basic principles of multisensor tools which are the candidates to be used in food detection are discussed and their applications for spoilage identification are also reviewed. New ideas for detecting instruments to monitor the food production lines are substantial needs in the food industry (Peris & Escuder-Gilabert, 2013) and as the paper presents, the use of such detection systems is the future of food spoilage evaluation domain and consequently promising future could be imagined for industrial and commercial usage of such systems in food supply chain, from production to consumption.

2. The nature of food spoilage and factors involved in the process

Food spoilage remains a global economic problem that is not yet under control. It is estimated that annually about 1.3 billion tonnes of food, amounting to 30% of global food production intended for human consumption is lost or wasted. This loss occurs at all levels of the food supply chain 'from farm to fork' with spoilage an important contributing factor (FAO, 2011).

Food spoilage describes a variety of cumulative undesirable changes in a food product that renders it unacceptable to consumers (Huis in't Veld., 1996). Food spoilage is a complex process and loss of quality is associated with two main events; changes in the physical and chemical characteristics of the food product and the microbial activity of a wide range of microorganisms (Dalgaard et al., 2006; Ercolini et al., 2006). It should be noted that the distinction between both processes is not always clear. For instance, undesirable enzymes in milk are responsible for producing the rancidity and bitterness associated with spoilage. These enzymes can either be indigenous or of microbial origin (The et al., 2004) but together catalyse the proteolytic and lipolytic reactions that lead to undesirable changes in the product.

Physicochemical spoilage processes are usually observed as changes in the flavour and colour of a food product and are also often interlinked. Physical treatments such as excessive heat, high hydrostatic pressure and ultrasound technologies can initiate chemical changes in food. Likewise, chemical reactions such as lipolysis and lipid/enzyme oxidation can cause colour change and increased viscosity, gelation or sedimentation (Ghanbari et al., 2013; Zhou et al., 2010).

Biochemical and microbial changes after harvest have a major impact on the final quality and shelf life of food products. Apart from physical and chemical damage, other changes to the sensory quality of a food product such as slime production, off-flavours, off-odours and blown pack spoilage of vacuum-packaged foods can be attributed to the metabolic activities of microorganisms (Brightwell et al., 2007; Parlapani et al., 2015; Wang et al., 2017; Yang and Bedoni, 2013).

A vast range of bacterial and fungal species play an important role in food spoilage therefore the microbial aspects of spoilage have been the subject of intensive research for decades. Initial studies used conventional microbiology methods for identifying microbial populations involved in food spoilage (Dainty and Mackay, 1992; Dalgaard, 1995). However, the evolution of more powerful molecular tools, particularly those based on 16S rRNA bacterial species classification and culture independent techniques allow for a more accurate assessment of the overall microbial food ecosystem and in some cases a reconsideration of the diversity of food spoilage flora (Ercolini et al., 2006; Jaaskelainen et al., 2016; Jaffres et al., 2009; Sade et al., 2017).

An important point to note is that not all microorganisms present or growing in food product cause spoilage. Microbial species that directly contribute to food spoilage have been described using terms such as 'specific spoilage organisms (SSO) or 'metabiotic spoilage associations', the latter term was introduced to recognize the importance of microbial interactions in food spoilage (Jorgensen et al., 2000; Gram et al., 2002).

Many studies have reported on the major microbial species associated with spoilage for a wide range of food types (for reviews see Andre et al., 2017; Casaburi et al., 2015; Hungaro et al., 2016; Quigely et al., 2013) . It is generally acknowledged that every food product has a distinct microbial flora associated with it during each stage of processing and storage. The composition of this microbial community depends on the microorganisms present on the raw product as well as the conditions under which the food is processed, preserved or stored (Gram et al., 2002; Parpalani et al., 2014).

Many interrelated factors influence the shelf life and quality indicators of a food product. Intrinsic, processing and extrinsic factors individually or in combination determine the selection of SSOs that will dominate and cause deterioration of a specific food product (Mossel et al., 1995; Nychas et al., 2008). Intrinsic factors describe the inherent physical, chemical and structural properties of the food product such as water activity (a_w), pH, nutrient availability and the presence of antimicrobial compounds for e.g. bacteriocins. Common characteristics of highly perishable foods such as milk, poultry, fish and meat is their high protein and moisture content, a_w > 0.998 and neutral to acidic pH. These conditions provide a suitable growth environment for a diverse range of bacterial and fungal species.

Physical or chemical preservation methods are applied during processing to inhibit the survival and growth of microorganisms. Baked products are usually poorly susceptible to microbial spoilage as the heat treatment during the baking process eliminates most of the raw microbial flora. Post-processing contamination thus becomes an important contributory factor to spoilage.

The conditions under which food is stored markedly influences the composition of the microbial flora that will contribute to the spoilage of the food product (Doulgeracki et al., 2010). Extrinsic factors relate to the environment the food is exposed to during processing and storage. Temperature and the gaseous phase surrounding a food are the most important factors that affect microbial growth (Ercolini et al., 2008; Casaburi et al., 2015). Modifications to these conditions e.g. refrigeration, modified atmosphere or vacuum packaging can be used to delay spoilage by slowing down microbial metabolic activity.

As previously mentioned, SSOs typically represent a small percentage of microbial species associated with a food product. This is because antagonistic and synergistic interactions between the factors described above, referred to as implicit parameters, will select for specific specie(s) adapted to occupy these ecological niches depending on their physiology and nutrient assimilation ability (Mossel et al., 1995). Table 1 summarises the influence of these factors on the microbial species associated with major food products.

For example, lactic acid bacteria (LAB) such as *Carnobacterium* spp. have been shown to dominate the spoilage microbiota of different meat and fish products stored at low temperature under modified atmospheres (Paludan-Muller et al., 1998; Barakat et al., 2000; Laursen et al., 2005). However, in similar products stored aerobically within the same temperature range, psychrotolerant aerobes like *Pseudomonas* spp. often dominate (Del Rio et al., 2007; Nychas et al., 2008; Paparlani and Boziaris, 2016).

Table 1. Reports on spoilage microorganisms in selected food products as influenced by intrinsic and extrinsic factors

3. Traditional methods and recent developments

Food spoilage is of great economic significance. The ability to predict shelf-life during the development of new products and to determine remaining shelf life during storage of food products is important for all stakeholders in the food value chain. This has necessitated the development of fast, accurate and reproducible methods for monitoring food spoilage (Blixt and Borsh, 1999). Traditional methods used for quality control typically rely on microbiological, chemical and sensory analysis (Haugen et al., 2006; Gobbi et al., 2010; Spadafora et al., 2016).

Early studies focused on determining the microbiological status of food products relied mainly on total viable counts (TVC) and phenotyping microbial isolates using biochemical tests (Dainty and Mackey, 1992; Haugen et al., 2006). These methods are time consuming and sometimes provide limited information as the extent of spoilage does not always correspond to the number of microorganisms present in the food (Blixt and Borsh, 1999; Ramirez-Guizar et al., 2017). Furthermore, they often underestimate the true microbial community. More recently, molecular approaches based on rRNA gene sequences or metagenomics are increasingly used to identify microbial communities involved in spoilage (Jaaskelainen et al., 2016; Jaffres et al., 2009; Sade et al., 2017).

Chemical methods can be used as an indirect means to detect and quantify microbial contamination of food based on the analysis of certain chemical markers. The quantity of cell wall components such as chitin and ergosterol are used to assess spoilage of oil seeds during storage (Gancarz et al., 2017). The colour change associated with spoilage of chicken meat can be measured using colorimetry and spectrophotometry

(Mancini et al., 2005). The amounts of total volatile basic nitrogen (TVBN) and trimethylamine can be indicative of fish spoilage (Jaffres et al., 2011) but as these markers only increase in fish during the late stages of storage, they cannot be used as an indication of freshness (Oehlenschangler, 2014). Organic acid profile and pH are also routinely measured. A drawback of some of these methods is the requirement for laborious sampling and extraction procedures. Despite technological advances, sensory analysis using trained panellists remains an important aspect of investigating the direct quantification of spoilage (Parpalani et al., 2014; Lytou et al., 2017); however this is not always practical for routine analysis as it is time consuming and requires skilled personnel.

Nowadays, the detection of characteristic volatile compounds (VOC) of microbial origin has become a viable option to investigate the presence and growth of spoilage organisms in food and has been used in clinical settings (Tait et al., 2014). Wang et al., (2016) recently reviewed the range of methods used for the sampling, detection and analysis of these microbial volatile organic compounds in foods.

Solid phase microextraction (SPME) coupled with gas chromatography/mass spectroscopy (GC/MS) is one of the most common methods for studying volatile organic compounds. The use SPME-GCMS to evaluate the degree of spoilage in several food products including yoghurt (Ndagijimana et al., 2008), shrimp (Jaffres et al., 2011), ham (Martin et al., 2010) has been reported. However, VOC profiles are influenced by sample preparation, extraction and chromatographic procedures which may create inconsistencies (Ramirez-Guizar, 2017).

The development of more rapid and efficient identification methods continues to be the focus of intensive research. While traditional methods are for the most part cost effective, they do not always provide accurate, sensitive and reliable information.

Instrumentation overcomes this hurdle but widespread routine use for quality control during processing and storage is limited by cost of equipment and technical skills required by personnel (Concina et al., 2009; Wang et al., 2016). Furthermore, they mainly focus on compounds produced when food is spoiled, limiting their use for at-site quality monitoring.

In recent decades, there have been developments towards the use of gas sensors in devices such as the electronic nose for odour detection and electronic tongue (Gil-Sanchez et al., 2011) and biosensors. Despite all advancements in this research area, the complexity of the microbiological and biochemical processes involved in spoilage remains a challenge to developing a single quality monitoring technique for individual food products (Remenant et al., 2015).

4. Production of chemical compounds (gas and substrate) in spoiled foods

As described previously, various sensory defects such as off-odours, off-flavours and discolouration in spoiled food can be attributed to the presence and metabolic activity of spoilage microorganisms. During exponential growth, spoilage microorganisms preferentially utilize the carbohydrates, sugars, proteins and fats in food to provide their metabolic needs. For example, during storage at low temperatures, bacteria present in meat use glucose as a carbon and energy source. When glucose is depleted, other substrates such as lactate, pyruvate, amino acids and nucleic acids may be metabolized (Casaburi et al., 2015). Primary metabolites such as polysaccharides, amino acids, lipids and vitamins act as precursors for the production of a range of compounds. These chemical compounds serve as indicators of spoilage and comprise of organic acids, biogenic amines and a range of VOCs (alcohols, aldehydes, ketones, esters, volatile fatty acids and sulphur compounds) (Doyle, 2007; Wang et al., 2016).

The composition and concentration of VOCs produced in food is for the most part determined by the combined effect of both intrinsic and extrinsic factors. For example, some amino acids can be decarboxylated by microbial enzymes to produce biogenic amines such as histamine, tyramine, putrescine and cadaverine (Naila et al., 2010). Biogenic amine accumulation in fermented meat products has been reported to be influenced by fermenting strains, pH, sausage diameter (intrinsic) as well as storage temperature and relative humidity (extrinsic). These conditions favour proteolytic and decarboxylase reactions required for biogenic amine formation (Suzzia and Gardini, 2003; Lattore-Moratalla et al., 2012).

A list of some compounds associated with the spoilage of selected food products is reported in Table 2. Several authors have reported the detection and measurement of these molecules in spoiled food and there have been attempts to identify VOCs that are likely specific to both SSO and substrate (Concina et al., 2009; Spadafora et al., 2016). This has paved the way for more focused studies to determine the so called chemical spoilage index (CSI), a profile of microbial VOCs (MVOCs) for a particular food product (Parpalani et al., 2014). The concentration of these CSI metabolites should increase in tandem with the growth of the SSOs as well as loss of sensory quality and therefore can be used to estimate shelf life (Jay, 1986; Miks-Krajnik et al., 2016).

Table 2. Some spoilage substrates and metabolites typically found in spoiled food

Correlating sensory impressions of spoilage to the metabolic activity of SSOs is not always clear. This reflects both the complex nature of food spoilage and the limited information available regarding the metabolism of the microbial species involved.

Some VOCs can be produced from reactions catalysed by both SSOs and food matrix enzymes, others from complex metabolic reactions involving different microbial species (Remenant et al., 2015). Species of LAB, *Enterobacteriaceae* and *Clostridia* have been implicated in 'blown pack' spoilage (BPS) of refrigerated, vacuum packed meat products (Brightwell et al., 2007; Hernandez-Macedo et al., 2012). The 'blown pack' effect has been attributed to gas production but it remains unclear which species is directly implicated although some authors have attributed BPS to be largely due to the metabolic activities of *Clostridium esterthеticum* (Cavill et al., 2016; Rajagopal et al., 2016). In addition, MVOCs identified from culture media experiments as potential CSI candidates may not be detected in food (Yu et al., 2000).

5. Multisensor systems

5. 1. Electronic nose and its performance

The human nose is much more complicated than other human senses like the ear and the eye. It is still the primary 'instrument' to assess the smell of various products and it is is currently used to identify a diverse range of food spoilage. Sensory evaluation using the human sense of smell is subjective; careful design and rigorous training of assessors allows it to become a more objective, but still expensive option. Instrumental methods, such as gas chromatography/ mass spectrometry (GC/MS), are also expensive and require trained personnel. The concept of the electronic nose has attracted attention in many branches of industry for its potential in routine odour analysis.

The electronic nose is an electronic system that tries to mimick the structure of the human nose, but trying to reduce its limitations. An accepted definition was given by

Gardner in 1994: "an electronic nose is an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours" (Gardner & Bartlett, 1994). The similarity of electronic nose with the biological sense of smell can be observed in the smelling process: the first step in both is the interaction between volatile compounds (usually a complex mixture) with the appropriate receptors: olfactory receptors in the biological nose and a sensor array in the case of the electronic nose. The next step is the storage of the signal generated by the receptors in the brain or in a pattern recognition database (learning stage) and later the identification of one of the odour stored (classification stage). An electronic nose uses currently a number of individual sensors (typically 5-100) whose selectivities towards different molecules overlap. The response from a chemical sensor is usually measured as the change of some physical parameter, e.g. conductivity or current. There are some significant drawbacks for these devices, like the lack of selectivity and the sensors drift, that are one of the main research topics in this field. On the other hand, they have the advantage of high portability for making in situ and on-line measurements with lower costs and good reliability.

An electronic nose generally consists of an aroma extraction system, a sensor array, a control and measurement system, and a pattern recognition method. A simple flow chart of the typical structure of an electronic nose is shown in Fig. 1 (Lozano, 2006).

Fig. 1. Block diagram of an electronic nose system.

The aroma extraction system or sampling method carries the volatile compounds from the samples to the sensor chamber and it significantly contributes to the capability and reliability in an odour sensing system. Various techniques of the sample flow, static and preconcentrator systems are available for using with an electronic nose and the most appropriate aroma extraction system should be selected for the project taking into account the type of samples, the application and the portability of the system.

There is a basic classification of sampling methods if concentrator is used or not. A concentrator is often used to enhance the sensitivity and can be used to autonomously enhance the selectivity of a sensor array. On the other hand, there are two main types of aroma extracting systems, the sample flow system and the static system. In the first one, the sensors are placed in the vapour flow, which allows the rapid exchange of vapour and hence many samples can be measured within a short time. In the static system, there is no vapour flow around the sensor, and measurements are usually made on the steady-state responses of the sensors exposed to vapour at a constant concentration. The most common techniques used for solid or liquid samples in food applications are static headspace (HS), purge and trap (P&T) and solid phase micro extraction (SPME) (Lozano, Santos, Gutiérrez, & Horrillo, 2007).

The most important part of an electronic nose is the detection system or chemical sensors, that are capable of converting a chemical change in the environment into an electric signal in the gas sensors and respond to the concentration of specific compounds from gases or liquids (Nagle, 2006). Chemical sensors can be based on electrical, thermal, mass or optical principles. Several examples of chemical sensors used in electronic noses are: conducting polymers (Guadarrama, Fernández, Íñiguez, Souto, & De Saja, 2000), semiconductor devices (Jose Pedro Santos & Lozano, 2015) quartz resonators (Sharma et al., 2015), and surface acoustic sensor (SAW) (Jose Pedro Santos et al., 2005).

Conducting polymers (based on polypyrrole, polyaniline, thiophenes, indoles, or furans) have been used as the active layers of gas sensors since early 1980s. The sensors made of conducting polymers have many improved characteristics: high sensitivities and short response time at room temperature. The electronic interface is straightforward, and they are suitable for portable instruments. Conducting polymers are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivations. Most of the conducting polymers are doped/undoped by redox reactions; therefore, their doping level can be altered by transferring electrons from or to the analytes. Electron transferring can cause the changes in resistance and work function of the sensing material. The work function of a conducting polymer is defined as the minimal energy needed to remove an electron from bulk to vacuum energy level. This process occurred when the sensing films are exposed to redox-active gases. They can remove electrons from the aromatic rings of conducting polymers. When this occurs at a p-type conducting polymer, the doping level as well as the electric conductance of the conducting polymer is enhanced. An opposite process will occur when detecting an electro-donating gas.

Semiconductor chemical sensors detect gases and aromas in samples by a chemical reaction that takes place when the gas comes in direct contact with the sensor surface. This chemical reaction and the presence of the gases can be detected since the electrical resistance in the sensor is modified when it is exposed to the monitored gas. This change in resistance is measured and can be used to identify the presence of a gas, to predict the the gas concentration or other tasks. Tin dioxide in different structures (thin or thick film, nanostructures, nanowires, etc.) is the most common material used in semiconductor sensors, that are commonly used to detect hydrogen, oxygen, alcohol vapor, and harmful gases such as carbon monoxide in different applications related with environment, health, food quality, etc. Operating the device at different temperatures and varying the type and thickness of the material, the sensitivity and selectivity can be optimized.

The piezoelectric family of sensors has two main members: quartz crystal microbalance (QCM) and surface acoustic-wave (SAW) devices. They can measure temperature, mass changes, pressure, force, and acceleration, but in the electronic nose, they are configured as mass-change-sensing devices.

The QCM type consists of a resonating disk a few millimeters in diameter, with metal electrodes on each side connected to a lead wire. The device resonates at a characteristic (10 MHz to 30 MHz) frequency when excited with an oscillating signal. During manufacture, a polymer coating is applied to the disk to serve as the active sensing material. In operation, a gas sample is adsorbed at the surface of the polymer, increasing the mass of the disk-polymer device and thereby reducing the resonance frequency. The reduction is inversely proportional to odorant mass adsorbed by the polymer.

The SAW sensor differs from QCM in several important ways. First, the wave travels over the surface of the device, not throughout its volume. SAW sensors operate at much higher frequencies, and so can generate a larger change in frequency. A typical SAW device operates in the hundreds of megahertz, while 10 MHz is more typical for a QCM, but SAW devices can measure changes in mass to the same order of magnitude as QCMs. Even though the frequency change is larger, increased surface-to-volume ratios mean the signal-to-noise ratio is usually poorer. Hence, SAW devices can be less sensitive than QCMs in some instances.

With QCMs, many polymer coatings are available, and as with the other sensor types, differential measurements can eliminate common-mode effects. For example, two adjacent SAW devices on the same substrate (one with an active membrane and another without) can be operated as a differential pair to remove temperature variations and power line noise. A disadvantage of both QCM and SAW devices is more complex electronics than are needed by the conductivity sensors. Another is their need for frequency detectors, whose resonant frequencies can drift as the active membrane ages.

The control and measurement system includes all electronic circuits needed for the measurements of signals generated by the sensors such as interface circuits, signal conditioning and A/D converters. This sensor electronics usually amplify and condition the sensor signal. The signal must be converted into a digital format to be processed by a computer, and this is carried out by an analogue to digital converter (e.g. a 12 bit converter) followed by a multiplexer to produce a digital signal which either interfaces to a serial port on the microprocessor (e.g. RS-232, USB) or a digital bus (e.g. GPIB). The microprocessor is programmed to carry out a number of tasks, including the pre-processing of the time-dependent sensor signals to compute the input vectors x_j and classify them against known vectors stored in memory. Finally, the output of the sensor array and the odour classification can be displayed on a LCD or on a PC monitor.

The main goal of an electronic nose is to identify an odorant sample and perhaps to estimate its concentration. The multivariate information obtained by the sensor array can be sent to a display so a human can read that information and do an action or an analysis. Also, that information, that is an electronic fingerprint of the volatile compound measured, can be sent to a computer to perform an automated analysis and emulate the human sense of smell. These automated analysis that comes from methods of statistical pattern recognition, neural arrays and chemometrics (Aguilera, Lozano, Paredes, Alvarez, & Suárez, 2012), is a key part in the development of a gas sensor array capable to detect, identify or quantify different volatile compounds responsible for food spoilage. This process may be subdivided into the following steps: preprocessing and feature extraction, dimensionality reduction, classification or prediction, and decision-making.

Preprocessing compensates for sensor drift, compresses the transient response of the sensor array, and reduces sample-to-sample variations. Typical techniques include: manipulation of sensor baselines; normalization of sensor response ranges for all the sensors in an array (the normalization constant may sometimes be used to estimate the odorant concentration); and compression of sensor transients. Feature extraction has two purposes: to reduce the dimensionality of the measurement space, and to extract information relevant for pattern recognition. For example, in an electronic nose with 32 sensors, tipically one feature is extracted from each raw response of the sensor and the measurement space has 32 dimensions.

A dimensionality reduction stage projects this initial feature vector onto a lower dimensional space in order to avoid problems associated with high-dimensional, sparse datasets. Maybe, some of them probably respond in a similar (but not identical) way. This means that the number of dimensions in the data set can be reduced without any loss of information. It is generally performed with linear transformations such as the classical principal component analysis (PCA) and linear discriminant analysis (LDA). The resulting low-dimensional feature vector is further used to solve a given prediction problem, generally classification, regression or clustering.

Classification is a general process related to categorization, the process in which ideas and objects are recognized, differentiated, and understood. In this case, the identification of an unknown sample into previously learned classes is usually performed by artificial neural networks (ANNs). An artificial neural network is an information processing system that has certain performance characteristics in common with biological neural networks. It allows the electronic nose to function in the way a brain function when it interprets responses from olfactory sensors in the human nose. During training, the ANN adapts the synaptic weights to learn the patterns of the different odorants. After training, when presented with an unidentified odorant, the ANN feeds its pattern through the different layers of neurons and assigns the class label that provides the largest response.

Finally, the classifier produces an estimate of the class for an unknown sample along with an estimate of the confidence placed on the class assignment. A final decision-making stage may be used if any application-specific knowledge is available, such as confidence thresholds or risk associated with different classification errors. Cross validation is usually employed and training is stopped at the point of the smallest error in the validation set to detect and avoid overtraining.

5.2. Electronic tongue

The analysis of the substances dissolved in liquid samples with multisensor systems was firstly developed in mid-1980s (Otto & Thomas, 1985). In the beginning of the 1990s, the first taste sensor was built, based on ion-selective electrodes (Hayashi, Yamanaka, Toko, & Yamafuji, 1990; Iiyama, Miyazaki, Hayashi, Toko, Yamafuji, Ikezaki, & Sato, 1992). The sensitive membrane was made of various lipid membranes immobilized onto polyvinyl chloride (Toko, 2000). Later, in 1995, the concept of electronic tongue was introduced. It was based on inorganic chalcogenide glass sensors, being used for both qualitative and quantitative determinations (Legin, Rudnitskaya, Di Natale, Mazzone, & D'Amico, 2000; Vlasov, Legin, Rudnitskaya, Di Natale, & D'Amico, 2005).

This concept has been developed, and in the last years the bioelectronic tongue system was introduced (del Valle, Cetó, & Gutierrez-Capitán, 2014; Ghasemi-Varnamkhasti, Rodríguez-Méndez, Mohtasebi, Apetrei, Lozano, Ahmadi, Razavi, de Saja, 2012). It contains an array of biosensors and is able to qualitatively and quantitatively characterize multicomponent liquid samples (Cetó, Voelcker, & Prieto-Simón, 2016; Song, Jin, Ahn, Kim, Lee, Kim, Simons, Hong, & Park, 2014; Rodriguez-Méndez, Medina-Plaza, García-Hernández, de Saja, Fernández-Escudero, Barajas-Tola, & Medrano, 2014).

Conceptually speaking, electronic tongues are analytical tools which artificially determine the gustatory perceptions (del Valle, 2012; Smyth & Cozzolino, 2013). These systems consist of an array of sensors coupled with chemometric means of data processing for the characterization of complex liquid samples (Winquist, Olsson, & Eriksson, 2011; Martínez-Bisbal, Loeff, Olivas, Carbó, García-Castillo, López-Carrero, Tormos, Tejadillos, Berlanga, Martínez-Máñez, Alcañiz,& Soto, 2017; Kumar, Ghosh, Tudu & Bandyopadhyay, 2017; Rudnitskaya , Schmidtke, Reis, Domingues, Delgadillo, Debus, Kirsanov, Legin, 2017). Following adequate calibration and training, the electronic tongue is able to determine the qualitative and quantitative chemical composition of more chemical species in complex samples (Lvova, Di Natale & Paolesse, 2017; Gutiérrez, Haddi, Amari, Bouchikhi, Mimendia, Cetó, & del Valle, 2013; Immohr, Hedfeld, Lang, & Pein, 2017).

The general scheme which describes the concept of electronic tongue is outlined in Fig. 2.

Fig. 2. General scheme of an electronic tongue system

Electronic tongue comprises three components: (1) automatic sampler, which may be necessary, but it is featured in the majority of commercial systems; (2) array of sensors with different selectivity and sensitivity and (3) chemometric software with proper algorithms for processing the signals from sensors and delivering the results (del Valle, 2012; Ciosek & Wróblewski, 2007; Kalit, Marković, Kalit, Vahčić, & Havranek, 2014; Tahara & Toko, 2013).

Usually, the initial studies dedicated to the development of electronic tongues with sensors based on various detection systems focused on the qualitative and quantitative analysis of the solutions which represent basic tastes (sweet, sour, salty, bitter and umami), as well as of other gustatory sensations or perceptions (astringency, pungency) (Riul Jr., dos Santos Jr., Wohnrath, Di Tommazo, Carvalho, Fonseca, Oliveira Jr., Taylor, & Mattoso, 2002; Eckert, Pein, Reimann, & Breitkreutz, 2013; Tian, Feng, Xiao, Song, Li, Liu, Mao, & Li, 2015; Pioggia, Di Francesco, Marchetti, Ferro, Leardi, Ahluwalia, 2007; Jain, Panchal, Pradhan, Patel, & Pasha, 2010; Rudnitskaya, Polshin, Kirsanov, Lammertyn, Nicolai, Saison, Delvaux, Delvaux, & Legin, 2009; Toko, 1998; Legin, Rudnitskaya, Clapham, Seleznev, Lord, & Vlasov, 2004; Khan, Khalilian, & Kang, 2016; Arrieta, Rodriguez-Mendez, & de Saja, 2003; Apetrei, Rodríguez-Méndez, Parra, Gutierrez, & de Saja, 2004; Arrieta, Apetrei, Rodríguez-Méndez, & de Saja, 2004). This is absolutely necessary in order to prove that the sensor responds to compounds with various organoleptic properties. The main compounds analyzed, as well as their sensorial properties, are presented in Table 3.

Table 3. The main sensorial properties and their relative compounds.

For developing the arrays of sensors, more types of sensors have been used: electrochemical (potentiometric, voltammetric, amperometric, impedimetric, conductimetric), optic or enzymatic (biosensors).

Most electronic tongue systems reported in the specialized literature are based on potentiometric sensors (Mimendia, Gutiérrez, Leija, Hernández, Favari, Muñoz, & del Valle, 2010; Ciosek & Wróblewski, 2011; Cuartero, Carretero, Garcia, & Ortuño, 2015). By using the potentiometric methods, one measures the potential between two electrodes in the absence of an external flow of current. The value of potential measured under these circumstances is used for the quantitative determination of the analytical species of interest in the multicomponent liquid solution (Bard & Faulkner, 2001; Zoski, 2007; Wang, 2000).

Potentiometric sensors present a number of advantages, such as: their functioning principle is well-known, there is a possibility to obtain selective sensors, low cost, high possibility of industrial production, and the detection is very similar to the principle of molecular recognition, i.e., with the principle of biologic detection of the substances responsible of taste. Their disadvantages are their being temperature dependant and the fact that the adsorption of the solution compounds in the sensitive element modifies the value of the measured potential (Bratov, Abramova, & Ipatov, 2010; Bobacka, Ivaska, & Lewenstam, 2008).

Potentiometric sensors are most often used in the development of electronic tongues with various applications: fermentation processes monitoring, identification of the botanic origin of honey, evaluation of the impact of micro-oxygenation in the process of wine aging in the presence of oak chips, etc. (Gerstl, Joksch, & Fafilek, 2013; Peris

& Escuder-Gilabert, 2013; Dias, Veloso, Sousa, Estevinho, Machado, & Peres, 2015; Schmidtke, Rudnitskaya, Saliba, Blackman, Scollary, Clark, Rutledge, Delgadillo, & Legin, 2010; Mednova, Kirsanov, Rudnitskaya, Kilmartin, & Legin, 2009; Gutiérrez-Capitán, Vila-Planas, Llobera, Jiménez-Jorquera, Capdevila, Domingo, & Puig-Pujol, 2014).

Another category of sensors which has been widely used for the development of electronic tongues are the voltammetric sensors (Bard & Faulkner, 2001; Zoski, 2007; Wang, 2000). In this case, a potential, either fix or, most often, variable, is introduced into the system, and the electroactive compounds present in the sample are oxidized or reduced, which leads to the generation of a flow of anodic or cathodic current. When the sample to be analyzed is a complex one, containing more chemical species with redox properties, the selectivity of this type of sensors is limited for a specific analyte present in the sample. The greatest disadvantage of this type of sensors is their reduced selectivity, but this aspect can be improved by using nanomaterials or by employing pulse techniques (differential pulse voltammetry and square-wave voltammetry) or by optimization of the experimental conditions (Brett & Fungaro, 2000; Gupta, Jain, Radhapyari, Jadon, Agarwal, 2011; Reza Ganjali, Garkani Nejad, Beitollahi, Jahani, Rezapour, & Larijani, 2017; Rodríguez-Méndez, Apetrei, & de Saja, 2008).

The complexity of the voltammetric signals is even more complicated in the case of sensors which contain electroactive substances immobilized onto the sensitive element. The interpretation of results is often difficult, as the interactions are extremely complex, electrocatalytic, synergetic or inhibition effects may occur. This is why, in most cases, it is necessary to use analytical methods for multivariate data

(Cetó, Apetrei, del Valle, & Rodríguez-Méndez, 2014; Winquist, 2008; Bueno, de Araujo, Salles, Kussuda, & Paixão, 2014; del Valle, 2010).

Numerous research groups have developed various multisensory systems based on voltammetric sensors (metallic electrodes, electrodes based on nanocomposite materials, chemically-modified electrodes, etc.) for the studies of different industrial products (Campos, Alcañiz, Aguado, Barat, Ferrer, Gil, Marrakchi, Martínez-Mañez, Soto, & Vivancos, 2012; Domínguez, Moreno-Barón, Muñoz, & Gutiérrez, 2014; Campos Sánchez, Bataller Prats, Gandía Romero, Soto Camino, Martínez Mañez, & Gil Sánchez, 2013; Winquist, 2008; Cetó, Capdevila, Puig, & del Valle, 2014; Apetrei & Apetrei, 2014).

The detection principle of the conductimetric sensors is based on the change in the conductivity of the sensible material as a result of the interaction with various chemical species present in the solution to be analysed. There are only a few studies in the literature which tackle the use of conductimetric sensors in the development of electronic tongues (Winquist, Holmin, Krantz-Rückler, Wide, Lündström, 2000; Sha, 2013).

The measurement principle of impedance sensors is based on measuring the impedance at a certain frequency value or for a range of frequencies with the help of impedance spectroscopy. This type of sensors, based on various materials, has been largely used in the development of electronic tongues with various applications (Cabral, Bergamo, Dantas, Riul Jr, & Giacometti, 2009; Guo, Chen, Yang, & Wang, 2005).

The detection principle of piezoelectric sensors is based on the piezoelectric phenomenon. The result of the exposure of these sensors to various substances is the modification of their mass due to adsorption or absorption processes, which modify the resonance frequency of the sensor. Therefore, the electric current is modified, i.e., the exit signal provided by the sensor. The advantages of these types of sensors are: high sensibility, durability, low costs, and reduced size. The detection principle is based on mass modification (Pearce, Schiffman, Troy Nagle, Gardner, 2006). The advantages of these types of sensors are: high sensibility, durability, low costs, and reduced size. The electronic tongues with piezoelectric sensors arrays have been used for various applications in food analysis (Sehra, Cole, & Gardner, 2004; Kalit, Marković, Kalit, Vahčić, Havranek, 2014).

Colorimetric sensors are based on the interaction between electromagnetic radiation and matter, from which various phenomena, such as reflection, fluorescence or absorption, result. This type of sensors contains a source of light or a series of filters for a specific wave length for increasing selectivity, an indicator, and a detector. The properties of the indicator are modified as a result of the interaction with the substance to be analysed, and consequently, a change in absorbance or fluorescence occurs. The changes are quantified by the detector, which converts the optical signal in electrical signal. Colorimetric sensors present the following advantages: simplicity, low cost, and high selectivity. In addition, it is possible for these sensors to detect non-electroactive substances which cannot be detected by electrochemical sensors. The disadvantages of the colorimetric sensors are: low durability and distortion of the exit signal, which greatly limits their applications (Piriya, Joseph, Daniel, Lakshmanan, Kinoshita, Muthusamy, 2017; Kangas, Burks, Atwater, Lukowicz, Williams, & Holmes, 2017). In the literature, there are several papers which report on the use of electronic tongues based on colorimetric sensors in food analysis

(Gutiérrez, Llobera, Vila-Planas, Capdevila, Demming, Büttgenbach, Mínguez, & Jiménez-Jorquera, 2010; Chung, Park, Park, Kim, Park, Son, Bae, & Cho, 2015) .

Bioelectronic tongue systems are endowed with biosensors arrays which can specifically determine a number of analytes of interest for a certain sample. However, when using certain detection methods, interferences are significant, and there can be obtained signals which may be assimilated to a chemical impression, which can be used for the discrimination and classification of the analyzed samples (Ahn, An, Song, Park, Lee, Kim, Jang, & Park, 2016; Song, Jin, Ahn, Kim, Lee, Kim, Simons, Hong, & Park, 2014). Bioelectronic tongue systems have been successfully used in the qualitative and quantitative analysis of various foods (Zeravik, Hlavacek, Lacina, & Skládal, 2009).

The comparison between electronic tongues based on different type of sensors were reported in literature. For instance, a hybrid electronic tongue based on six chemically modified graphite-epoxy voltammetric sensors and 15 potentiometric sensors was applied in the recognition of beer types (Gutiérrez, Haddi, Amari, Bouchikhi, Mimendia, Cetó, & del Valle, 2013). In other study the data obtained with two sets of voltammetric sensors, prepared using different strategies, have been combined in an electronic tongue to evaluate the antioxidant properties of red wines (Cetó, Apetrei, del Valle, & Rodríguez-Méndez, 2014). Furthermore, the purpose of a complex study was to compare the performance characteristics of six different e-tongues applied to the same set of pharmaceutical samples. Two commercially available electronic tongues (from AlphaMOS and Insent) and four laboratory prototypes (one potentiometric system from St. Petersburg University, two potentiometric systems from Warsaw University operating in flow and static modes, one voltammetric system from Barcelona University) were employed (Pein, Kirsanov, Ciosek, del Valle, Yaroshenko, Wesoły, Zabadaj, Gonzalez-Calabuig, Wróblewski, &Legin, 2015).

The advantages of electronic tongues compared to the classical analytical methods include: high sensitivity, easy building and use, low costs of equipment and price per analysis, as well as short time necessary for analysis. Through miniaturizing and automating, electronic tongues can be used for on-line, in-line or real-time analyses, another advantage being that it is a non-destructive analytical method (Khan, Khalilian, & Kang, 2016; Cetó, González-Calabuig, del Valle, 2015; Medina-Plaza, García-Hernandez, de Saja, Fernandez-Escudero, Barajas, Medrano, García-Cabezon, Martin-Pedrosa, & Rodriguez-Mendez, 2015).

Nevertheless, research in this field is necessary in what concerns aspects such as: sensor-obtaining technologies, data processing, system calibration and validation of results. Researchers in this field grant special attention to these themes, and most of the recent studies are more and more thorough and present clear applications in various fields.

5.3. Biosensors

Biosensors are analytical devices which integrate a bioreceptor (enzymes, organelles, living cells, tissues, nucleic acids, aptamers, etc.) in a compatible transducing system, and which are capable to specifically determine certain chemical compounds (Rotariu, Lagarde, Jaffrezic-Renault, & Bala, 2016; Scognamiglio, Arduini, Palleschi, & Rea, 2014; Di Rosa, Leone, Cheli, & Chiofalo, 2017). The most frequently used transducers are: electrochemical, optical, mass, thermal, but there are other types as well (Compagnone, Di Francia, Di Natale, Neri, Seeber, & Tajani, 2017; Ali, Najeeb, Ali, Aslam, & Raza, 2017; Almeida Silva, Cruz Moraes, Campos Janegitz, Fatibello-Filho, 2017; Chauhan, Maekawa, & Kumar, 2017). An electric signal which can be measured and recorded is produced as a result of the specific interaction between the analyte and the biocomponent. The analytes or target compounds comprise a large and various number of chemical species, from inorganic compounds to organic compounds with small molecules and even with large molecules such as proteins (Abdulbari & Basheer, 2017; El-Nour, Salam, Soliman, &. Orabi, 2017; Matysik, 2017; Leca-Bouvier & Blum, 2005). The scheme of analytes detection with biosensors is presented in Fig. 3.

Fig. 3. Biosensor detection scheme

When compared to classical methods of analysis, biosensors present a number of advantages, such as: extremely high selectivity, which allows the detection of the target molecule in real complex samples, without requiring the pre-treatment of the sample, short time of analysis (from a few seconds to a few minutes), relatively low costs, possibility of miniaturizing and turning them into portable devices, which allows fast and precise on-site, in-line, on-line or real time analytical determinations (Scognamiglio, Rea, Arduini, & Palleschi, 2017; Shao, Wang, Wu, Liu, Aksay, & Lina, 2010; Mehrotra, 2016).

Food quality control, as well as the detection or monitoring of the food spoilage processes, requires methods and tools for the precise analysis of various parameters. Biosensors can accomplish these functions, which is why the special interest in developing new biosensors which can be used in food analysis for example, for determining freshness or spoilage, is fully justified (Dornelles Mello & Tatsuo

Kubota, 2002; Poltronieri, Mezzolla, Primiceri, & Maruccio, 2014; Pividori & Alegret, 2010).

The main research directions include the analysis of compounds of interest for food quality and that of contaminates, compounds which accidentally appear in food and which should not be there under normal conditions (McGrath, Elliott, & Fodey, 2012; Dragone, Grasso, Muccini, & Toffanin, 2017). Moreover, focus is laid on monitoring various chemical or biochemical processes related to fermentation, degradation, spoilage, maturation or freshness of foods with the help of the biosensors (Mutlu, 2016; Vasilescu, Nunes, Hayat, Latif, & Marty, 2016; Adley, 2014; Ispas, Crivat, & Andreescu, 2012; Park, Kim, Lee, & Jang, 2015). Other studies lay importance on the characterization of foods in terms of biologic or geographic origins, as well as authenticity, fraud or adulteration of foods (Apetrei & Ghasemi-Varnamkhasti, 2013; Bassi, Lee, & Zhu, 1998; Narsaiah, Jha, Bhardwaj, Sharma, & Kumar, 2012; Campuzano, Ruiz-Valdepeñas Montiel, Torrente-Rodríguez, Reviejo, & Pingarrón, 2016).

The classification of the biosensors can be made according to several criteria, the most often being the biochemical recognition mechanism (Thévenot, Toth, Durst, Wilson, 2001; Monošík, Streďanský, Šturdík, 2012; Apetrei & Ghasemi-Varnamkhasti, 2013; Gorton, 2005).

Enzyme-based biosensors are the most frequently used in foods analysis (Kumar & Neelam, 2016; Prodromidis & Karayannis, 2002). Two basic principles are used in practice, one being the direct detection of the analyte (substrate) resulted from an enzymatic process, the other being the inhibition of the enzymatic activity (Upadhyay & Nishant, 2013; Murugaboopathi, Parthasarathy, Chellaram, Prem Anand, &

Vinurajkumar, 2013). Enzymes in the class of oxidoreductases (laccase, tyrosinase, peroxidase, dehydrogenases) are used for substrate detection, and the main electroactive compounds detected by these biosensors are o-quinone derivatives, hydrogen peroxide or reduced forms of nicotinamide adenine dinucleotide (Amine, Mohammadi, Bourais, & Palleschi, 2006; Mello & Kubota, 2002; Tembe & D'Souza, 2015). The enzyme sources can be purified enzymes commercially available, but also organelles, cells, tissues, microorganisms, etc. (Apetrei & Apetrei, 2016; Rodríguez-Delgado, Alemán-Nava, Rodríguez-Delgado, Dieck-Assad, Martínez-Chapa, Barceló, Parra, 2015; Gul, Sheeraz Ahmad, Saqlan Naqvi, Hussain, Wali, Farooqi, & Ahmed, 2017; Liu, Wu, Cai, Hu, Zhou, & Wang, 2014; Hasan, Nurunnabi, Morshed, Paul, Polini, Kuila, Al Hariri, Lee, & Jaffa, 2014; Lim, Ha, Lee, Lee, & Kim, 2015). For the detection of inhibitors of enzymatic activity, the activity of the enzyme is determined in the absence and in the presence of the inhibitor, determining the inhibition degree based on inhibitor concentration. The detection of target compounds does not involve its transformation (Upadhyay & Nishant, 2013; Murugaboopathi, Parthasarathy, Chellaram, Prem Anand, & Vinurajkumar, 2013).

The detection principle of affinity biosensors is based on molecular recognition systems, such as the interaction between DNA (Deoxyribonucleic acid) strands, antigen – antibody or hormone – receptor interactions (Patel, 2006; Turner, 2013; Rogers, 2000). Another class of compounds used in the production of this types of biosensors is molecularly imprinted polymers (Song, Xu, Chen, Wei, & Xiong, 2014; Frasco, Truta, Sales, & Moreira, 2017; Wackerlig & Schirhagl, 2016).

Nano biosensors are emerging as a promising tools for the applications in the food analysis. They are integrating knowledge of physical sciences, biology, chemistry, biotechnology, molecular engineering, and nanotechnology offering important improvements in selectivity and sensitivity compared to classical chemical and biological methods. Nano biosensors can be used for detection and quantification of microorganisms, contaminants, and food freshness (Pérez-López, & Merkoçi, 2011; Grumezescu, 2016).

6. Literature evidence multisensor systems to food spoilage detection

6.1. Electronic nose

There are several electronic nose systems, including different types of and gas sensors and systems combined with other techniques and using different data processing methods for the detection and characterization of food spoilage. Some successful experiments performed by different authors have been described in the bibliography. As a general rule, there are some chemical compounds that are responsible for defects and off-flavors in food and beverages. These compounds are known by consumers as the first alarm signal linked to spoilage. It is very important to optimize the measurement system to detect these compounds. Table 4 summarizes the sensors and sensory systems applications for detection and characterization of spoilage in the food industry.

Table 4. A summarized overview on the application of electronic nose to food spoilage detection

There are different prototypes designed by some research groups with different features that are appropriate for different applications. In the bibliography, Laboratory equipment as well as portable instruments are designed for food spoilage detection. The following reference (Jose Pedro Santos & Lozano, (2015) shows a hand-held wireless portable electronic nose applied to the real-time detection of two common aromatic defects in beer: acetaldehyde and ethyl acetate. An image of the electronic nose is illustrated in Fig. 4. These aromatic defects in beer have been measured at level between the organoleptic threshold and five times this quantity (25 ppm for acetaldehyde and 21 ppm for ethyl acetate). PCA were applied to these responses to see the data distribution among classes. Although there is some confusion between some classes corresponding to different concentrations, non-defect beer samples were separated from the other samples. In a qualitative classification among beer without defects (blank) and beer with one of the defects (ethyl acetate or acetaldehyde) regardless the concentration, the measurements were grouped into three classes: blank, ethyl acetate and acetaldehyde. The PCA score plot for the whole measurement set is shown in Fig. 4. Some partial overlapping is observed among the classes, although the ANN analysis gave a 94 % success rate in validation. Few samples are wrongly classified among the three clases. Authors explain that these results could be improved using other types of classifiers and improving the measurement system in order to a better control of the operation temperatures and flows and reducing the measurement noise.

Fig. 4. Portable e-nose system for the defect discrimination in beer and PCA score plot of measurements of beer defects.

It is usually recognized that electronic noses have not achieved the market penetration that was expected in the mid-90s. The prototype presented in Lozano et al., (2015) could be a first step for implementation in the wine industry. It is installed in a wine cellar for on-line monitoring of wine evolution during 9 months. The system has a novel sampling method that extracts the aroma directly from the tanks where wine is stored; and it automatically carries the volatile compounds to the sensor cell with tin oxide multisensor. Linear techniques as principal component analysis (PCA) and nonlinear ones as Artificial Neural Arrays (ANN) are used for pattern recognition, and Partial Least Squares (PLS) is used for predicting GC-MS analysis. Results showed that system can detect the evolution of two different wines along 9 months stored in the monitored tanks. The evolution of the wine is confirmed with chemical and sensory analysis. Moreover, GC-MS analysis was performed to the wine of the tanks. In the whole, 19 odorants were analysed. The chemical compounds analysed were acids (butyric acid, decanoic acid, hexanoic acid, isobutyric acid, isovaleric acid, and octanoic acid), alcohols (1-hexanol and 2-phenilethanol), esters (hexyl acetate, ethyl butyrate, ethyl decanoate, ethyl hexanoate, ethyl isovalerate, ethyl lactate, ethyl octanoate, isoamyl acetate, isobutyl acetate, diethyl succinate and phenyl ethyl acetate) and phenols (4-vinyl-guaiacol). The aforementioned 19 compounds analysed in GC-MS profiles were used as predictor variables. Then, a model was created in order to predict these responses from sensor measurements. In this way, the concentration of chemical compounds in wine determined by GC–MS were correlated with electronic nose response PLS regression analysis. Correlation coefficients near to 1 are obtained in the prediction of several volatile organic compounds (VOCs), i.e. ethyl butyrate, isobutyric acid, isobutyl acetate, hexyl acetate and ethyl octanoate. This system could be trained for monitoring wine preservation and evolution in tanks and therefore detecting off-odours of wine and warning the wine expert to correct it as soon as possible, preventing the wine spoilage and improving its final quality.

Based on the body of scientific literature, numerous considerable works on spoilage detection using electronic nose has been conducted on meat and fish products. Chemical reaction between volatile compounds involved in spoiled meat with gas sensors has imperative results and this measuring principle is the basis of the spoilage detection in meat products (Wojnowski, Majchrzak, Dymerski, Gębicki, Namieśnik, 2017).

Meat spoilage as a tremendously complex phenomenon is affected by many parameters such as storage conditions, packaging type and materials used, temperature and so on. Innovative instrumental approaches such as electronic nose have shown promising results to be used as a potential candidate for inspection of meat and its spoilage. A list of the most applications on such products is summarized in Table 4. For instance, two cases of the more recent applications are discussed here.

Estelles-Lopez et al., (2017) conducted a research to develop the appropriate models for predicting minced beef spoilage. For this aim, a commercial electronic nose ((LibraNose, Technobiochip, Napoli, Italy) comprising eight quartz crystal microbalance (QMB) sensors coated with different poly-pyrrole derivatives was used. Based on the planned experimental protocol, few grams of the meat was inserted in a container and left for a moment to collect the adequate headspace as called static sampling. Then the volatile compounds present in the headspace were passed over the sensors and the responses registered and saved. The authors have also used four analytical instruments to fuse the data with electronic nose. They were Gas Chromatography-Mass Spectrometry (GC–MS), High Performance Liquid Chromatography (HPLC), multispectral imaging (MSI), and Fourier Transformed Infrared Spectroscopy (FT-IR). For data fusion and analyses, numerous techniques as given in Table 4, were used and modeled. In final, they developed an on line platform to identify different types on microorganisms present in spoiled meat. Electronic nose showed satisfactory contribution for this aim.

Lipid oxidation as a spoilage indicator was studied by Gu, Sun, Tu, & Pan (2017) who aimed their research at evaluating the odor of Chinese-style sausage as a high-fat meat product during processing and storage using electronic nose. During lipid oxidation, some chemical changes occur in the sausage where some volatile compounds involved in the sample headspace are found such as certain aldehydes, ketones and alcohols. Monitoring these compounds could help in lipid oxidation prediction and spoilage detection consequently. They used a portable electronic nose (PEN 3, Win Muster Air-sense Analytics Inc., Germany) consisting of ten metal oxide sensors which were extremely sensitive to a lot of volatile compounds as nitrogen oxides, ammonia and aromatic compounds, Benzene, hydrogen, alkenes and aromatic compounds, Propane, methane, sulphur compounds, alcohols, sulphur organic compounds, alkane). The sensors were non selective and partial sensitive to aromatic compounds. The time of the measurement was 60 s and 110 s for odor injection and purging periods, respectively. Win Muster software was exploited to transform the information to digital signals. As mentioned in Table 4, many data processing algorithms were used to classify the samples. The authors concluded that the results show great potential use of electronic nose in judging the lipid oxidation of the high-fat meat products.

6.2. Electronic tongue

Electronic tongues have been successfully used for qualitative and quantitative determinations of the spoilage of many foods of interest (Haddi, El Barbri, Tahri, Bougrini, El Bari, Llobet, & B. Bouchikhi, 2015; Śliwinska, Wisniewska, Dymerski, Namiesnik, & Wardencki, 2014). As it is well-known, the foods spoilage is a complex biochemical and microbiologic process which involves atmospheric oxygen, the activity of some specific enzymes and microorganisms, etc. (Sahu & Bala, 2017; de Blackburn, 2006).

Thus, for the quantitative case, a number of toxic compounds formed during the spoilage process has been determined, especially biogenic amines, which result from amino acids decarboxylation. The amino acids involved in these processes are free amino acids present in foods, but also the ones which originate in proteins hydrolysis (Naila, Steve Flint, Fletcher, Bremer, & Meerdink, 2010; Karovičová & Kohajdová, 2005). Other quantitatively determined compounds are inosine 5'-monophosphate, inosine and xanthine and hypoxanthine, which originate from adenosine triphosphate (ATP) degradation (Vilas, Alonso, Herrera, García-Blanco, & García, 2017) (Fig. 5).

Fig. 5. Decomposition of ATP in the muscles (Nelson & Cox, 2017)

Where, ATP: Adenosine triphosphate; ADP: Adenosine diphosphate; AMP: Adenosine monophosphate, IMP: Inosine monophosphate; Ino: Inosine; Hx: Hypoxanthine; Xa: Xanthine; PI: phosphate ion.

Quantitative determination is generally acquired from statistic models obtained according to the data recorded with the sensor system of the electronic tongue, which allow quantitative estimations of certain physical-chemical or sensorial parameters (e.g. partial least squares–discriminant analysis (PLS-DA) or PLS2 regression models) (Haddi, El Barbri, Tahri, Bougrini, El Bari, Llobet, & B. Bouchikhi, 2015; Rodríguez-Méndez, Gay, Apetrei, & de Saja, 2009).

More types of foods have been analyzed and the systems used and the main results obtained are presented in the following paragraphs.

The concept of meat freshness is quite complex, including various physicochemical, biochemical and microbiologic characteristics related to two different processes – the former, aging, determined by the storage period required by meat in order to acquire the proper taste for consumption, and the latter, also in relation to the period of storage, which leads to meat spoilage due to bacterial growth and autolysis (Iulietto, Sechi, Borgogni & Cenci-Goga, 2015; Dave & Ghaly, 2011).

Gil et al. (2011) presented a case study of the use of potentiometric electronic tongue in the study of the spoilage process of a whole piece of pork loin stored under refrigeration (Gil, Barat, Baigts, Martínez-Máñez, Soto, Garcia-Breijo, Aristoy, Toldrá, Llobet, 2011). The sensors array used in the developing of the electronic tongue consisted of six electrodes made of Au, Ag, Cu, Pb, Zn and C, and a reference electrode. By using more methods in the multivariate data analysis (PCA and artificial neural arrays - multilayer perceptron and fuzzy ARTMAP), the authors proved that the potentiometric electronic tongue is capable to determine the storage time, which is in relation to the degradation of the pork loin.

For data validation and for establishing the correlation with the results of classical analytical methods, a number of physical-chemical, microbial and biochemical parameters were analysed. These analyses consisted in pH determination, microbial count, concentrations of inosine 5’-monophosphate, inosine and hypoxanthine. Using the PLS regression method, a very good correlation was found between pH and the data obtained from potentiometric sensors, as well as between K-index (simultaneously measures the variation in the adenosine triphosphate) and the data obtained with the electronic tongue. The conclusion of the study was that the potentiometric electronic tongues are very useful in the qualitative or semiquantitative evaluation of freshness in meat samples and they can have numerous applications in food industry in quality control of pork meat.

Another study, presented by Kaneki et al., (2004) described the use of a potentiometric electronic tongue based on simple solid electrodes (i.e. Pt, CuS and Ag_2S) which are able to detect certain compounds responsible for the initial stage of meat putrefaction. This system was successfully used in the study of pork meat freshness (Kaneki, Miura, Shimada, Tanaka, Ito, Hotori, Akasaka, Ohkubo, & Asano, 2004).

Microbiological contamination in dry-cured ham can occur at various stages of the maturation process, and the development of a large number of microorganisms involved in spoilage may lead to the alteration of the end product (Dikeman & Devine, 2014). These processes lead to some unpleasant and non-common odours, which are detected by an expert taster, who follows a procedure called “cala”, by which he classifies hams as good and altered hams (Paarup, Nieto, Peláez, & Reguera, 1999). Girón et al. (2015) produced a potentiometric electronic tongue based on an array of sensors which contains three types of sensors, silver, nickel and copper electrodes. This electronic tongue was used for the classification of altered and unaltered hams before the classification of hams by an expert tester. The results of the analyses showed that, in the case of altered hams, the Ag potentials have the lowest values and the Cu potentials, the highest values. Starting from these experimentally observed differences, a model of classification of hams was built, but further studies are required for the system validation for industrial practice (Girón, Gil-Sánchez, García-Breijo, Pagána, Barat, & Grau, 2015).

Gil-Sánchez et al. (2011) presented the use of a combined multisensor system for the analysis of the spoilage of wine when it is in contact with air (Gil-Sánchez, Soto, Martínez-Máñez, Garcia-Breijo, Ibáñez, & Llobet, 2011). The system consists of a potentiometric electronic tongue and a humid electronic nose. The potentiometric electronic tongue was used for the evolution in time of the wine samples in the presence of air. The classical method of analysis used for monitoring the wine spoilage was the determination of the titratable (total) acidity. The electronic tongue used in this study is based on potentiometry. Potentiometric sensors were built using thick-film serigraphic techniques. The paste used for making the sensors was commercial, generally used for the production of thick-film resistances and conductors for hybrid electronic circuits. Each paste contains an active element, which are, in this case, Ag, Au, Cu, Ru, AgCl, and C. These sensitive materials are often used in the production of non-specific electrodes. Some materials were used in duplicate for the production of sensors, by modifying, for instance, the thickness of the sensitive layer, 9 potentiometric sensors being included in the multisensor system. Fig. 6 presents the distribution of the sensors on the multisensor pad and the tracks and pads for connecting to measuring equipment.

Fig. 6. The sensor array used for the potentiometric electronic tongue (Gil-Sánchez, Soto, Martínez-Máñez, Garcia-Breijo, Ibáñez, & Llobet, 2011).

Ruiz-Rico et al. (2013) studied the shelf-life assessment of fresh cod in cold storage using a voltammetric electronic tongue (Ruiz-Rico, Fuentes, Masot, Alcañiz, Fernández-Segovia, & Barat, 2013). The electronic tongue system is based on an array of sensors, specialised software installed on a PC and electronic equipment. Measurements relied on pulse voltammetry, the voltage pulses being applied to sensors by the electronic equipment, and the generated currents being measured afterwards. For each sensor, 1,000 values were recorded, which correspond to the time evolution of the current generated in the system after applying the voltage pulse. The sensor system is made up of 8 metallic electrodes, separated into two subsystems, one made up of 4 electrodes based on noble metals (iridium, rhodium, platinum and gold) and the other, of 4 metallic electrodes based on non-noble metals (silver, cobalt, copper and nickel). Therefore, a total of 8,000 values are registered by the electronic tongue for each sample under study. For the validation of the analytical system, data resulted from physical-chemical and microbial analyses were used. For all samples analysed, the limits of the main parameters related to fish freshness, such as total volatile basic nitrogen, mesophilic and Enterobacteriaceae, were exceeded on the fourth day of storage, which means that fish has a shelf-life less than four days. The results of physical-chemical and microbial analyses showed an obvious loss of freshness from day 0 to day 4. Also, the voltammetric tongue results showed a clear difference between the freshness of fish on days 0 and 1 of storage and that in the following days. The regression patterns based on partial least squares for Total Volatile Basic Nitrogen (TVB-N) and mesophilic counts proved that the predicted values concord with the experimental results, which confirms the usefulness of voltammetric electronic tongue for assessing cod spoilage.

Haddi et al. (2015) implemented a voltammetric electronic tongue based on an array of seven working electrodes, a platinum counter electrode and an Ag/AgCl reference electrode (Haddi, El Barbri, Tahri, Bougrini, El Bari,. Llobet, & Bouchikhi, 2015). The working electrodes were made of platinum, gold, silver, glassy carbon, palladium, copper and nickel. They were assembled in the form of an array of sensors in a stainless steel tube. The wires of each electrode were connected to a portable potentiostat through a relay box. The responses of the array of sensors in the presence of the samples to be analyzed were recorded by cyclic voltammetry.

With the help of this system, it was objectively and rapidly assessed whether there were any significant differences between meat types (beef, goat and mutton), and between the same piece of meat in various spoilage states. The electronic tongue system, made up of 7 voltammetric sensors, was used for the detection of the specific electroactive compounds for each of the three types of meat. Data analysis was pursued using discrimination and classification methods, Principal Component Analysis (PCA) and Support Vector Machines (SVMs). The results obtained proved that the system is capable of distinguishing meats based on their biologic origin. Also, for each type of meat, the number of days passed in cold storage can be determined.

A number of studies reported in the literature relied on the use of voltammetric electronic tongues based on sensors modified with electroactive substances (phthalocyanines or conducting polymers), both regular and screen-printed electrodes.

A study reported the use of a novel array of voltammetric sensors used for the detection of the principal biogenic amines resulted from the spoilage process of Tench fish (Rodríguez-Méndez, Gay, Apetrei, & de Saja, 2009). The array of sensors consisted of screen-printed electrodes modified with phthalocyanines. The method conveyed in this study entailed the global detection of the chemical products resulted from the process of spoilage of fish, including the biogenic amines.

The sensors proved very good sensitivity to biogenic amines present in the solution to be analysed (ammonia, dimethylamine, trimethylamine, cadaverine and histamine). It was observed that biogenic amines have great influence on the chemical behaviour of the sensors, due to the fact that some biogenic amines are electroactive and that all biogenic amines have basic and nucleophilic properties. The developed sensors are very sensitive, reproducible, and present good stability on long term.

The array of sensors was used for the determination of the freshness degree of fish kept at $4^{o}C$ in the refrigerator for 12 days. The responses recorded by cyclic voltammetry were successfully used for assessing freshness and for determining the post-mortem period. The voltammetric signals displayed increasing intensity with the increasing of storage time.

The ability of discriminating fish samples based on their freshness was demonstrated by principal component analysis. The ability of classifying the fish samples according to their freshness, as well as the prediction of freshness of some samples was calculated by partial least squares-discriminant Analysis (PLS-DA). The results proved that voltammetric electronic tongue is able for determining the degree of fish freshness by monitoring the production of spoilage products. In addition, this method is able to determine the stage of the spoilage process, which comprises 4 states.

Another paper reported the use of a voltammetric electronic tongue for monitoring the freshness of Pontic shad fish samples (Apetrei, Rodriguez-Mendez, Apetrei, de Saja, 2013). The samples were Pontic shad (*Alosa Pontica*), a species living in the north-western part of the Black Sea. Pontic shad migrates in the Danube River for spawning. The array of sensors was made up of a series of sensors based on carbon screen printed electrodes modified with polypyrrole doped with different doping agents. The electrochemical signals are complex and present redox processes related to the electrochemical activity of the amines, and redox peaks associated to the electrochemical activity of the electroactive material. The viability of the voltammetric electronic tongue was tested for fish freshness monitoring. From the analysis of the signals registered by sensors, a growth of the signal currents associated to biogenic amines was observed in the analysed samples with the increase of the storage time.

The voltammetric signals obtained with the help of the array of sensors were used to discriminate and evaluate the state of fish freshness. Principal component analysis confirmed the ability of the voltammetric electronic tongue to monitor the fish freshness. The partial least squares–discriminant analysis (PLS-DA) model showed that this electronic tongue is able to determine the post-mortem time elapsed, being highly useful in practice.

Another study was dedicated to the detection and quantification of putrescine and ammonia resulted from the spoilage of dehydrated beef, as well as to monitoring beef freshness under refrigeration conditions (Apetrei & Apetrei, 2016).

The array of sensors used in this study was a hybrid one, made up of screen-printed electrodes modified with bisphthalocyanines and polypyrrole doped with different doping agents. The electrochemical responses of the sensors were analysed for two compounds of interest in beef spoilage, namely ammonia and putrescine.

The electrochemical signals are related to the redox properties of the substances used for modifying the electrodes, which are greatly influenced by the compounds present in the solution to be analysed. At first, it was determined that the sensors were capable to detect amine compounds in beef extract powder with good sensitivity to the levels of concentration at which the respective compounds are found in the initial spoilage stages. The sensor array made up of sensors with the best performance was used for beef freshness monitoring. The methods conveyed for the analysis of experimental data, PCA and PLS-DA, demonstrated that the electronic tongue system is able to discriminate and classify samples according to their refrigeration time.

6.3. Biosensors

Various types of biosensors have been used for the specific determination of some analytes directly related to the spoilage process (Rotariu, Lagarde, Jaffrezic-Renault, Bala, 2016). The most important are biogenic amines and the compounds resulted from the decomposition of nucleic acids, as is the case of xanthine, hypoxanthine and other metabolites (Ghaly, Dave, Budge, & Brooks, 2010). The following section reviews the most relevant results reported in the specialized literature, according to the type of food under analysis.

Meat and meat products are the foods which have been most often studied using biosensors for spoilage detection. The reason is that the products which result from the spoilage process are toxic and may lead to intoxication, allergies, and even death when ingested in large quantities (Stadler & Lineback, 2008). In order to be fitted with consumption, beef must be subject to a refrigeration process for a few days, a process that is named “aging” (Perry, 2012). During its refrigeration, besides aging, the unwanted process of bacterial spoilage may also occur. Therefore, in order to obtain aged meat with optimal organoleptic properties, the simultaneous monitoring of aging and bacterial spoilage is necessary. For highlighting the bacterial spoilage process, it is necessary to monitor the concentration of putrescine and cadaverine, two biogenic amines, which can be considered markers of the spoilage process (Perry, 2012; Dashdorj, Tripathi, Cho, Kim, & Hwang, 2016; Apetrei & Apetrei, 2016).

Yano et al. (1996) developed a direct sensing method in order to determine the quality of beef (Yano, Yokoyama, Tamiya, & Karube, 1996). The biosensor was made of an Ag/AgCl electrode and a platinum electrode onto which two enzymes were immobilized, namely putrescine oxidase or xanthine oxidase. The detection method used was potential-step chronoamperometry, the potential was stepped in the range from 0.3 V to 0.6 V. The experimental conditions, such as pH and selectivity, were adequate and the target compounds could be analysed on the beef surface. Sensitivity, selectivity and stability of the biosensor were very good in detecting putrescine, cadaverine and hypoxanthine. The experimental results demonstrated that the method of direct determination with this biosensor could be successfully used in the non-destructive assessment of beef quality.

Kress-Rogers et al. (1993) developed a prototype biosensor (in the form of an array of biosensors) in view of ultra-fast assessment of pork meat freshness (Kress-Rogers, D'Costa, Sollars, Gibbs, & Turner, 1993). The biosensors array allows the measurement of glucose concentration at 2 and 4 mm depth under the meat surface. The array of biosensors was used to monitor the spoilage process of refrigerated pork carrying a slaughterhouse flora. The assessment of meat freshness was pursued based on the three-dimensional profile of glucose near the meat surface. This method can be applied as a marker for the fast evaluation of complex foods, in what concerns the microbial and oxidative spoilage, maturation and the fermentation process.

Fish and fish products spoilage is also of great interest in food industry, as fish is susceptible to spoilage due to storage conditions. Fish spoilage under refrigeration conditions is attributed to the metabolic degradation of trimethylamine N-oxide (TMAO) to trimethylamine (TMA) by psychrophilic bacteria. TMA accumulation in tissues is responsible for the specific smell of degrading fish, while the TMA concentration depends on the stage of the spoilage process (Barrett & Kwan, 1985; Muzaddadi, Devatkal, & Oberoi, 2016).

Gamati et al. (1991) developed a biosensor for monitoring the trimethylamine concentration, based on the difference in the oxygen uptake response of two microbial electrodes (Gamati, Luong & Mulchandani, 1991). One of the electrodes was produced using *Pseudomonas aminovorans* grown on TMA. It was particularly sensitive to TMA, trimethylamine N-oxide, dimethylamine and monomethylamine. The other electrode was produced using *Pseudomonas aminovorans* grown on TMAO, and it was sensitive to TMA, trimethylamine N-oxide, dimethylamine and monomethylamine. The response of biosensor is linear with TMA concentration and the limit of detection is in pM domain. Besides, the relative standard deviation of the biosensor response is low, the response is stable and reproducible. The results obtained with the help of this sensor were validated by HPLC. The biosensor is useful for TMA determination in fish tissue extracts.

Another biosensor for the TMA detection was developed by Bourigua et al. (2011). It was based on polypyrrole–flavin-containing monooxygenase (FMO3) and ferrocene. The detection techniques employed were amperometry and impedance spectroscopy. The biosensor presents high selectivity and sensitivity to TMA in real samples. The validation of the biosensor was carried out using GC/SM and the real sample was fish extract after deterioration during storage (Bourigua, El Ichi, Korri-Youssoufi, Maaref, Dzyadevych, & Jaffrezic Renault, 2011).

In food industry, fish processing is difficult because of its low commercial life and high variability of the raw material, starting from the biologic species and ending with fishing and storage. An important biomarker of fish spoilage is the level of xanthine:

above certain values, it is certain that the spoilage process has begun (Costa & Miertus, 1993).

Fish freshness is the most important feature of this raw material for its processing in food industry under safe, qualitative conditions. After the fish's death, breathing and biosynthesis of adenosine triphosphate (ATP) nucleotide cease. Consequently, the ATP in the muscles is degraded, according to the scheme presented in Fig. 5.

Among the spoilage products, IMP is the main factor which contributes to fish freshness flavour, and the spoilage product hypoxanthine is what gives the fish meat its specific bitter taste. Dervisevic et al. (2015) produced a biosensor based on a host matrix nanocomposite for immobilization of xanthine oxidase made up of MWCNT incorporate in poly (GMA-co-VFc) copolymer film (Dervisevic, Custiuc, Çevik, & Senel, 2015). The inclusion of MWCNT in the polymer matrix resulted in a substantial growth of the sensitivity of the biosensor. The fabrication process of the sensitive layer of the biosensor was characterized by scanning electron microscopy. The electrochemical behaviour of the biosensor was studied by cyclic voltammetry and electrochemical impedance spectroscopy. The biosensor presents maximum response to xanthine at pH 7.0 and 45°C, when +0.35 V is applied. The biosensor reaches 95% of steady-state current in approximately 4 seconds. The limit of detection of the biosensor to xanthine detection is of 0.12 μM, positive results being obtained for the measurement of xanthine concentration in fish meat. The response of the biosensor is stable and the interferences are very low.

Dervisevic et al. (2015) studied the detection of xanthine molecules, which is an indicator of meat spoilage (Dervisevic, Custiuc, Çevik, Durmus, Senel, Durmus, 2015). Xanthine is formed as a result of the decomposition of guanine. To this end, they developed a novel biosensor by embedding reduced expanded graphene oxide sheets decorated with iron oxide (Fe_3O_4) nanoparticles into poly (glycidyl methacrylate-covinylferrocene) phase, and by covalent immobilization of xanthine oxidase onto the surface of P(GMA-co-VFc)/REGO-Fe_3O_4 nanocomposite film. The experimental conditions were studied and optimized for the high sensitivity detection of xanthine (response time, linear range, operation and storage stability, pH and temperature) a limit of detection of 0.17 μM being obtained. The xanthine biosensor was used for the analysis of xanthine content in fish real samples after 5, 8, 10, 13, 15, and 20 days of storage. The novel biosensor proved that it could be successfully employed in the analysis of real samples and also that it could be successfully used as a reliable fish freshness controlling technique.

Apetrei et al. (2015) developed a biocomposite screen-printed biosensor based on immobilization of tyrosinase onto the carboxyl functionalised carbon nanotube for assaying tyramine in fish products (Apetrei & Apetrei, 2015). Tyramine is a biogenic amine which is especially found in fermented food products, but also in smoked, salted or soused fish (Luten, 2006). This compound can be used as a biomarker for spoilage monitoring. The detection principle employed was the amperometric one, by applying the optimum potential for the electrochemical reduction of the o-quinone formed in the enzymatic process at the surface of the sensitive layer of the biosensor. The biosensor presented very good analytical performance in what tyramine detection is concerned. These results are related to the presence of carboxyl functionalized carbon nanotube in the sensitive layer which facilitates the transfer of the electrodes involved in the electrochemical process.

Histamine is a biogenic amine of low molecular weight, with biologic activity. Histamine intoxication is also known as “scombroid fish poisoning”. Histamine concentration is used as an indicator of fish spoilage (Luten, 2006; Feng, Teuber, & Gershwin, 2016).

Histamine is accumulated in seafood after the beginning of bacterial spoilage and causes histamine poisoning even though the fish may not be altered in what the visual aspect and smell is concerned (Luten, 2006; Feng, Teuber, & Gershwin, 2016).

Keow et al. (2007) developed a biosensor based on diaminoxidase for the detection of histamine in tiger prawn (*Penaeus monodon*) (Keow, Bakar, Salleh, Heng, Wagiran, & Bean, 2007). The response time of the biosensor is below 1 minute under optimal pH conditions of 7.4. The limit of detection is in the sub-ppm domain (under 50 ppm, the level established by FDA USA), which recommends it for practical usage.

For the validation of the biosensor on real samples, the variation of histamine concentration was studied on tiger prawn samples after a 5-hour exposure at 30 ± 2°C temperature. The results obtained were comparable to the results determined by HPLC. There is good linear correlation between the two methods, with the determination coefficient higher than 0.95. The biosensor is reusable and may be used for the determination and quantification of histamine without further sample processing, being appropriate for the analysis of histamine in tiger prawn and also for spoilage monitoring.

Bóka et al. (2012) developed a novel amperometric biosensor based on putrescine oxidase for the selective detection and quantification of putrescine, a characteristic which may function as an indicator of microbial spoilage (Bóka, Adányi, Szamos, Virág, & Kiss, 2012). Putrescine oxidase was isolated from Kocuria rosea

(*Micrococcus rubens*). The purified enzyme was immobilized onto the surface of a graphite electrode in a hydrogel containing horseradish peroxidase, as a mediator of electron transfer and poly (ethylene glycol) (400) diglycidyl ether as a reticular agent.

This biosensor was used in an amperometric electrochemical cell in flow together with the reference electrode Ag/AgCl (0.1 M KCl) and a platinum wire as an auxiliary electrode. Under optimal conditions of pH, flow rate and applied potential, a vast linearity domain was obtained between the response of the biosensor and the putrescine concentration, with a detection limit appropriate for applications in foods analysis. The validation of the biosensor was pursued by analysing beer samples and comparing the results obtained with the results of the reference method HPLC.

The formation of volatile compounds, such as acetaldehyde and ethylene in plants and fruits is related to the state of their metabolism. For example, the synthesis speed of ethylene in apples increases with the time spent after harvest, while the acetaldehyde production is related to the anaerobic metabolism which grows in fruits after harvesting. The quantity of ethylene and acetaldehyde is related to the metabolic state and to the quality of fruit (Chen, Zhang, Hao, Chen, & Cheng, 2015; Maffei, 2010).

Weber et al. (2009) developed and implemented a hybrid dual-channel catalytic-biological sensor system, able to quantify the two volatile substances in situ (Weber, Luzi, Karlsson, & Fussenegger, 2009). This biosensor is based on a mammalian cell line engineered for constitutive expression of an *Aspergillus nidulans*, which triggers quantitative reporter gene expression in the presence of acetaldehyde. Ethylene oxidized to acetaldehyde through Wacker process can be quantified with the same biosensor. The quantification of metabolites allowed the accurate assessment of the quality of fruits, the fresh apples being clearly differentiated from the old and rotten apples.

By placing in relation the catalytic processes and the detection technology of the biosensors, it was possible to determine the metabolic state of food. Consequently, this could be used in the assessment of foods which suffer biochemical transformations, as well as in control processes for detecting and preventing food spoilage (Zhang & Keasling, 2011).

Fumarate is a very important intermediary in Krebs cycle (the tricarboxylic acid cycle) and has a key role in the fundamental processes which produce energy, as well as in the biosynthesis of amino acids and lipids (Nelson & Cox, 2017).

The accumulation of fumarate in organism above a certain limit, due to fumarate hydratase mutation, is one of the main causes of hereditary leiomyomatosis and renal cell cancer, being considered an oncometabolite (Yang, Soga, Pollard, & Adam, 2012)

On the other hand, fumarate is present in beverages, baking powders and candy, as a result of the microbial activity which leads to spoilage. Another source of contamination is represented by the impurities present in certain synthetic additives. Accordingly, fumarate is an important and relevant indicator of food quality, which can be used as a biomarker of food freshness (Hurrell, 2010; Kvasničk & Voldřich, 2000). Nevertheless, a cost-effective and fast analytical method for the detection and quantification of fumarate is desired. Si et al. (2015) produced an electrochemical whole-cell biosensing system for the quantification of fumarate in foods (apple juice) (Si, Zhai, Liao, Gao, & Yong, 2015). A sensitive inwards electric output (electron flow from electrode into bacteria) is sensitive to fumarate in *Shewanella oneidensis*

MR-1. Therefore, the electrochemical fumarate biosensing system delivered symmetric current peak immediately upon fumarate addition in the sample. The peak area increases in direct ratio with fumarate concentration in vast concentration domain with a limit of detection of 0.83 μM. This biosensing system showed to be specific to fumarate, as the interferences are very low. The validation of this biosensing system was pursued by the successful quantification of fumarate in samples of apple juice. The advantages of this biosensing system are: simplicity, low cost, limited time required for analysis and its robustness in fumarate quantification.

7. Challenges and future trends

Commercial electronic noses are designed for general-purpose use and besides selectivity and sensitivity of the sensors in the array; they do not match the needs for a particular application. It is necessary to design an array of sensors with optimized conditions for each application in order to increase the performance for food spoilage detection.

So far, electronic noses as sensory detectors of food spoilage have been widely used in the laboratory of different research groups. It is also clear that the utility of using electronic noses in an industrial or consumer context is high; the chemical compounds responsible of food spoilage are usually detected by electronic noses at lower concentrations than human nose, so efforts must be made by researchers to transfer this technology to them. For the food industry, faster and more efficient sampling techniques suitable for successive batches need to be developed in the future. On the sensors side, major focus must be given to the design and development of high sensitivity and selectivity drift free sensors that can be used reliably over long temporal horizons. Novel and promising materials like grapheme or silicene should be used for developing ambient temperature sensors and novel nanostructures like nanowires and nanofibers and other nanostructures could enhance the response and reduce the time of response and consumption. Data processing methods not only must be made for classification and prediction problems, but also for sensor replacements, compensating drift, stability and reliability of the sensors. It will allow a long-term use that will be a convincing factor for industry when considering the uptake of such a device. On the consumers' side, there are now available in the market miniature gas sensors with low size (less than 2x3mm) and consumption (less than 7mw) that will allow to develop very small electronic noses systems for consumers in order to advise them if food they are going to consume is of adequate quality. Moreover, mobile phones have been increasing the number of sensors they contain; from one or two sensors in 2003 to more than 16 sensors in 2016. Predictions of the sensor market say that in the near future, smart phones will include gas sensors, and with it hundreds of apps for detecting compounds, odours and aromas related with food spoilage.

The future of the electronic tongue systems and the biosensors are closely related because improving the sensitivity and selectivity of the sensor array remain challenging tasks.

It seems that the trends will include the development of novel sensitive nanomaterials and the nanotechnologies for the preparation of the sensors as well as the use of hybrid array of sensors. The inclusion of the biosensors in the sensors arrays could be a factor that will improve the multi-analyte detection, the quantitative analyses becoming more significant and more precise. This is necessary in the detection of food spoilage in early stage, when it starts and not when the food product is spoiled and not suitable for human consumption. Other important research directions will include the miniaturization of the systems able to measure in-flow in real-time analysis, coupled with wireless signal transmitters, expert systems for data analysis and feed-back action. These multisensory systems will assure a rapid and accurate control of food spoilage, important for the producers and for the consumers.

8. Conclusion

In this paper, we have outlined the major contributions of electronic nose, biosensors, and electronic tongue technologies related with food spoilage. There is a great interest for handheld instruments that respond to simple questions related with food spoilage posed by producers, food inspectors and general consumers. A great number of references can be found with different applications of food spoilage detection, including wine spoilage monitoring and detection of off-flavors, beer defects, microbial contamination in tomatoes, egg quality detection, grain spoilage, enterobacteriaceae in vegetable soups, spoilage of bakery products, contamination of soft drinks, apple defects, milk spoilage and olive oil defects, fish freshness monitoring, meats freshness, seafood spoilage, apple juice spoilage, among others. Electronic noses and gas sensors have shown in the last years an important enhancement in the time response and time life as well as a decrease in the size and consumption. The latest works about the electronic tongue systems for detection of food spoilage demonstrates one significant progress in the terms of high sensitive sensor arrays based on different methods of detection and the use of improved data analyses. The biosensors were used in the detection of target analytes related to food spoilage with high sensitivity, improved selectivity, and low detection limit. These superior analytical characteristics are principally related to the use of nanomaterials and nanotechnologies in the development of biosensors.

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Captions of Figures

Fig. 1. Block diagram of an electronic nose system.

Fig. 2. General scheme of an electronic tongue system

Fig. 3. Biosensor detection scheme

Fig. 4. Portable electronic nose system for the defect discrimination in beer

Fig. 5. Decomposition of ATP in the muscles (Nelson & Cox, 2017)

Fig. 6. The sensor array used for the potentiometric electronic tongue (Gil-Sánchez, Soto, Martínez-Máñez, Garcia-Breijo, Ibáñez, & Llobet, 2011).

Table 3. The main sensorial properties and their relative compounds.

Taste	Compounds
Sweetness	Glucose, Sucrose, Fructose, D-Amino acids, Sweeteners (natural or artificial)
Sourness	Acetic acid, Citric acid, Tartaric acid, Lactic acid, Phosphoric acid
Saltiness	NaCl, KCl
Bitterness	Quinine, Caffeine, $MgCl_2$, Humulone, L-Amino acids
Umami	Monosodium glutamate, Glutamic acid, Disodium inositate, Disodium guanilate
Astringency	Tannins
Pungency	Capsaicin, piperine

Table 4. A summarized overview on the application of electronic nose to food spoilage detection

Application	Sensor technology	Number of sensors	Additional Techniques	Data processing algorithm	References
Wine monitoring	MOX	16	GC-MS	PCA, PNN	(J. Lozano et al., 2015)
Acetic Acid in wine	MOX(PEN3)	10	-	PCA, MLP	(Macías et al., 2012)
	MOX	4	-	PCA, RBFNN	(Lozano et al., 2011)
Wine spoilage, off-flavors	Humid e-nose	5	E-tongue	PCA, K-means	(Gil-Sanchez et al., 2011)
	MOX(FOX 3000)	12	-	PCA, CLA	(Cabañes, Sahgal, Bragulat, & Magan, 2009)
	MOX (FOX4000)	18	-	PCA, DFA	(Ragazzo-Sanchez, Chalier, Chevalier-Lucia, Calderon-Santoyo, & Ghommidh, 2009)
	MOX (FOX 3000)	12	MS	PLS	(Berna, Trowell, Cynkar, & Cozzolino, 2008)
Red wine spoilage induced by Brettanomyces yeast	MS-enose	-	GC-MS	PCA, SLDA, PLS	(Cynkar, Cozzolino, Dambergs, Janik, & Gishen, 2007)
Threshold detection wine compounds	MOX	16	Sensory panel	PCA, NN	(José Pedro Santos et al., 2010)
Beer defects	MOX	4	-	PCA, NN	(Jose Pedro Santos &

					Lozano, 2015)
Fried potato	MOX (Figaro)	8	Biochemical assays	Fuzzy logic, PCA, ANOVA	(Chatterjee, Bhattacharjee, & Bhattacharyya, 2014)
Microbial contamination in tomatoes	MOX (EOS835 – Sacmi)	6	DHS-GC-MS	PCA, Pearson correlation	(Concina et al., 2009)
Egg quality	MOX	8	-	PCA, LDA, BPNN, GANN, QPSR	(Yongwei, Wang, Zhou, & Lu, 2009)
Grain spoilage (review)	MOX	17	-	DFA, Neural Networks	(N. Magan & Evans, 2000)
Spoiled Rapeseed	MOX (Agrinose)	8	HPLC, Colony Forming Units, Fourier Transform Infrared (FT-IR) Spectra	PCA	(Gancarz et al., 2017)
Enterobacteriaceae in vegetable soups	MOX (EOS507C)	4	GC-MS	PCA,LDA, Pearson correlation	(Emanuela Gobbi et al., 2015)
Spoilage of bakery products	MS-enose	-	HPLC	PLS	(Marín et al., 2007)
Contamination of soft drinks	MOX (EOS835)	6	PCR, HPLC	PCA, LDA, kNN, SVM	(Concina et al., 2010)
Alicyclobacillus spp. spoilage of fruit juices	MOX (EOS835)	6	DHS-GC-MS	PCA, Pearson correlation	(E. Gobbi et al., 2010)
Zygosaccharomyces spoilage in apple juice	MOX (PEN3)	10	Sensory panel	LDA, PLS	(Wang et al., 2016)
Apple defects	CP (Cyranose 320)	32	-	PCA, MANOVA, DA	(Pathange, Mallikarjunan, Marini, O'Keefe, & Vaughan, 2006)
	CP	32	Z-nose	PCA, PNN, Bayesian	(Li, Heinemann, & Sherry,

	(Cyranose 320)				2007)
Medicinal off-flavor in apple juice	MOX (PEN3)	10	GC-MS, Test panel	PCA, LDA, ANOVA	(Huang, Guo, Yuan, Luo, & Yue, 2015)
Spoilage of milk and fish	SAW	6	-	Fuzzy c-means, PCA, RBNN	(Verma & Yadava, 2015)
Milk spoilage (bacteria and yeasts)	CP (BH-114)	14	-	DFA, PCA, Dendrogram, NN	(Naresh Magan, Pavlou, & Chrysanthakis, 2001)
Olive oil defects	MOX (EOS)	6	GC-MS, Test panel	PCA, SIMCA	(Esposto et al., 2006)
	MOX (EOS507)	6	Test panel	LDA, MLR, NN	(Lerma-García et al., 2010)
Rancidity of oil	MOX (EOS507)	18	Rancidity analysis	PCA, HCPC	(Upadhyay, Sehwag, & Mishra, 2017)
Classification of Chicken meat freshness and bacterial population prediction	MOX	8	GC-MS	BPNN	Timsorn et al., 2016
Prediction of total volatile basic nitrogen (TVB-N) content in chicken meat	Colorimetric sensors array	-	Hyperspectral imaging system, Texture analysis	Data fusion techniques	Khulal et al., (2017)
Microbiological examination of beef fillets	QMB	8	Microbiological and sensory analyses	SVM, DFA	Papadopoulou et al., 2013
Identification of spoiled beef	CP	32	Microbiological analysis	ANNs	Panigrahi et al., 2006a
Determining the spoilage of vacuum packaged beef	MOSFET	10	Microbiological and sensory analyses	PLSR	Blixt & Borch, 1999
Spoilage classification of beef	MOX (M-	9	Microbiological analyses	LDA, QDA	Panigrahi et al., 2006b

	Module E-nose)				
Monitoring the spoilage of beef fillets under storage	QCM	8	Microbiological analyses	Fuzzy-Wavelet Network	Kodogiannis, 2017
Odor spoilage sensing of beef and fish	MOS	8	-	SVM, ANNs	ul Hasan et al., (2012)
Developing an automated ranking platform to predict minced beef spoilage	QMB (LibraNose)	8	HPLC, FT-IR, GC–MS and MSI	OLS-R, SL-R, PCR, PLS-R, SVM-R, RF-R and kNN-R	Estelles-Lopez et al., 2017
Spoilage detecting in hairtail fish and pork	MOX	8	Measuring total volatile basic nitrogen (TVBN)	PCA	Tian et al., 2012
Spoilage Classification of Red Meat	MOS	6	Microbiological analyses	PLS, SVM	El Barbri et al., 2008
Detection of Acetone and Ethanol in spoiled meat	MOS (TGS822)	1	Microbiological analysis	Statistical analysis	Benabdellah et al., 2017
Reduction of *Salmonella* and the spoilage bacteria on fresh chilled pork	MOS (PEN3)	10	Chemical analyses	One-way ANOVA	Wang et al., 2017
Study of lipid oxidation of Chinese-style sausage	MOS (PEN3)	10	Measuring acid value (AV) and peroxide value (POV)	PLSDA, FLDA, MLR, ANNs, SVM, HCA	Gu et al., 2017
Identification of pork meat samples spoiled by *R. aquatilis*	Heracles II	Columns: MXT-5 and MXT-17	PCR and microbiological analyses	ANOVA, Tukey's post-hoc test	Godziszewska et al., 2017
Spoilage detection of modified	MOSFET,	10	Microbiological and	PLSR, ANNs	Rajamaki et al., 2006

atmosphere packaged poultry meat	NST 3320 instrument		sensory analyses		
Evaluation of Spoilage of the blue crab (Crab (*Callinectes sapidus*) meat	CP (Cyranose)™	32	Microbiological and sensory analyses	Canonical discriminant analysis (CDA), stepwise discriminant analysis (SDA)	Sarnoski et al., 2008
Quality and spoilage identification in smoked salmon	MOX - FishNose system	6	GC-MS	Partial least-squares regression (PLSR)	Haugen et al., 2006

Table 1. Reports on spoilage microorganisms in selected food products as influenced by intrinsic and extrinsic factors

Food product	Extrinsic				Intrinsic			Spoilage organism(s)	Reference
	Temperature		Atmospheric conditions		pH		Preservative		
	Low	High	Aerobic	Anaerobic	Low	High			
Baked products		x	x		(x)			*Bacillus* spp. Moulds	Valerio et al., (2012); Vytrasova et al., 2002
Meat	x			x	x			Lactic acid bacteria, Enterobactericeae, *Clostridium*, *Shewanella*	Cavill et al., 2011; Doulgeracki et al., (2010); Hernandez-Macedo et al., 2012;
Meat	x		x		x			*Pseudomonas*, *Brochothrix thermosphacta*, *Photobacterium*,	Ercolini et al., 2006; Nychas et al., 2008; Pennachia et al., 2011
Meat		x	x		x			Enterobactericeae, *Pseudomonas*, *Acinetobacter*	Gill and Newton, 1979
Meat	x			x	x		Nisin	Enterobactericeae, *Pseudomonas*	Ferrocino et al., 2013
Marinated broiler	x			x	x		Spices	*Leuconostoc gasicomaticum*	Susuiluito et al., (2003)
Raw milk (refrigeration)	x		x		Neutral			*Pseudomonas*, *Lactococcus*, *Acinetobacter*	von Neubeck et al., (2015)
Minimally processed vegetable	x		x		(x)			*Pseudomonas*, *Enterobactericeae*, *Cryptococcus*	Ragaert et al., (2007)

Table 1 (contd.). Reports on spoilage microorganisms in selected food products as influenced by intrinsic and extrinsic factors

Food product	Extrinsic				Intrinsic			Spoilage organism(s)	Reference
	Temperature		Atmospheric conditions		pH		Preservative		
	Low	High	Aerobic	Anaerobic	Low	High			
Filtered milk	x		x		ND			*Acinetobacter*, *Chryseobacterium*, *Psychrobacter*, *Sphingomonas*, *Paenibacillus*, *Bacillus*	Schmidt et al., 2012
Fish	x			x		x	Essential oil	*Aeromonas*, *Lactococcus*	Zhang et al., 2017
Fish		x	x			x		*Pseudomonas*, H_2S producing bacteria, Enterobactericeae	Parpalani et al., 2014
Fish	x			x		x		*Pseudomonas*, *Photobacterium*, *Lactococcus*, *Brocothrix thermosphacta*	Koutsoumanis et al., (2000); Mace et al., 2012
Smoked fish	x			x		x		Lactic acid bacteria, *Phospobacterium*¸ psychothrophic Enterobactericeae	Lovdal, 2015
Seafood		x	x			x		*Proteus*, *Vibrio*	Yang et al., 2017
Fruits		x	x		x			Yeasts	Gram et al., 2002
Fermented alcoholic beverages – sake and beer	x			x	x		Ethanol as by product of fermentation	*Lactobacillus* spp, *Pediococcus* spp., *Pectinatus* spp., *Megaspaera* spp.	Jespersen and Jackobsen, (1996); Suzuki (2011)

Table 2. Some spoilage substrates and metabolites typically found in spoiled food

Sensory characteristic	Spoilage compound	Spoilage substrate	Food product	Reference
Blown pack	CO_2	sugars	vacuum packed meat	Hernandez-Macedo et al. (2012)
Ropiness/Slime	EPS	glucose	wine	Delarheche et al. (2004)
		starch	bread	Valerio et al. (2008)
		sugars	vacuum packed cooked meats	Korkeala et al. (1988)
Off odours				
Fruity	ethylhexanoate, ethyloctanonate, ethyldecnoate	glucose	air stored beef	Ercolini et al. 2010
	ethyl butanoate	ethanol	meat	La Storia et al. (2012)
	hexanal	lipids	fish	Leduc et al. (2012)
Pungent/alcoholic/ fermented	3-methyl-1-butanol, 2-butanol, ethanol	sugars	fish	Miks-Krajnik et al. (2016); Parpalani et al. (2017)
	1-pentanol	sugars	RTE salads	Dias-Lula et al. (2017)
	acetic acid	glucose	fish	Mace et al. (2013)
			bell peppers	Pothakos et al. (2014)
Fishy	Trimethylamine	trimethylamine oxide	seafood	Lopez-Caballero et al. (2001)
Musty, mushroom	1-octen-3-ol	unsaturated fatty acids	baby spinach	Dias-Lula et al. (2017)
			fish	Leduc et al. (2012)
			rapeseed	Gancarz et al., 2017
Cheesy	Acetoin	glucose	fish	Miks-Krajnik et al. (2016)
	Butanoic acid	triglycerides/amino acids	meat	Ercolini et al. (2011)
	2,3-heptanedione		shrimps	Jaffres et al. (2011)
Sulphide off-odour	H_2S	sulphur containing amino acids	fish	Fonnechbech Vogel et al. (2005)
	Dimethyl sulfoxide	sulphur containing amino acids	baby spinach	Dias-Lula et al. (2017)

[a]The combination of acrolein with polyphenols leads to the production of bitter compounds.

Table 2 (contd.). Some spoilage substrates and metabolites typically found in spoiled food

Sensory characteristic	Spoilage compound	Spoilage substrate	Food product	Reference
		sulphur containing amino acids	fish	Parpalani et al. (2017)
Off flavours				
Rancid	Volatile fatty acids	triglycerides	milk	Deeth
Bitter		protein	milk	Cleto et al., (2012)
	acrolein[a]	glycerol	beer and wine	Garai-Ibabe et al., (2008)

[a]The combination of acrolein with polyphenols leads to the production of bitter compounds.

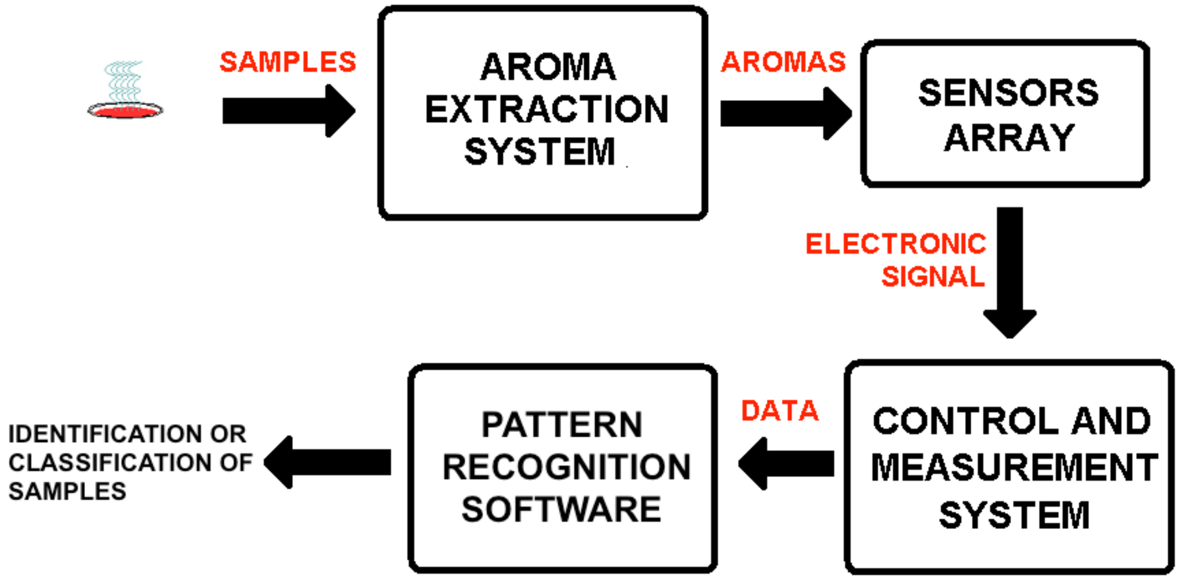

Fig. 1. Block diagram of an electronic nose system.

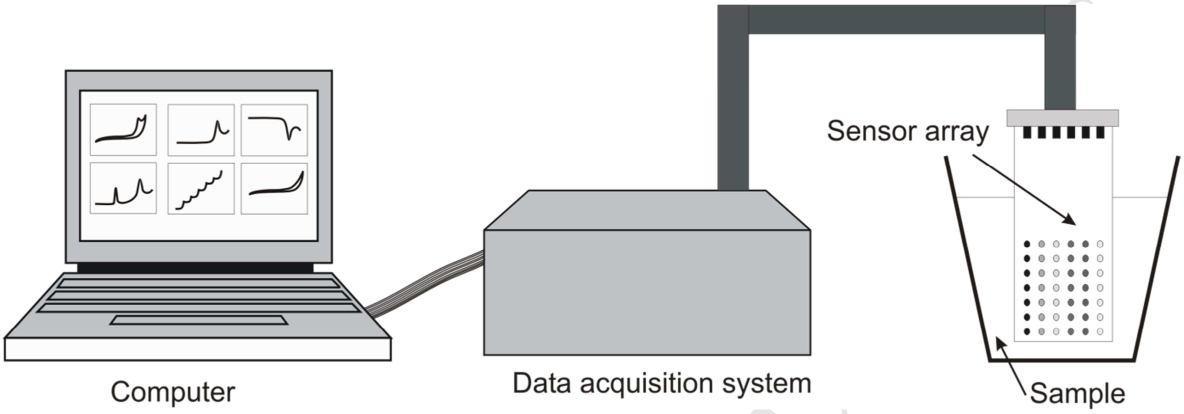

Fig. 2. General scheme of an electronic tongue system

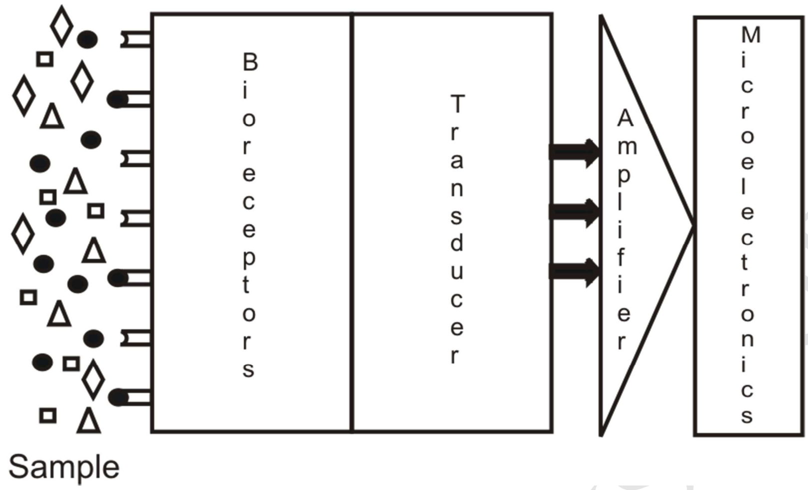

Fig. 3. Biosensor detection scheme

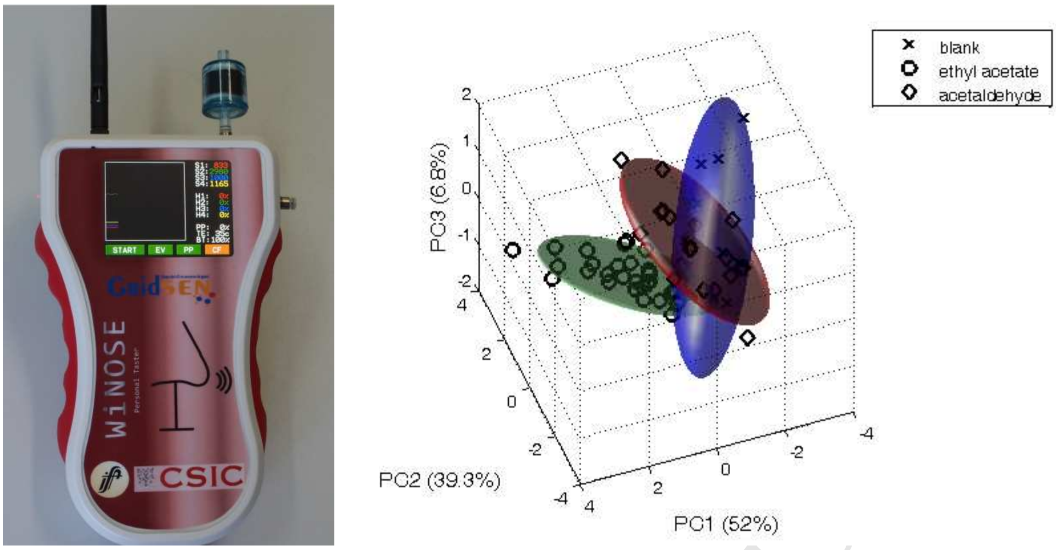

Fig. 4. Portable electronic nose system for the defect discrimination in beer and PCA score plot of measurements of beer defects.

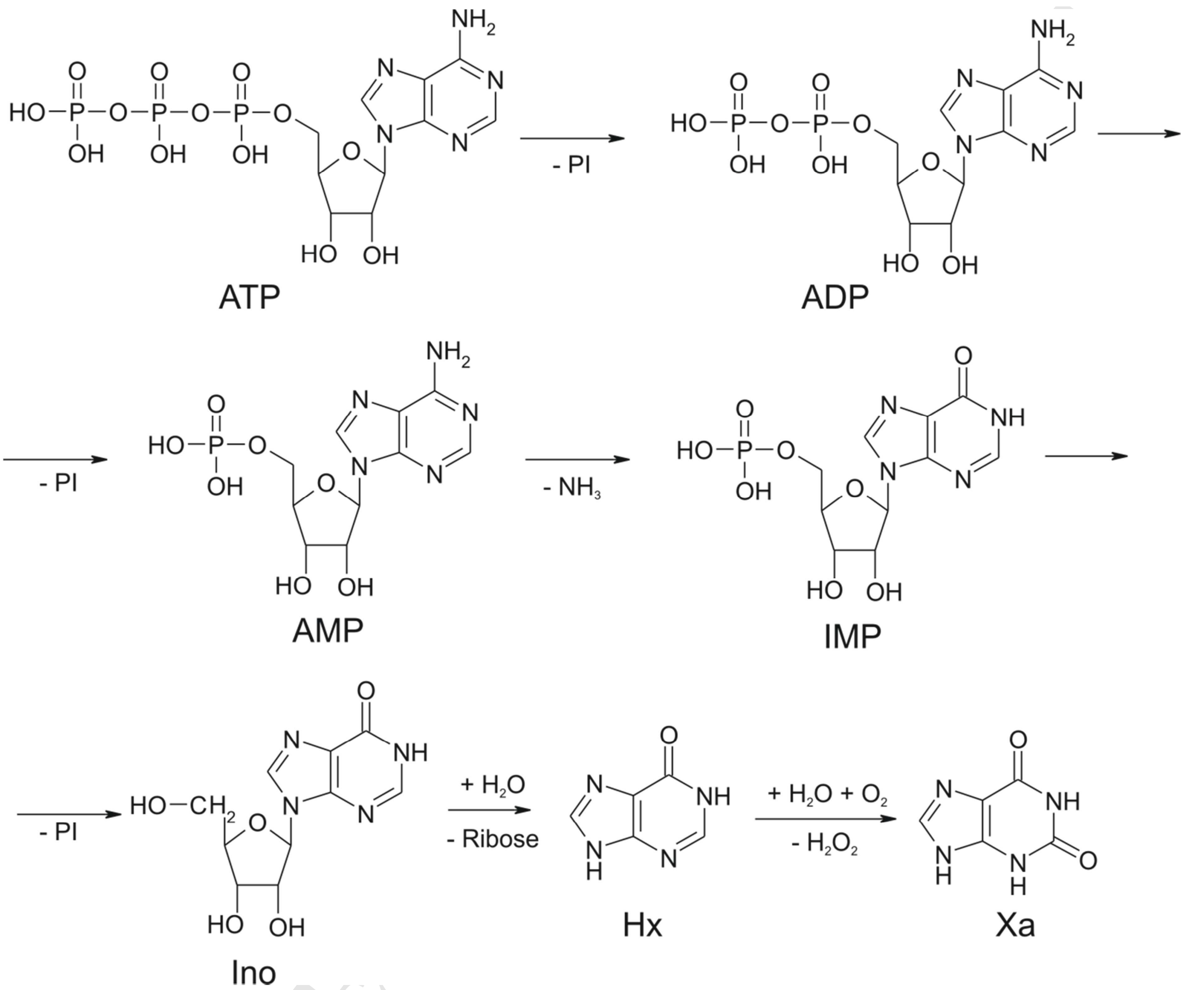

Fig. 5. Decomposition of ATP in the muscles (Nelson & Cox, 2017)

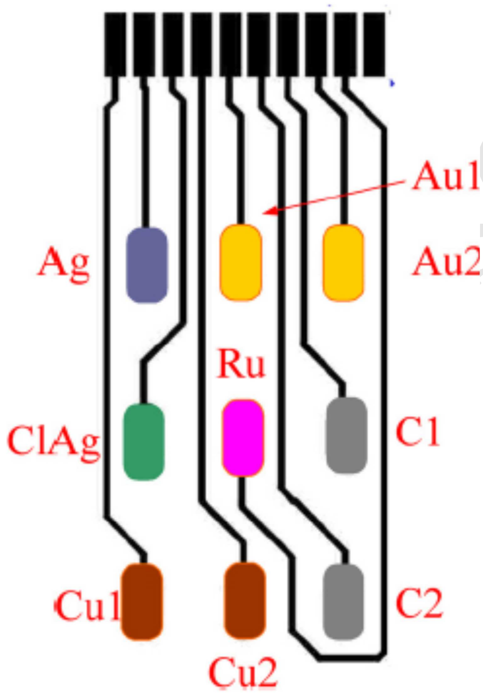

Fig. 6. The sensor array used for the potentiometric electronic tongue (Gil-Sánchez, Soto, Martínez-Máñez, Garcia-Breijo, Ibáñez, & Llobet, 2011).

There is an urgent need for the development of rapid, reliable, precise and non-expensive systems to be used in the food supply and production chain.

In recent decades, some diagnostic tools such as electronic noses, electronic tongues and biosensors have attracted much interest for detection of food spoilage.

The future of the electronic tongue systems and the biosensors are closely related because improving the sensitivity and selectivity of the sensor array remain challenging tasks.

Electronic noses and gas sensors have shown in the last years an important enhancement in the time response and time life as well as a decrease in the size and consumption.