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

119 indigenous or of microbial origin (The et al., 2004) but together catalyse the
120 proteolytic and lipolytic reactions that lead to undesirable changes in the product.

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

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

133 A vast range of bacterial and fungal species play an important role in food spoilage
134 therefore the microbial aspects of spoilage have been the subject of intensive research
135 for decades. Initial studies used conventional microbiology methods for identifying
136 microbial populations involved in food spoilage (Dainty and Mackay, 1992; Dalgaard,
137 1995). However, the evolution of more powerful molecular tools, particularly those
138 based on 16S rRNA bacterial species classification and culture independent
139 techniques allow for a more accurate assessment of the overall microbial food
140 ecosystem and in some cases a reconsideration of the diversity of food spoilage flora
141 (Ercolini et al., 2006; Jaaskelainen et al., 2016; Jaffres et al., 2009; Sade et al., 2017).

142 An important point to note is that not all microorganisms present or growing in food
143 product cause spoilage. Microbial species that directly contribute to food spoilage

144 have been described using terms such as ‘specific spoilage organisms (SSO) or
145 ‘metabiotic spoilage associations’, the latter term was introduced to recognize the
146 importance of microbial interactions in food spoilage (Jorgensen et al., 2000; Gram et
147 al., 2002).

148 Many studies have reported on the major microbial species associated with spoilage
149 for a wide range of food types (for reviews see Andre et al., 2017; Casaburi et al.,
150 2015; Hungaro et al., 2016; Quigely et al., 2013) . It is generally acknowledged that
151 every food product has a distinct microbial flora associated with it during each stage
152 of processing and storage. The composition of this microbial community depends on
153 the microorganisms present on the raw product as well as the conditions under which
154 the food is processed, preserved or stored (Gram et al., 2002; Parpalani et al., 2014).

155 Many interrelated factors influence the shelf life and quality indicators of a food
156 product. Intrinsic, processing and extrinsic factors individually or in combination
157 determine the selection of SSOs that will dominate and cause deterioration of a
158 specific food product (Mossel et al., 1995; Nychas et al., 2008). Intrinsic factors
159 describe the inherent physical, chemical and structural properties of the food product
160 such as water activity (a_w), pH, nutrient availability and the presence of antimicrobial
161 compounds for e.g. bacteriocins. Common characteristics of highly perishable foods
162 such as milk, poultry, fish and meat is their high protein and moisture content, $a_w >$
163 0.998 and neutral to acidic pH. These conditions provide a suitable growth
164 environment for a diverse range of bacterial and fungal species.

165 Physical or chemical preservation methods are applied during processing to inhibit the
166 survival and growth of microorganisms. Baked products are usually poorly
167 susceptible to microbial spoilage as the heat treatment during the baking process

168 eliminates most of the raw microbial flora. Post-processing contamination thus
169 becomes an important contributory factor to spoilage.

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

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

185 For example, lactic acid bacteria (LAB) such as *Carnobacterium* spp. have been
186 shown to dominate the spoilage microbiota of different meat and fish products stored
187 at low temperature under modified atmospheres (Paludan-Muller et al., 1998; Barakat
188 et al., 2000; Laursen et al., 2005). However, in similar products stored aerobically
189 within the same temperature range, psychrotolerant aerobes like *Pseudomonas* spp.
190 often dominate (Del Rio et al., 2007; Nychas et al., 2008; Paparlani and Boziaris,
191 2016).

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

194 3. Traditional methods and recent developments

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

202 Early studies focused on determining the microbiological status of food products
203 relied mainly on total viable counts (TVC) and phenotyping microbial isolates using
204 biochemical tests (Dainty and Mackey, 1992; Haugen et al., 2006). These methods are
205 time consuming and sometimes provide limited information as the extent of spoilage
206 does not always correspond to the number of microorganisms present in the food
207 (Blixt and Borsh, 1999; Ramirez-Guizar et al., 2017). Furthermore, they often
208 underestimate the true microbial community. More recently, molecular approaches
209 based on rRNA gene sequences or metagenomics are increasingly used to identify
210 microbial communities involved in spoilage (Jaaskelainen et al., 2016; Jaffres et al.,
211 2009; Sade et al., 2017).

212 Chemical methods can be used as an indirect means to detect and quantify microbial
213 contamination of food based on the analysis of certain chemical markers. The quantity
214 of cell wall components such as chitin and ergosterol are used to assess spoilage of oil
215 seeds during storage (Gancarz et al., 2017). The colour change associated with
216 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

265 of organic acids, biogenic amines and a range of VOCs (alcohols, aldehydes, ketones,
266 esters, volatile fatty acids and sulphur compounds) (Doyle, 2007; Wang et al., 2016).

267 The composition and concentration of VOCs produced in food is for the most part
268 determined by the combined effect of both intrinsic and extrinsic factors. For
269 example, some amino acids can be decarboxylated by microbial enzymes to produce
270 biogenic amines such as histamine, tyramine, putrescine and cadaverine (Naila et al.,
271 2010). Biogenic amine accumulation in fermented meat products has been reported to
272 be influenced by fermenting strains, pH, sausage diameter (intrinsic) as well as
273 storage temperature and relative humidity (extrinsic). These conditions favour
274 proteolytic and decarboxylase reactions required for biogenic amine formation
275 (Suzzia and Gardini, 2003; Lattore-Moratalla et al., 2012).

276 A list of some compounds associated with the spoilage of selected food products is
277 reported in Table 2. Several authors have reported the detection and measurement of
278 these molecules in spoiled food and there have been attempts to identify VOCs that
279 are likely specific to both SSO and substrate (Concina et al., 2009; Spadafora et al.,
280 2016). This has paved the way for more focused studies to determine the so called
281 chemical spoilage index (CSI), a profile of microbial VOCs (MVOCs) for a particular
282 food product (Parpalani et al., 2014). The concentration of these CSI metabolites
283 should increase in tandem with the growth of the SSOs as well as loss of sensory
284 quality and therefore can be used to estimate shelf life (Jay, 1986; Miks-Krajnik et al.,
285 2016).

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

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

290 Some VOCs can be produced from reactions catalaysed by both SSOs and food
291 matrix enzymes, others from complex metabolic reactions involving different
292 microbial species (Remenant et al., 2015). Species of LAB, *Enterobacteriaceae* and
293 *Clostridia* have been implicated in 'blown pack' spoilage (BPS) of refrigerated,
294 vacuum packed meat products (Brightwell et al., 2007; Hernandez-Macedo et al.,
295 2012). The 'blown pack' effect has been attributed to gas production but it remains
296 unclear which species is directly implicated although some authors have attributed
297 BPS to be largely due to the metabolic activities of *Clostridium estertheticum* (Cavill
298 et al., 2016; Rajagopal et al., 2016). In addition, MVOCs identified from culture
299 media experiments as potential CSI candidates may not be detected in food (Yu et al.,
300 2000).

301 **5. Multisensor systems**

302 *5. 1. Electronic nose and its performance*

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

312 The electronic nose is an electronic system that tries to mimick the structure of the
313 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

435 emulate the human sense of smell. These automated analysis that comes from
436 methods of statistical pattern recognition, neural arrays and chemometrics (Aguilera,
437 Lozano, Paredes, Alvarez, & Suárez, 2012), is a key part in the development of a gas
438 sensor array capable to detect, identify or quantify different volatile compounds
439 responsible for food spoilage. This process may be subdivided into the following
440 steps: preprocessing and feature extraction, dimensionality reduction, classification or
441 prediction, and decision-making.

442 Preprocessing compensates for sensor drift, compresses the transient response of the
443 sensor array, and reduces sample-to-sample variations. Typical techniques include:
444 manipulation of sensor baselines; normalization of sensor response ranges for all the
445 sensors in an array (the normalization constant may sometimes be used to estimate the
446 odorant concentration); and compression of sensor transients. Feature extraction has
447 two purposes: to reduce the dimensionality of the measurement space, and to extract
448 information relevant for pattern recognition. For example, in an electronic nose with
449 32 sensors, tipically one feature is extracted from each raw response of the sensor and
450 the measurement space has 32 dimensions.

451 A dimensionality reduction stage projects this initial feature vector onto a lower
452 dimensional space in order to avoid problems associated with high-dimensional,
453 sparse datasets. Maybe, some of them probably respond in a similar (but not identical)
454 way. This means that the number of dimensions in the data set can be reduced without
455 any loss of information. It is generally performed with linear transformations such as
456 the classical principal component analysis (PCA) and linear discriminant analysis
457 (LDA). The resulting low-dimensional feature vector is further used to solve a given
458 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).

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

510 Fig. 2. General scheme of an electronic tongue system

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

517 Usually, the initial studies dedicated to the development of electronic tongues with
518 sensors based on various detection systems focused on the qualitative and quantitative
519 analysis of the solutions which represent basic tastes (sweet, sour, salty, bitter and
520 umami), as well as of other gustatory sensations or perceptions (astringency,
521 pungency) (Riul Jr., dos Santos Jr., Wohnrath, Di Tommazo, Carvalho, Fonseca,
522 Oliveira Jr., Taylor, & Mattoso, 2002; Eckert, Pein, Reimann, & Breitkreutz, 2013;
523 Tian, Feng, Xiao, Song, Li, Liu, Mao, & Li, 2015; Pioggia, Di Francesco, Marchetti,
524 Ferro, Leardi, Ahluwalia, 2007; Jain, Panchal, Pradhan, Patel, & Pasha, 2010;
525 Rudnitskaya, Polshin, Kirsanov, Lammertyn, Nicolai, Saison, Delvaux, Delvaux, &
526 Legin, 2009; Toko, 1998; Legin, Rudnitskaya, Clapham, Seleznev, Lord, & Vlasov,
527 2004; Khan, Khalilian, & Kang, 2016; Arrieta, Rodriguez-Mendez, & de Saja, 2003;
528 Apetrei, Rodríguez-Méndez, Parra, Gutierrez, & de Saja, 2004; Arrieta, Apetrei,
529 Rodríguez-Méndez, & de Saja, 2004). This is absolutely necessary in order to prove
530 that the sensor responds to compounds with various organoleptic properties. The main
531 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

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

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

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

652 from Barcelona University) were employed (Pein, Kirsanov, Ciosek, del Valle,
653 Yaroshenko, Wesoły, Zabadaj, Gonzalez-Calabuig, Wróblewski, &Legin, 2015).

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

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

667

668 *5.3. Biosensors*

669 Biosensors are analytical devices which integrate a bioreceptor (enzymes, organelles,
670 living cells, tissues, nucleic acids, aptamers, etc.) in a compatible transducing system,
671 and which are capable to specifically determine certain chemical compounds (Rotariu,
672 Lagarde, Jaffrezic-Renault, & Bala, 2016; Scognamiglio, Arduini, Palleschi, & Rea,
673 2014; Di Rosa, Leone, Cheli, & Chiofalo, 2017). The most frequently used
674 transducers are: electrochemical, optical, mass, thermal, but there are other types as

675 well (Compagnone, Di Francia, Di Natale, Neri, Seeber, & Tajani, 2017; Ali, Najeeb,
676 Ali, Aslam, & Raza, 2017; Almeida Silva, Cruz Moraes, Campos Janegitz, Fatibello-
677 Filho, 2017; Chauhan, Maekawa, & Kumar, 2017). An electric signal which can be
678 measured and recorded is produced as a result of the specific interaction between the
679 analyte and the biocomponent. The analytes or target compounds comprise a large
680 and various number of chemical species, from inorganic compounds to organic
681 compounds with small molecules and even with large molecules such as proteins
682 (Abdulbari & Basheer, 2017; El-Nour, Salam, Soliman, &. Orabi, 2017; Matysik,
683 2017; Leca-Bouvier & Blum, 2005). The scheme of analytes detection with
684 biosensors is presented in Fig. 3.

685 Fig. 3. Biosensor detection scheme

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

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

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

701 The main research directions include the analysis of compounds of interest for food
702 quality and that of contaminates, compounds which accidentally appear in food and
703 which should not be there under normal conditions (McGrath, Elliott, & Fodey, 2012;
704 Dragone, Grasso, Muccini, & Toffanin, 2017). Moreover, focus is laid on monitoring
705 various chemical or biochemical processes related to fermentation, degradation,
706 spoilage, maturation or freshness of foods with the help of the biosensors (Mutlu,
707 2016; Vasilescu, Nunes, Hayat, Latif, & Marty, 2016; Adley, 2014; Ispas, Crivat, &
708 Andreescu, 2012; Park, Kim, Lee, & Jang, 2015). Other studies lay importance on the
709 characterization of foods in terms of biologic or geographic origins, as well as
710 authenticity, fraud or adulteration of foods (Apetrei & Ghasemi-Varnamkhasti, 2013;
711 Bassi, Lee, & Zhu, 1998; Narsaiah, Jha, Bhardwaj, Sharma, & Kumar, 2012;
712 Campuzano, Ruiz-Valdepeñas Montiel, Torrente-Rodríguez, Reviejo, & Pingarrón,
713 2016).

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

718 Enzyme-based biosensors are the most frequently used in foods analysis (Kumar &
719 Neelam, 2016; Prodromidis & Karayannis, 2002). Two basic principles are used in
720 practice, one being the direct detection of the analyte (substrate) resulted from an
721 enzymatic process, the other being the inhibition of the enzymatic activity (Upadhyay
722 & 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

748 improvements in selectivity and sensitivity compared to classical chemical and
749 biological methods. Nano biosensors can be used for detection and quantification of
750 microorganisms, contaminants, and food freshness (Pérez-López, & Merkoçi, 2011;
751 Grumezescu, 2016).

752 **6. Literature evidence multisensor systems to food spoilage detection**

753 *6.1. Electronic nose*

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

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

766 There are different prototypes designed by some research groups with different
767 features that are appropriate for different applications. In the bibliography, Laboratory
768 equipment as well as portable instruments are designed for food spoilage detection.
769 The following reference (Jose Pedro Santos & Lozano, (2015) shows a hand-held
770 wireless portable electronic nose applied to the real-time detection of two common

771 aromatic defects in beer: acetaldehyde and ethyl acetate. An image of the electronic
772 nose is illustrated in Fig. 4. These aromatic defects in beer have been measured at
773 level between the organoleptic threshold and five times this quantity (25 ppm for
774 acetaldehyde and 21 ppm for ethyl acetate). PCA were applied to these responses to
775 see the data distribution among classes. Although there is some confusion between
776 some classes corresponding to different concentrations, non-defect beer samples were
777 separated from the other samples. In a qualitative classification among beer without
778 defects (blank) and beer with one of the defects (ethyl acetate or acetaldehyde)
779 regardless the concentration, the measurements were grouped into three classes:
780 blank, ethyl acetate and acetaldehyde. The PCA score plot for the whole measurement
781 set is shown in Fig. 4. Some partial overlapping is observed among the classes,
782 although the ANN analysis gave a 94 % success rate in validation. Few samples are
783 wrongly classified among the three clases. Authors explain that these results could be
784 improved using other types of classifiers and improving the measurement system in
785 order to a better control of the operation temperatures and flows and reducing the
786 measurement noise.

787

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

790 It is usually recognized that electronic noses have not achieved the market penetration
791 that was expected in the mid-90s. The prototype presented in Lozano et al., (2015)
792 could be a first step for implementation in the wine industry. It is installed in a wine
793 cellar for on-line monitoring of wine evolution during 9 months. The system has a
794 novel sampling method that extracts the aroma directly from the tanks where wine is

795 stored; and it automatically carries the volatile compounds to the sensor cell with tin
796 oxide multisensor. Linear techniques as principal component analysis (PCA) and
797 nonlinear ones as Artificial Neural Arrays (ANN) are used for pattern recognition,
798 and Partial Least Squares (PLS) is used for predicting GC-MS analysis. Results
799 showed that system can detect the evolution of two different wines along 9 months
800 stored in the monitored tanks. The evolution of the wine is confirmed with chemical
801 and sensory analysis. Moreover, GC-MS analysis was performed to the wine of the
802 tanks. In the whole, 19 odorants were analysed. The chemical compounds analysed
803 were acids (butyric acid, decanoic acid, hexanoic acid, isobutyric acid, isovaleric acid,
804 and octanoic acid), alcohols (1-hexanol and 2-phenilethanol), esters (hexyl acetate,
805 ethyl butyrate, ethyl decanoate, ethyl hexanoate, ethyl isovalerate, ethyl lactate, ethyl
806 octanoate, isoamyl acetate, isobutyl acetate, diethyl succinate and phenyl ethyl
807 acetate) and phenols (4-vinyl-guaiacol). The aforementioned 19 compounds analysed
808 in GC-MS profiles were used as predictor variables. Then, a model was created in
809 order to predict these responses from sensor measurements. In this way, the
810 concentration of chemical compounds in wine determined by GC–MS were correlated
811 with electronic nose response PLS regression analysis. Correlation coefficients near to
812 1 are obtained in the prediction of several volatile organic compounds (VOCs), i.e.
813 ethyl butyrate, isobutyric acid, isobutyl acetate, hexyl acetate and ethyl octanoate.
814 This system could be trained for monitoring wine preservation and evolution in tanks
815 and therefore detecting off-odours of wine and warning the wine expert to correct it as
816 soon as possible, preventing the wine spoilage and improving its final quality.

817 Based on the body of scientific literature, numerous considerable works on spoilage
818 detection using electronic nose has been conducted on meat and fish products.
819 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

869 activity of some specific enzymes and microorganisms, etc. (Sahu & Bala, 2017; de
870 Blackburn, 2006).

871 Thus, for the quantitative case, a number of toxic compounds formed during the
872 spoilage process has been determined, especially biogenic amines, which result from
873 amino acids decarboxylation. The amino acids involved in these processes are free
874 amino acids present in foods, but also the ones which originate in proteins hydrolysis
875 (Naila, Steve Flint, Fletcher, Bremer, & Meerdink, 2010; Karovičová & Kohajdová,
876 2005). Other quantitatively determined compounds are inosine 5'-monophosphate,
877 inosine and xanthine and hypoxanthine, which originate from adenosine triphosphate
878 (ATP) degradation (Vilas, Alonso, Herrera, García-Blanco, & García, 2017) (Fig. 5).

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

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

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

889 More types of foods have been analyzed and the systems used and the main results
890 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 semi-

915 quantitative evaluation of freshness in meat samples and they can have numerous
916 applications in food industry in quality control of pork meat.

917 Another study, presented by Kaneki et al., (2004) described the use of a
918 potentiometric electronic tongue based on simple solid electrodes (i.e. Pt, CuS and
919 Ag_2S) which are able to detect certain compounds responsible for the initial stage of
920 meat putrefaction. This system was successfully used in the study of pork meat
921 freshness (Kaneki, Miura, Shimada, Tanaka, Ito, Hotori, Akasaka, Ohkubo, & Asano,
922 2004).

923 Microbiological contamination in dry-cured ham can occur at various stages of the
924 maturation process, and the development of a large number of microorganisms
925 involved in spoilage may lead to the alteration of the end product (Dikeman &
926 Devine, 2014). These processes lead to some unpleasant and non-common odours,
927 which are detected by an expert taster, who follows a procedure called “cala”, by
928 which he classifies hams as good and altered hams (Paarup, Nieto, Peláez, & Reguera,
929 1999). Girón et al. (2015) produced a potentiometric electronic tongue based on an
930 array of sensors which contains three types of sensors, silver, nickel and copper
931 electrodes. This electronic tongue was used for the classification of altered and
932 unaltered hams before the classification of hams by an expert tester. The results of the
933 analyses showed that, in the case of altered hams, the Ag potentials have the lowest
934 values and the Cu potentials, the highest values. Starting from these experimentally
935 observed differences, a model of classification of hams was built, but further studies
936 are required for the system validation for industrial practice (Girón, Gil-Sánchez,
937 García-Breijo, Pagána, Barat, & Grau, 2015).

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

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

957 Ruiz-Rico et al. (2013) studied the shelf-life assessment of fresh cod in cold storage
958 using a voltammetric electronic tongue (Ruiz-Rico, Fuentes, Masot, Alcañiz,
959 Fernández-Segovia, & Barat, 2013). The electronic tongue system is based on an
960 array of sensors, specialised software installed on a PC and electronic equipment.
961 Measurements relied on pulse voltammetry, the voltage pulses being applied to
962 sensors by the electronic equipment, and the generated currents being measured

963 afterwards. For each sensor, 1,000 values were recorded, which correspond to the
964 time evolution of the current generated in the system after applying the voltage pulse.
965 The sensor system is made up of 8 metallic electrodes, separated into two subsystems,
966 one made up of 4 electrodes based on noble metals (iridium, rhodium, platinum and
967 gold) and the other, of 4 metallic electrodes based on non-noble metals (silver, cobalt,
968 copper and nickel). Therefore, a total of 8,000 values are registered by the electronic
969 tongue for each sample under study. For the validation of the analytical system, data
970 resulted from physical-chemical and microbial analyses were used. For all samples
971 analysed, the limits of the main parameters related to fish freshness, such as total
972 volatile basic nitrogen, mesophilic and Enterobacteriaceae, were exceeded on the
973 fourth day of storage, which means that fish has a shelf-life less than four days. The
974 results of physical-chemical and microbial analyses showed an obvious loss of
975 freshness from day 0 to day 4. Also, the voltammetric tongue results showed a clear
976 difference between the freshness of fish on days 0 and 1 of storage and that in the
977 following days. The regression patterns based on partial least squares for Total
978 Volatile Basic Nitrogen (TVB-N) and mesophilic counts proved that the predicted
979 values concord with the experimental results, which confirms the usefulness of
980 voltammetric electronic tongue for assessing cod spoilage.

981 Haddi et al. (2015) implemented a voltammetric electronic tongue based on an array
982 of seven working electrodes, a platinum counter electrode and an Ag/AgCl reference
983 electrode (Haddi, El Barbri, Tahri, Bougrini, El Bari,. Llobet, & Bouchikhi, 2015).
984 The working electrodes were made of platinum, gold, silver, glassy carbon,
985 palladium, copper and nickel. They were assembled in the form of an array of sensors
986 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°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

1035 analysis of the signals registered by sensors, a growth of the signal currents associated
1036 to biogenic amines was observed in the analysed samples with the increase of the
1037 storage time.

1038 The voltammetric signals obtained with the help of the array of sensors were used to
1039 discriminate and evaluate the state of fish freshness. Principal component analysis
1040 confirmed the ability of the voltammetric electronic tongue to monitor the fish
1041 freshness. The partial least squares–discriminant analysis (PLS-DA) model showed
1042 that this electronic tongue is able to determine the post-mortem time elapsed, being
1043 highly useful in practice.

1044 Another study was dedicated to the detection and quantification of putrescine and
1045 ammonia resulted from the spoilage of dehydrated beef, as well as to monitoring beef
1046 freshness under refrigeration conditions (Apetrei & Apetrei, 2016).

1047 The array of sensors used in this study was a hybrid one, made up of screen-printed
1048 electrodes modified with bisphthalocyanines and polypyrrole doped with different
1049 doping agents. The electrochemical responses of the sensors were analysed for two
1050 compounds of interest in beef spoilage, namely ammonia and putrescine.

1051 The electrochemical signals are related to the redox properties of the substances used
1052 for modifying the electrodes, which are greatly influenced by the compounds present
1053 in the solution to be analysed. At first, it was determined that the sensors were capable
1054 to detect amine compounds in beef extract powder with good sensitivity to the levels
1055 of concentration at which the respective compounds are found in the initial spoilage
1056 stages. The sensor array made up of sensors with the best performance was used for
1057 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,

1154 they developed a novel biosensor by embedding reduced expanded graphene oxide
1155 sheets decorated with iron oxide (Fe_3O_4) nanoparticles into poly (glycidyl
1156 methacrylate-covinylferrocene) phase, and by covalent immobilization of xanthine
1157 oxidase onto the surface of P(GMA-co-VFc)/REGO-Fe_3O_4 nanocomposite film. The
1158 experimental conditions were studied and optimized for the high sensitivity detection
1159 of xanthine (response time, linear range, operation and storage stability, pH and
1160 temperature) a limit of detection of 0.17 μM being obtained. The xanthine biosensor
1161 was used for the analysis of xanthine content in fish real samples after 5, 8, 10, 13, 15,
1162 and 20 days of storage. The novel biosensor proved that it could be successfully
1163 employed in the analysis of real samples and also that it could be successfully used as
1164 a reliable fish freshness controlling technique.

1165 Apetrei et al. (2015) developed a biocomposite screen-printed biosensor based on
1166 immobilization of tyrosinase onto the carboxyl functionalised carbon nanotube for
1167 assaying tyramine in fish products (Apetrei & Apetrei, 2015). Tyramine is a biogenic
1168 amine which is especially found in fermented food products, but also in smoked,
1169 salted or soused fish (Luten, 2006). This compound can be used as a biomarker for
1170 spoilage monitoring. The detection principle employed was the amperometric one, by
1171 applying the optimum potential for the electrochemical reduction of the o-quinone
1172 formed in the enzymatic process at the surface of the sensitive layer of the biosensor.
1173 The biosensor presented very good analytical performance in what tyramine detection
1174 is concerned. These results are related to the presence of carboxyl functionalized
1175 carbon nanotube in the sensitive layer which facilitates the transfer of the electrodes
1176 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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References

Abdulbari, H. A., Basheer, E. A. M. (2017) Electrochemical Biosensors: Electrode Development, Materials, Design, and Fabrication. *ChemBioEng Reviews* **4**, 92 – 105. doi:10.1002/cben.201600009.

Adley, C. C. (2014) Past, Present and Future of Sensors in Food Production. *Foods* **3**, 491 –510.

Aguilera, T., Lozano, J., Paredes, J. A., Alvarez, F. J., & Suárez, J. I. (2012). Electronic nose based on independent component analysis combined with partial least squares and artificial neural arrays for wine prediction. Sensors (Basel, Switzerland), 12(6), 8055–72. http://doi.org/10.3390/s120608055

Ahn, S.R, An, J.H., Song, H.S., Park, J.W., Lee, S.H., Kim, J.H., Jang, J., Park, T.H. (2016) Duplex Bioelectronic Tongue for Sensing Umami and Sweet Tastes Based on Human Taste Receptor Nanovesicles. *ACS Nano* **10**, 7287 - 7296.

1344 Ali, J., Najeeb, J., Ali, M.A., Aslam, M.F., Raza, A. (2017) Biosensors: Their
1345 Fundamentals, Designs, Types and Most Recent Impactful Applications: A Review.
1346 *Journal of Biosensors & Bioelectronics* **8**, 235. doi: 10.4172/2155-6210.1000235.
1347
1348 Almeida Silva, T., Cruz Moraes, F., Campos Janegitz, B., Fatibello-Filho, O. (2017)
1349 Electrochemical Biosensors Based on Nanostructured Carbon Black: A Review.
1350 *Journal of Nanomaterials* **2017**, Article ID 4571614, 14 pages.
1351 Amine, A., Mohammadi, H., Bourais, I., Palleschi, G. (2006) Enzyme inhibition-
1352 based biosensors for food safety and environmental monitoring. *Biosensors and*
1353 *Bioelectronics* **21**, 1405 – 1423.
1354
1355 Andre, S., Vallaeys, T., Planchon, S. (2017) Spore-forming bacteria responsible for
1356 food spoilage. *Research in Microbiology* 52, 123-138.
1357
1358 Apetrei, C., Ghasemi-Varnamkhasti, M. (2013) *Biosensors in food PDO*
1359 *authentication*. Comprehensive Analytical Chemistry, Volume 60, 279 - 297.
1360 Apetrei, C., Rodríguez-Méndez, M. L., Parra, V., Gutierrez, F., de Saja, J.A. (2004)
1361 Array of voltammetric sensors for the discrimination of bitter solutions. *Sensors and*
1362 *Actuators B: Chemical* **103**, 145 – 152.
1363
1364 Apetrei, I.M., Apetrei, C. (2014) Detection of virgin olive oil adulteration using a
1365 voltammetric e-tongue. *Computers and Electronics in Agriculture* **108**, 148 – 154.
1366 Apetrei, I.M., Apetrei, C. (2015) The biocomposite screen-printed biosensor based on
1367 immobilization of tyrosinase onto the carboxyl functionalised carbon nanotube for
1368 assaying tyramine in fish products. *Journal of Food Engineering* **149**, 1 – 8.

Apetrei, I.M., Apetrei, C. (2016) Amperometric biosensor based on diamine oxidase/platinum nanoparticles/graphene/chitosan modified screen-printed carbon electrode for histamine detection. *Sensors* **16**, Article number 422, doi: 10.3390/s16040422.

Apetrei, I.M., Apetrei, C. (2016) Application of voltammetric e-tongue for the detection of ammonia and putrescine in beef products. *Sensors and Actuators B: Chemical* **234**, 371 - 379.

Apetrei, I.M., Rodriguez-Mendez, M.L., Apetrei, C., de Saja, J.A. (2013) Fish freshness monitoring using an E-tongue based on polypyrrole modified screen-printed electrodes. *IEEE Sensors Journal* **13**, 2548 – 2554.

Arrieta, A., Rodriguez-Mendez, M. L., de Saja, J.A. (2003) Langmuir–Blodgett film and carbon paste electrodes based on phthalocyanines as sensing units for taste. *Sensors and Actuators B: Chemical* **95**, 357 – 365.

Arrieta, A.A. Apetrei, C., Rodríguez-Méndez, M. L., de Saja, J. A. (2004) Voltammetric sensor array based on conducting polymer-modified electrodes for the discrimination of liquids. *Electrochimica Acta* **49**, 4543 – 4551.

Barakat, R.K., Griffiths, M.W., Harris, L.J. (2000) Isolation and characterization of *Carnobacterium, Lactococcus* and *Enterococcus* spp. from cooked, modified atmosphere packaged, refrigerated, poultry meat. *International Journal of Food Microbiology* 62, 83 – 94.

Bard, A. J., Faulkner, L. R. (2001) *Electrochemical Methods: Fundamentals and Applications*, 2nd Edition, John Willey & Sons, Inc., New York.

Barrett, E.L., Kwan, H.S. (1985) Bacterial reduction of trimethylamine oxide. *Annual Review of Microbiology* **39**, 131 - 149.

Bassi, A.S., Lee, E., Zhu J.-X. (1998) Carbon paste mediated, amperometric, thin film biosensors for fructose monitoring in honey. *Food Research International* **31**, 119 – 127.

Benabdellah, N. Bourhaleb, M., Benazzi, N., Nasri, M., Dahbi, S. 2017. The detection of smell in spoiled meat by TGS822 gas sensor for an electronic noseused in rotten food. Advances in Intelligent Systems and Computing. 520, 279-286.

Berna, A. Z., Trowell, S., Cynkar, W., & Cozzolino, D. (2008). Comparison of metal oxide-based electronic nose and mass spectrometry-based electronic nose for the prediction of red wine spoilage. Journal of Agricultural and Food Chemistry, 56(9), 3238–3244. http://doi.org/10.1021/jf7037289

Blixt, Y., Borch, E. (1999) Using an electronic nose for determining the spoilage of vacuum packaged beef. Int J. Food. Microbiol. 46, 123 -134.

Bobacka, J., Ivaska, A., Lewenstam, A. (2008) Potentiometric Ion Sensors. *Chemical Reviews* **108**, 329 - 351.

Bóka, B., Adányi, N., Szamos, J., Virág, D., Kiss A. (2012) Putrescine biosensor based on putrescine oxidase from *Kocuria rosea. Enzyme and Microbial Technology* **51**, 258 – 262.

Bourigua, S., El Ichi, S., Korri-Youssoufi, H., Maaref, A., Dzyadevych, S., Jaffrezic Renault, N. (2011) Electrochemical sensing of trimethylamine based on polypyrrole–flavin-containing monooxygenase (FMO3) and ferrocene as redox probe for evaluation of fish freshness. Biosensors and Bioelectronics 28, 105-111.

Bratov, A., Abramova, N., Ipatov A. (2010) Recent trends in potentiometric sensor arrays—A review. *Analytica Chimica Acta* **678**, 149 – 159.

Brett, C.M.A., Fungaro, D. A. (2000) Modified Electrode Voltammetric Sensors for Trace Metals in Environmental Samples. *Journal of the Brazilian Chemical Society* **11**, 298 – 303.

Brightwell, G., Clemens, R., Urlich, S., Boerema, J. (2007) Possible involvement of psychrotolerant *Enterobactericeae* in blown pack spoilage of vacuum-packaged raw meats. *International Journal of Food Microbiology* **119**, 334 – 339.

Bueno, L., de Araujo, W. R., Salles, M. O., Kussuda, M. Y., Paixão, T. R. L. C. (2014) Voltammetric Electronic Tongue for Discrimination of Milk Adulterated with Urea, Formaldehyde and Melamine. *Chemosensors* **2**, 251-266.

1441 Cabañes, F. J., Sahgal, N., Bragulat, M. R., & Magan, N. (2009). Early discrimination
1442 of fungal species responsible of ochratoxin A contamination of wine and other grape
1443 products using an electronic nose. Mycotoxin Research, 25(4), 187–192.
1444 http://doi.org/10.1007/s12550-009-0027-x.

1445

1446 Cabral, F.P., Bergamo, B.B., Dantas, C.A., Riul Jr., A., Giacometti, J.A. (2009)
1447 Impedance e-tongue instrument for rapid liquid assessment. *Review of Scientific*
1448 *Instruments* **80**, 026107. doi: 10.1063/1.3084210.
1449 Campos Sánchez, I., Bataller Prats, R., Gandía Romero, J.M., Soto Camino, J.,
1450 Martínez Mañez, R., Gil Sánchez, L. (2013) Monitoring grape ripeness using a
1451 voltammetric electronic tongue. *Food Research International* **54**, 1369 - 1375.

1452

1453 Campos, I., Alcañiz, M., Aguado, D., Barat, R., Ferrer, J., Gil, L., Marrakchi, M.,
1454 Martínez-Mañez, R., Soto, J., Vivancos, J.-L. (2012) A voltammetric electronic
1455 tongue as tool for water quality monitoring in wastewater treatment plants. *Water*
1456 *Research* **46**, 2605 – 2614.

1457

1458 Campuzano, S., Ruiz-Valdepeñas Montiel, V., Torrente-Rodríguez, R. M., Reviejo,
1459 Á. J., Pingarrón, J. M. (2016) *Electrochemical Biosensors for Food Security:*
1460 *Allergens and Adulterants Detection*, 287-307. In book: Biosensors for Security and
1461 Bioterrorism Applications. Springer.

1462

1463 Casaburi, A., Nasi, A., Ferrochino, L., Di Monaco, R., Mauriello, G., Villiani, F.,
1464 Ercolini, D. (2011) Spoilage-related activity of *Carnobacterium maltaromaticum*

1465 strains in air stored and vacuum packed meat. *Applied and Environmental*
1466 *Microbiology* **77**, 7382 - 7393.

1467

1468 Casaburi, A., Piombino, P., Nychas, G-J., Villiani, F. (2015) Bacterial populations
1469 and the volatilome associated to meet spoilage. *Food Microbiology* **45**, 83 – 102.

1470

1471 Cetó, X., Apetrei, C., Del Valle, M., Rodríguez-Méndez, M.L. (2014) Evaluation of
1472 red wines antioxidant capacity by means of a voltammetric e-tongue with an
1473 optimized sensor array. *Electrochimica Acta* **120**, 180 – 186.

1474

1475 Cetó, X., Capdevila, J., Puig, A., del Valle, M. (2014) Cava wine authentication
1476 employing a voltammetric electronic tongue. *Electroanalysis* **26**, 1504 - 1512.

1477

1478 Cetó, X., González-Calabuig, A., del Valle, M. (2015) Use of a Bioelectronic Tongue
1479 for the Monitoring of the Photodegradation of Phenolic Compounds. *Electroanalysis*
1480 **27**, 225 – 233.

1481

1482 Cetó, X., Voelcker, N. H., Prieto-Simón, B. (2016) Bioelectronic tongues: New trends
1483 and applications in water and food analysis. *Biosensors and Bioelectronics* **79**, 608 –
1484 626.

1485

1486 Chatterjee, D., Bhattacharjee, P., & Bhattacharyya, N. (2014). Development of
1487 methodology for assessment of shelf-life of fried potato wedges using electronic

noses: Sensor screening by fuzzy logic analysis. Journal of Food Engineering, 133, 23–29. http://doi.org/10.1016/j.jfoodeng.2014.02.009

Chauhan, N., Maekawa, T., Kumar, D. (2017) Graphene based biosensors—Accelerating medical diagnostics to new-dimensions. *Journal of Materials Research*, 1 - 23. doi:10.1557/jmr.2017.91

Chen, S., Zhang, R., Hao, L., Chen, W., Cheng, S. (2015) Profiling of Volatile Compounds and Associated Gene Expression and Enzyme Activity during Fruit Development in Two Cucumber Cultivars. *PLoS One* **10**, e0119444. doi: 10.1371/journal.pone.0119444

Chung, S., Park, T. S., Park, S. H., Kim, J. Y., Park, S., Son, D., Bae, Y. M., Cho S. I. (2015) Colorimetric Sensor Array for White Wine Tasting. *Sensors* **15**, 18197 - 18208.

Ciosek, P., Wróblewski W. (2007) Sensor arrays for liquid sensing – electronic tongue systems. *Analyst* **132**, 963 – 978.

Ciosek, P., Wróblewski, W. (2011) Potentiometric Electronic Tongues for Foodstuff and Biosample Recognition—An Overview. *Sensors* **11**, 4688 - 4701.

Cleto, S., Matos, S., Kluskens, L., Vieira, M.J. (2012) Characterization of contaminants from a sanitized milk processing plant. PLoS One. 7, e40189.

Compagnone, D., Di Francia, G., Di Natale, C., Neri, G., Seeber, R., Tajani A. (2017) Chemical Sensors and Biosensors in Italy: A Review of the 2015 Literature. *Sensors* **17**, 868; doi:10.3390/s17040868.

Concina, I., Bornšek, M., Baccelliere, S., Falasconi, M., Gobbi, E., & Sberveglieri, G. (2010). Alicyclobacillus spp.: Detection in soft drinks by Electronic Nose. Food Research International, 43(8), 2108–2114. http://doi.org/10.1016/j.foodres.2010.07.012

Concina, I., Falasconi, M., Gobbi, E., Bianchi, F. Musci, M., Mattarozzi, M., Pardo, M., Mangia, A., Careri, M., Sberveglieri, G., (2009) Early detection of microbial contamination in processed tomatoes by electronic nose. Food Control, 20, 873-880.

Costa, C., Miertus, S. (1993) *Trends in Electrochemical Biosensors: Proceedings of the Conference*. World Scientific, Singapore.

Cuartero, M., Carretero, A., Garcia, M. S., Ortuño, J. A. (2015) New Potentiometric Electronic Tongue for Analysing Teas and Infusions. *Electroanalysis* **27**, 782 – 788.

Cynkar, W., Cozzolino, D., Dambergs, B., Janik, L., & Gishen, M. (2007). Feasibility study on the use of a head space mass spectrometry electronic nose (MS e_nose) to monitor red wine spoilage induced by Brettanomyces yeast. Sensors and Actuators, B: Chemical, 124(1), 167–171. http://doi.org/10.1016/j.snb.2006.12.017

Dainty, R.H., Mackey, B.M., (1992) The relationship between phenotypic properties of bacteria from chill-stored meat and spoilage processes. *Society of Applied Bacteriology Symposium Series* **73**, 103S – 114S.

Dalgaard, P. (1995) Qualitative and quantitative characterization of spoilage bacteria from packed fish. *International Journal of Food Microbiology* **26**, 319 – 333.

Dalgaard, P., Madsen, H., Samieian, N., Emborg, J. (2006) Biogenic amine formation and microbial spoilage in chilled garfish (Belone belone) effect of modified atmosphere packaging and previous frozen storage. *Journal of Applied Microbiology* **101**, 80 – 95.

Dashdorj, D., Tripathi, V. K., Cho, S., Kim, Y., Hwang, I. (2016) Dry aging of beef. *Journal of Animal Science and Technology* **58**: 20. doi: 10.1186/s40781-016-0101-9

Dave, D., Ghaly A. E. (2011). Meat Spoilage Mechanisms and Preservation Techniques: A Critical Review. *American Journal of Agricultural and Biological Sciences* 6, 486-510.

de Blackburn, C. (2006) *Food Spoilage Microorganisms*, 1st Edition, Elsevier.

Del Rio, E., Panizo-Moran, M., Prieto, M., Alonso-Calleja C., Capita, R. (2007) Effect of various chemical decontamination treatments on natural microflora and

1559 sensory characteristics of poultry. *International Journal of Food Microbiology* **76**,
1560 201 – 207.

1561

1562 del Valle M. (2010) Electronic Tongues Employing Electrochemical Sensors.
1563 *Electroanalysis* **22**, 1539 – 1555.

1564 del Valle, M. (2012) Sensor Arrays and Electronic Tongue Systems. *International*
1565 *Journal of Electrochemistry* **2012**, Article ID 986025, 11 pages.
1566 http://dx.doi.org/10.1155/2012/986025

1567 del Valle, M. (2012) Sensor Arrays and Electronic Tongue Systems. *International*
1568 *Journal of Electrochemistry* **2012**, Article ID 986025, 11 pages.
1569 doi:10.1155/2012/986025

1570 del Valle, M., Cetó, X., Gutierrez-Capitán, M. (2014) *BioElectronic tongues: When*
1571 *the sensor array incorporate biosensors*, pp. 211-246, in Multisensor Systems for
1572 Chemical Analysis: Materials and Sensors. Lvova, L., Kirsanov, D., Di Natale, C.,
1573 Legin, A. (Eds.) CRC Press.

1574 Dervisevic, M., Custiuc, E., Çevik, E., Durmus, Z., Senel, M., Durmus, A. (2015)
1575 Electrochemical biosensor based on REGO/Fe_3O_4 bionanocomposite interface for
1576 xanthine detection in fish sample. *Food Control* **57**, 402 – 410.

1577 Dervisevic, M., Custiuc, E., Çevik, E., Senel, M. (2015) Construction of novel
1578 xanthine biosensor by using polymeric mediator/MWCNT nanocomposite layer for
1579 fish freshness detection. *Food Chemistry* **181**, 277 – 283.

1580 Di Rosa, A. R., Leone, F., Cheli, F., Chiofalo V. (2017) Fusion of electronic nose,
1581 electronic tongue and computer vision for animal source food authentication and
1582 quality assessment - A review. *Journal of Food Engineering* **210**, 62 – 75.

1583 Dias, L. G., Veloso, A. C.A., Sousa, M. E. B. C., Estevinho, L., Machado, A. A. S. C.,
1584 Peres, A. M. (2015) A novel approach for honey pollen profile assessment using an
1585 electronic tongue and chemometric tools. *Analytica Chimica Acta* **900**, 36 – 45.

1586 Dikeman, M., Devine C., (Eds) (2014) *Encyclopedia of Meat Sciences*, 2nd edition,
1587 Elsevier.

1588 Domínguez, R. B., Moreno-Barón, L., Muñoz, R., Gutiérrez, J. M. (2014)
1589 Voltammetric Electronic Tongue and Support Vector Machines for Identification of
1590 Selected Features in Mexican Coffee. *Sensors* **14**, 17770 – 17785.

1591 Doulgeracki, A.I., Ercolini, D., Villani, F., Nychas, G.J. (2012) Spoilage microbiota
1592 associated to the storage of raw meat in different conditions. *International Journal of*
1593 *Food Microbiology* **157**, 130-141.

1594 Doyle, M.E. (2007) Microbial Food Spoilage – Losses and Control Strategies: a brief
1595 review of the literature. Food Research Institute. Briefings. University of Winsconsin
1596 – Madison. www.wisc.edu/fri.

1597 Dragone, R., Grasso, G., Muccini, M., Toffanin, S. (2017) Portable
1598 Bio/Chemosensoristic Devices: Innovative Systems for Environmental Health and
1599 Food Safety Diagnostics. *Frontiers in Public Health* **5**, 80. doi:
1600 10.3389/fpubh.2017.00080

1601 dry-cured ham, J. Food Sci. 75 M360–M365.

1602 Eckert, C., Pein, M., Reimann, J., Breitkreutz, J. (2013) Taste evaluation of
1603 multicomponent mixtures using a human taste panel, electronic taste sensing systems
1604 and HPLC. *Sensors and Actuators B: Chemical* **182**, 294-299.

1605 El Barbri, N., Llobet, E., El Bari, N., Correig, X., and Bouchikhi, B., 2008. Electronic
1606 Nose Based on Metal Oxide Semiconductor Sensors as an Alternative Technique for
1607 the Spoilage Classification of Red Meat. Sensors, 8, 142-156

1608 El-Nour, K. M. A., Salam, E. T. A., Soliman, H. M., Orabi A. S. (2017) Gold
1609 Nanoparticles as a Direct and Rapid Sensor for Sensitive Analytical Detection of
1610 Biogenic Amines. *Nanoscale Research Letters* **12**, 231. DOI 10.1186/s11671-017-
1611 2014-z

1612 Ercolini, D., Russo, F., Nasi, A., Ferranti, P., Villiani, F. (2009) Mesophilic and
1613 psychrothropic bacteria from meat and their spoilage potential in vitro and in beef.
1614 Applied and Environmental Microbiology **75**, 1990-2001.

1615 Ercolini, D., Russo, F., Torrieri, E., Masi, P., Villani, F. (2006) Changes in the
1616 spoilage –related microbiota of beef during refrigerated storage under different
1617 packaging conditions. *Applied and Environmental Microbiology* **72**, 4663-4671.

1618 Esposto, S., Servili, M., Selvaggini, R., Ricc, I., San, V., & Perugia, C. (2006).
1619 Discrimination of virgin olive oil defects - comparison of two evaluation methods :
1620 HS-SPME GC-MS and electronic nose, 315–318.

1621 Estelles-Lopez et al., 2017. An automated ranking platform for machine learning
1622 regression models for meat spoilage prediction using multi-spectral imaging and
1623 metabolic profiling. Food Research International, In press,
1624 http://dx.doi.org/10.1016/j.foodres.2017.05.013

1625 FAO. (2011) Global food losses and food waste – Extent, causes and prevention.

1626

1627 Feng, C., Teuber, S., Gershwin, M.E. (2016) Histamine (Scombroid) Fish Poisoning:
1628 a Comprehensive Review. *Clinical Reviews in Allergy & Immunology* **50**, 64-69.

Fonnesbech Vogel, B., Venkateswaran, K., Satomi, M., Gram, L. (2005) Identification of Shewanella baltica as the most important H2S-producing species during iced storage of Danish marine fish. Appl Environ Microbiol. 71, 6689-97.

Frasco, M. F., Truta, L. A. A. N. A., Sales, M. G. F., Moreira, F. T. C. (2017) Imprinting Technology in Electrochemical Biomimetic Sensors. *Sensors* **17**, 523. doi:10.3390/s17030523

Gamati, S., Luong, J. H. T., Mulchandani, A. (1991) A Microbial Biosensor for Trimethylamine Using *Pseudomonas aminovorans* Cells. *Biosensors and Bioelectronics* **6**, 125-131

Gancarz, M., Wawrzyniak, J., Gawrysiak-Witulska, M., Wiącek, D., Nawrocka, A., Tadla, M., & Rusinek, R. (2017). Application of electronic nose with MOS sensors to prediction of rapeseed quality. Measurement, 103, 227–234. http://doi.org/10.1016/j.measurement.2017.02.042

Ganjali, M. R., Nejad, F. G, Beitollahi, H., Jahani, S., Rezapour, M., Larijani B. (2017) Highly Sensitive Voltammetric Sensor for Determination of Ascorbic Acid Using Graphite Screen Printed Electrode Modified with ZnO/Al_2O_3 Nanocomposite. *International Journal of Electrochemical Science* **12**, 3231 – 3240.

Gardner, J. W., & Bartlett, P. N. (1994). A brief history of electronic noses. Sensors and Actuators B, 19, 18–19. http://doi.org/10.1016/0925-4005(94)87085-3

Gerstl, M., Joksch, M., Fafilek, G. (2013) Designing a Simple Electronic Tongue for Fermentation Monitoring. *Journal of Analytical & Bioanalytical Techniques* **S12**: 002. doi: 10.4172/2155-9872.S12-002

1653 Ghaly, A.E., Dave, D., Budge, S., Brooks, M.S. (2010) Fish Spoilage Mechanisms
1654 and Preservation Techniques: Review. *American Journal of Applied Sciences* **7**, 859 -
1655 877.

1656 Ghanbari, M., Ja,I, M., Domig, K.J., Kneifel, W. (2013) Seafood biopreservation by
1657 lactic acid bacteria – A review. *LWT Food Science and Technology* **54**, 315 – 324.

1658 Ghasemi-Varnamkhasti M, Aghbashlo M (2014) Electronic nose and electronic
1659 mucosa as innovative instruments for real time monitoring of food dryers Trends in
1660 Food Science & Technology 38:158-166.

1661 Ghasemi-Varnamkhasti M, Mohtasebi S, Rodriguez-Mendez M, Lozano J, Razavi S,
1662 Ahmadi H, Apetrei C (2012) Classification of non-alcoholic beer based on aftertaste
1663 sensory evaluation by chemometric tools. Expert Systems with Applications 39,4315-
1664 4327.

1665 Ghasemi-Varnamkhasti, M., Rodríguez-Méndez, M. L., Mohtasebi, S. S., Apetrei, C.,
1666 Lozano, J., Ahmadi, H., Razavi, S. H., de Saja, J. A. (2012) Monitoring the aging of
1667 beers using a bioelectronic tongue. *Food Control* **25**, 216-224.

1668 Gil, L., Barat, J. M., Baigts, D., Martínez-Máñez, R., Soto, J., Garcia-Breijo, E.,
1669 Aristoy, M. C., Toldrá, F., Llobet E. (2011) Monitoring of physical–chemical and
1670 microbiological changes in fresh pork meat under cold storage by means of a
1671 potentiometric electronic tongue. *Food Chemistry* **126**, 1261 – 1268.

1672 Gil-Sanchez, L., Soto, J., Martinez-Mañez, R., Garcia-Breijo, E., Ibañez, J., & Llobet,
1673 E. (2011). A novel humid electronic nose combined with an electronic tongue for
1674 assessing deterioration of wine. Sensors and Actuators, A: Physical, 171(2), 152–158.
1675 http://doi.org/10.1016/j.sna.2011.08.006.

1676 Gil-Sánchez, L., Soto, J., Martínez-Máñez, R., Garcia-Breijo, E., Ibáñez, J., Llobet, E.
1677 (2011) A novel humid electronic nose combined with an electronic tongue for
1678 assessing deterioration of wine. *Sensors and Actuators A* **171**, 152 – 158.
1679 Girón, J., Gil-Sánchez, L., García-Breijo, E., Pagána, M. J., Barat, J. M., Grau, R.
1680 (2015) Development of potentiometric equipment for the identification of altered dry-
1681 cured hams: A preliminary study. *Meat Science* **106**, 1 – 5.
1682 Gobbi, E., Falasconi, M., Concina, I., Mantero, G., Bianchi, F., Mattarozzi, M., …
1683 Sberveglieri, G. (2010). Electronic nose and Alicyclobacillus spp. spoilage of fruit
1684 juices: An emerging diagnostic tool. Food Control, 21(10), 1374–1382.
1685 http://doi.org/10.1016/j.foodcont.2010.04.011

1686 Gobbi, E., Falasconi, M., Concina, I., Mantero, G., Bianchi, F., Mattarozzi, M.,
1687 Musci, M., Sberveglieri, G., 2010. Electronic nose and Alicyclobacillus spp. spoilage
1688 of fruit juices: an emerging diagnostic tool. Food Control 21, 1374–1382.

1689 Gobbi, E., Falasconi, M., Zambotti, G., Sberveglieri, V., Pulvirenti, A., &
1690 Sberveglieri, G. (2015). Rapid diagnosis of Enterobacteriaceae in vegetable soups by
1691 a metal oxide sensor based electronic nose. Sensors and Actuators, B: Chemical,
1692 207(PB), 1104–1113. http://doi.org/10.1016/j.snb.2014.10.051

1693 Godziszewska, J., et al., 2017. A simple method of the detection of pork spoilage
1694 caused by *Rahnella aquatilis. LWT, IN press, DOI;* 10.1016/j.lwt.2017.05.049.
1695 Gorton L. (2005) *Biosensors and Modern Biospecific Analytical Techniques*. Elsevier.
1696 Gram, L., Ravn, L., Rasch, M., Bruhn, J.B., Christensen, A.B., Givskov, M. (2002)
1697 Food spoilage – interactions between food spoilage bacteria. *International Journal of*
1698 *Food Microbiology* **78**, 79-97.

1699 Grumezescu A. (Ed.) (2016) *Nanobiosensors*, Volume 8, 1st Edition. Academic Press,
1700 Amsterdam.
1701 Gu, X., Sun, Y., Tu, K., & Pan, L., 2017. Evaluation of lipid oxidation of Chinese-
1702 style sausage during processing and storage based on electronic nose. Meat Science,
1703 133, 1–9
1704 Guadarrama, A., Fernández, J. A., Íñiguez, M., Souto, J., & De Saja, J. A. (2000).
1705 Array of conducting polymer sensors for the characterisation of wines. Analytica
1706 Chimica Acta, 411(1–2), 193–200. http://doi.org/10.1016/S0003-2670(00)00769-8
1707 Gul, I., Sheeraz Ahmad, M., Saqlan Naqvi, S. M., Hussain, A., Wali, R., Farooqi, A.
1708 A., Ahmed, I. (2017) Polyphenol oxidase (PPO) based biosensors for detection of
1709 phenolic compounds: A Review. *Journal of Applied Biology & Biotechnology* **5**, 072
1710 – 085.
1711 Guo, X.S., Chen, Y.Q., Yang, X.L., Wang, L.R. (2005) Development of a novel
1712 electronic tongue system using sensor array based on polymer films for liquid phase
1713 testing. *2005 IEEE Engineering in Medicine and Biology*, 27th Annual Conference,
1714 Shanghai, 259 - 262.
1715 Gupta, V.K., Jain, R., Radhapyari, K., Jadon, N., Agarwal, S. (2011) Voltammetric
1716 techniques for the assay of pharmaceuticals-a review. *Analytical Biochemistry* **408**,
1717 179 - 96.
1718 Gutiérrez, J. M., Haddi, Z., Amari, A., Bouchikhi, B., Mimendia, A., Cetó, X., del
1719 Valle, M. (2013) Hybrid electronic tongue based on multisensor data fusion for
1720 discrimination of beers. *Sensors and Actuators B: Chemical* **177**, 989 – 996.
1721 Gutiérrez, M., Llobera, A., Vila-Planas, J., Capdevila, F., Demming, S., Büttgenbach,
1722 S., Mínguez, S., Jiménez-Jorquera, C. (2010) Hybrid electronic tongue based on

1723 optical and electrochemical microsensors for quality control of wine. *Analyst* **135**:
1724 1718 - 1725.
1725 Gutiérrez-Capitán, M., Vila-Planas, J., Llobera, A., Jiménez-Jorquera, C., Capdevila,
1726 F., Domingo, C., Puig-Pujol, A. (2014) Hybrid electronic tongues based on
1727 microsensors applied to wine quality control. *IEEE Sensors 2014 Proceedings,*
1728 Valencia, 2130 - 2133.
1729 Haddi, Z., El Barbri, N., Tahri, K., Bougrini, M., El Bari, N., Llobet, E., Bouchikhi,
1730 B. (2015) Instrumental assessment of red meat origins and their storage time using
1731 electronic sensing systems. *Analytical Methods* **7**, 5193 – 5203.
1732 Hasan, A., Nurunnabi, M., Morshed, M., Paul, A., Polini, A., Kuila, T., Al Hariri, M.,
1733 Lee, Y., Jaffa, A. A. (2014) Recent Advances in Application of Biosensors in Tissue
1734 Engineering. *BioMed Research International* **2014**, Article ID 307519, 18 pages.
1735 Haugen, J.E., 2006. Rapid control of smoked Atlantic salmon (Salmo salar) quality by
1736 electronic nose: Correlation with classical evaluation methods. Sensors and Actuators
1737 B 116, 72–77.
1738 Hayashi, K., Yamanaka, M., Toko, K., Yamafuji, K. (1990) Multi-channel taste
1739 sensor using lipid membranes. *Sensors and Actuators B: Chemical* **2**, 205 – 213.
1740 Hernandez-Macedo, M.L., Contreras-Castillo, C.J., Tsai, S.M., Da Cruz, S.H.,
1741 Sarantoupoulous, C.I.G.L., Padula, M., Dias, C.T.S. (2012) Gases and volatile
1742 compounds associated with microorganisms in blown pack spoilage of Brazilian
1743 vacuum-packed beef. *Letters in Applied Microbiology* **55**, 467-475.
1744 http://www.fao.org/docrep/014/mb060e/mb060e.pdf
1745 Huang, X. C., Guo, C. F., Yuan, Y. H., Luo, X. X., & Yue, T. L. (2015). Detection of
1746 medicinal off-flavor in apple juice with artificial sensing system and comparison with

1747 test panel evaluation and GC-MS. Food Control.
1748 http://doi.org/10.1016/j.foodcont.2014.11.037

1749 Huis int. Veld., J.H.J. (1996) Microbial and biochemical spoilage of food; an
1750 overview. *International Journal of Food Microbiology* **33**, 1-18.

1751 Hungaro, H.M., Caturla, M.Y.R., Horita, C.N., Furtado, M.M. Sant Ana, A.S. (2016)
1752 Blown pack spoilage in vacuum-packaged meat: a review on clostridia as causative
1753 agents, sources, detection methods, contributing factors and mitigation strategies.
1754 *Trends in Food Science and Technology*, **52**, 123 -138.

1755 Hurrell, R. (2010) Use of ferrous fumarate to fortify foods for infants and young
1756 children. *Nutrition Reviews* **68**, 522-530.

1757 Iiyama, S., Miyazaki, Y., Hayashi, K., Toko, K., Yamafuji, K., Ikezaki, H., Sato, K.
1758 (1992) Highly sensitive detection of taste substances using monolayer lipid
1759 membranes. *Sensors Materials* **4**, 21 – 27.

1760 Immohr, L. I., Hedfeld, C., Lang, A., Pein, M. (2017) Suitability of e-tongue sensors
1761 to assess taste-masking of pediatric liquids by different beverages considering their
1762 physico-chemical properties. *AAPS PharmSciTech* **18**, 330 – 340.

1763 Ispas, C. R., Crivat, G., Andreescu, S. (2012) Review: Recent Developments in
1764 Enzyme-Based Biosensors for Biomedical Analysis. *Analytical Letters* **45**, 168 – 186.

1765 Iulietto, M. F., Sechi, P., Borgogni, E., Cenci-Goga, B. T. (2015) Meat Spoilage: A
1766 Critical Review of a Neglected Alteration Due to Ropy Slime Producing Bacteria.
1767 *Italian Journal of Animal Science* **14**, Article 4011,
1768 http://dx.doi.org/10.4081/ijas.2015.4011

1769

1770 Jaaskelainen, E., Hultman, J., Parshintsev, J., Riekkola, M-L., Bjorkroth, J. (2016)
1771 Development of spoilage bacterial community and volatile compounds in chilled beef
1772 under vacuum or high oxygen atmospheres. *International Journal of Food*
1773 *Microbiology* **223**, 25-32.

1774 Jaffres, E., Lalanne, V., Mace, S., Cornet, J., Cardinal, M., Serot, T., Dousset, X.
1775 Joffraud, J.J., (2011) Sensory characteristics of spoilage and volatile compounds
1776 associated with bacteria isolated from cooked and peeled tropical shrimps using
1777 SPME-GC-MS analysis. *International Journal of Food Microbiology* **147**, 195 - 202.

1778 Jaffres, E., Sohier, D., Leroi, F., Pilet, M.F., Prevost, H., Joffraud, J.J., Dousset, X.
1779 (2009) Study of the bacterial ecosystem in tropical cooked and peeled shrimps using a
1780 polyphasic approach. *International Journal of Food Microbiology* **131**, 20-29.

1781 Jain, H., Panchal, R., Pradhan, P., Patel, H., Pasha, T. (2010) Electronic tongue: A
1782 new taste sensor. *International Journal of Pharmaceutical Sciences Review and*
1783 *Research* **5**, 91 – 96.

1784 Jay, J.M. (1986) Microbial spoilage indicators and metabolites. In: Pierson, M.D.,
1785 Sterm, N.J. (Eds.) Food-Borne Microorganisms and their toxins: Developing
1786 Methodology, Marcel Dekker, Inc., New York, N.Y., pp. 219-240.

1787 Jorgenson, L.V., Huss, H.H, Dalgaard, P. (2000) The effect of biogenic amine
1788 production by single bacterial cultures and metabiosis on cold-smoked salmon.
1789 *Journal of Applied Microbiology* **89**, 920 – 934.

1790 Kalit, M. T., Marković, K., Kalit, S., Vahčić, N., Havranek, J. (2014) Electronic nose
1791 and electronic tongue in the dairy industry. *Mljekarstvo* **64**, 228 – 244.

1792 Kaneki, N., Miura, T., Shimada, K., Tanaka, H., Ito, S., Hotori, K., Akasaka, C.,
1793 Ohkubo, S., Asano, Y. (2004) Measurement of pork freshness using potentiometric
1794 sensor. *Talanta* **62**, 217 - 221.
1795 Kangas, M. J., Burks, R. M., Atwater, J., Lukowicz, R. M., Williams, P., Holmes, A.
1796 E. (2017) Colorimetric Sensor Arrays for the Detection and Identification of Chemical
1797 Weapons and Explosives. *Critical Reviews in Analytical Chemistry* **47**, 138 – 153.
1798 Karovičová, J., Kohajdová, Z. (2005) Biogenic Amines in Food. *Chemical Papers* 59,
1799 70 – 79.
1800 Keow, C. M.,. Bakar, F. A, Salleh, A. B., Heng, L. Y., Wagiran, R., Bean, L. S.
1801 (2007) An amperometric biosensor for the rapid assessment of histamine level in tiger
1802 prawn (*Penaeus monodon*) spoilage. *Food Chemistry* **105**, 1636 – 1641.
1803 Khan, M. R. R., Khalilian, A., Kang S. W. (2016) A High Sensitivity IDC-Electronic
1804 Tongue Using Dielectric/Sensing Membranes with Solvatochromic Dyes. *Sensors* **16**,
1805 668. doi:10.3390/s16050668
1806 Khan, M. R. R., Khalilian, A., Kang, S.-W. (2016) A High Sensitivity IDC-Electronic
1807 Tongue Using Dielectric/Sensing Membranes with Solvatochromic Dyes. *Sensors* **16**,
1808 668. doi: 10.3390/s16050668.
1809 Khulal, U., Zhao, J., Hu, W., Chen, Q., 2017. Intelligent evaluation of total volatile
1810 basic nitrogen (TVB-N) contentin chicken meat by an improved multiple level data
1811 fusion model. Sensors and Actuators B 238 (2017) 337–345
1812 Kiani S, Minaei S, Ghasemi-Varnamkhasti M (2016) Fusion of artificial senses as a
1813 robust approach to food quality assessment Journal of Food Engineering 171:230-239.
1814 Kodogiannis, V.S., 2017. Application of an Electronic Nose Coupled with Fuzzy-
1815 Wavelet Network for the Detection of Meat Spoilage. Food Bioprocess Technology,
1816 10,730–749.

1817 Korkeala, H., Suortti, T., MäkeläRopy, P. (1998) Slime formation in vacuum-packed
1818 cooked meat products caused by homofermentative lactobacilli and a *Leuconostoc*
1819 species. International Journal of Food Microbiology, 7, 339-347.

1820 Koutsoumanis, K., Nychas, G.J.E. (2000) Application of a systematic experimental
1821 procedure to develop a microbial model for rapid fish shelf-life predictions.
1822 *International Journal of Food Microbiology*, 60, 171 -174.

1823 Kress-Rogers, E., D'Costa, E. J., Sollars, J. E., Gibbs, P. A., Turner, A. P. F. (1993)
1824 Measurement of meat freshness *in situ* with a biosensor array. *Food Control* **4**, 149 –
1825 154.

1826 Kumar, H., Neelam, R. (2016) Enzyme-based electrochemical biosensors for food
1827 safety: a review. *Nanobiosensors in Disease Diagnosis* **5**, 29 – 39.

1828 Kumar, S., Ghosh, A., Tudu, B., Bandyopadhyay, R. (2017) An equivalent electrical
1829 network of an electronic tongue: A case study with tea samples, *2017 ISOCS/IEEE*
1830 *International Symposium on Olfaction and Electronic Nose (ISOEN)*, Montreal, QC,
1831 Canada, 1 - 3.

1832 Kvasničk, F., Voldřich, M. (2000) Determination of fumaric acid in apple juice by on-
1833 line coupled capillary isotachophoresis–capillary zone electrophoresis with UV
1834 detection. *Journal of Chromatography A* **891**, 175 – 181.

1835 Latorre-Moratalla, M.L., Bover-Cidl, S., Bosch-Fuste, J., Vidal-Carou, M.C. (2012)
1836 Influence of technological conditions of sausage fermentation on the aminogenic
1837 activity of L. curvatus CTC273. *Food Microbiology* 29, 43 -48.

1838 Laursen, B.G., Bay, L., Cleenwerck, I., Vancanneyt, M., Swings, J., Dalgaard, P.,
1839 Leisner, J.J. (2005) *Carnobacterium divergens* and *Carnobacterium maltaromaticum*

1840 as spoilers or protective cultures in meat and seafood: phenotypic and genotypic
1841 characterization. *Systematic and Applied Microbiology* **28**, 151 – 164.

1842 Leca-Bouvier, B., Blum, L. J. (2005) Biosensors for Protein Detection: A Review.
1843 *Analytical Letters* **38**, 1491 – 1517.

1844 Ledenbach, L.H., and Marshall, R.T. (2009) Microbiological Spoilage of Dairy
1845 Products. In W.H. Sperber, M.P. Doyle (eds.), Compendium of the Microbiological
1846 Spoilage of Foods and Beverages, Food Microbiology and Food Safety, Springer
1847 Verlag New York.

1848 Leduc, F., Tournayre, P., Kondjoyan, N., Mercier, F., Malle,P., Kol, O., Berdagué,
1849 J.L., Duflos, G. (2012) Evolution of volatile odorous compounds during the storage of
1850 European seabass (Dicentrarchus labrax). Food Chemistry, 131, 1304-1311.

1851 Legin, A., Rudnitskaya, A., Clapham, D., Seleznev, B., Lord, K. & Vlasov, Y. (2004)
1852 Electronic tongue for pharmaceutical analytics: quantification of tastes and masking
1853 effects. *Analytical and Bioanalytical Chemistry* **380**, 36 – 45.

1854

1855 Legin, A., Rudnitskaya, A., Di Natale, C., Mazzone, E., D'Amico, A. (2000)
1856 Application of electronic tongue for qualitative and quantitative analysis of complex
1857 liquid media. *Sensors and Actuators B: Chemical* **65**, 232 – 234.

1858 Lerma-García, M. J., Cerretani, L., Cevoli, C., Simó-Alfonso, E. F., Bendini, A., &
1859 Toschi, T. G. (2010). Use of electronic nose to determine defect percentage in oils.
1860 Comparison with sensory panel results. Sensors and Actuators, B: Chemical, 147(1),
1861 283–289. http://doi.org/10.1016/j.snb.2010.03.058

1862 Li, C., Heinemann, P., & Sherry, R. (2007). Neural array and Bayesian array fusion
1863 models to fuse electronic nose and surface acoustic wave sensor data for apple defect

1864 detection. Sensors and Actuators, B: Chemical, 125(1), 301–310.
1865 http://doi.org/10.1016/j.snb.2007.02.027.

1866 Lim, J. W., Ha, D., Lee, J., Lee, S. K., Kim T. (2015) Review of
1867 Micro/Nanotechnologies for Microbial Biosensors. *Frontiers in Bioengineering and*
1868 *Biotechnology* **3**, 61. doi: 10.3389/fbioe.2015.00061

1869 Liu, Q., Wu, C., Cai, H., Hu, N., Zhou, J., Wang, P. (2014) Cell-Based Biosensors
1870 and Their Application in Biomedicine. *Chemical Reviews* **114**, 6423 – 6461.

1871 Lopez-Caballero, M.E., Sanchez-Fernandez, J.A., Moral, A., (2001) Growth and
1872 metabolic activity of *Shewanella putrefaciens* maintained under different CO_2 and O_2
1873 concentrations. *International Journal of Food Microbiology* 64, 277-287.

1874 Lovdal, T. (2015) The microbiology of cold salmon. Food Control 54, 360 – 373.

1875 Lozano, J. (2006) New technology in sensing odours: from human to artificial noses.
1876 In: Teixeira da Silva JA (Ed) (2006) Floriculture, Ornamental and Plant
1877 Biotechnology: Advances and Topical Issues (1st Edn, Vol IV), Global Science
1878 Books, London, pp 152-161

1879 Lozano, J., Álvarez, F., Santos, J.P., Horrillo, C., (2011). Detection of acetic acid in
1880 wine by means of an electronic nose. In: AIP Conference Proceedings - ISOEN11, pp.
1881 176–177.

1882 Lozano, J., Santos, J. P., Gutiérrez, J., & Horrillo, M. C. (2007). Comparative study of
1883 sampling systems combined with gas sensors for wine discrimination. Sensors and
1884 Actuators B: Chemical, 126(2), 616–623. http://doi.org/10.1016/j.snb.2007.04.018

1885 Lozano, J., Santos, J. P., Suarez, J. I., Cabellos, M., Arroyo, T., & Horrillo, C. (2015).
1886 Automatic Sensor System for the Continuous Analysis of the Evolution of Wine.

American Journal of Enology and Viticulture, 66(2), 148–155. http://doi.org/10.5344/ajev.2014.14103

Luten J.B. (2006) *Seafood Research from Fish to Dish: Quality, Safety and Processing of Wild and Farmed Fish*. Wageningen Academic Pub.

Lvova, L., Di Natale, C., Paolesse, R. (2017) Electronic tongue based on porphyrins for Apulian red wines defects detection, *2017 ISOCS/IEEE International Symposium on Olfaction and Electronic Nose (ISOEN)*, Montreal, QC, Canada, 1 - 2.

Lytou, A.E., Panagou, Z.E., Nychas, G.J.E (2017) Effect of different marinating conditions on the evolution of spoilage microbiota and metabolomic profile of chicken breast fillets. Food Microbiol. 66, 141 -179.

Mace, S., Cornet, J., Chevalier, F., Cardinal, M., Pilet, M-F., Dousset, X., Joffrau, J-J. (2012) Characterisation of the spoilage microbiota in raw salmon (Salmo salar) steaks stored under vacuum or modified atmosphere packaging combining conventional methods and PCR-TTGE. *Food Microbiology* **30**, 164-172.

Macías, M., Manso, A., Orellana, C., Velasco, H., Caballero, R., & Chamizo, J. (2012). Acetic Acid Detection Threshold in Synthetic Wine Samples of a Portable Electronic Nose. Sensors, 13(1), 208–220. http://doi.org/10.3390/s130100208

Maffei M.E. (2010) Sites of synthesis, biochemistry and functional role of plant volatiles. *South African Journal of Botany* **76**, 612 – 631.

Magan, N., & Evans, P. (2000). Volatiles as an indicator of fungal activity and differentiation between species, and the potential use of electronic nose technology for early detection of grain spoilage. Journal of Stored Products Research. http://doi.org/10.1016/S0022-474X(99)00057-0

1910 Magan, N., Pavlou, A., & Chrysanthakis, I. (2001). Milk-sense: A volatile sensing
1911 system recognizes spoilage bacteria and yeasts in milk. Sensors and Actuators, B:
1912 Chemical, 72(1), 28–34. http://doi.org/10.1016/S0925-4005(00)00621-3

1913 Mancini, R. A., & Hunt, M. C. (2005). Current research in meat colour. Meat Science,
1914 71, 100-121.

1915 Marín, S., Vinaixa, M., Brezmes, J., Llobet, E., Vilanova, X., Correig, X., … Sanchis,
1916 V. (2007). Use of a MS-electronic nose for prediction of early fungal spoilage of
1917 bakery products. International Journal of Food Microbiology, 114(1), 10–16.
1918 http://doi.org/10.1016/j.ijfoodmicro.2006.11.003

1919 Martin, A., Benito, M.J., Aranda, E., Ruiz-Moyano, S., Cordoba, J.J., Cordoba, M.J.
1920 (2010) Characterization by volatile compounds of microbial deep spoilage in Iberian

1921 Martínez-Bisbal, M. C., Loeff, E., Olivas, E., Carbó, N., García-Castillo, F. J., López-
1922 Carrero, J., Tormos, I., Tejadillos, F. J., Berlanga, J. G., Martínez-Máñez, R., Alcañiz,
1923 M., Soto, J. (2017) A Voltammetric Electronic Tongue for the Quantitative Analysis
1924 of Quality Parameters in Wastewater. *Electroanalysis* **29**, 1147 – 1153.
1925 Matysik F. M. (Ed.) (2017) *Trends in Bioelectroanalysis*. Springer International
1926 Publishing AG.
1927 McGrath, T.F., Elliott, C.T., Fodey, T.L. (2012) Biosensors for the analysis of
1928 microbiological and chemical contaminants in food. *Analytical and Bioanalytical*
1929 *Chemistry* **403**, 75 - 92.
1930 Medina-Plaza, C., García-Hernandez, C., de Saja, J.A., Fernandez-Escudero, J.A.,
1931 Barajas, E., Medrano, G., García-Cabezon, C., Martin-Pedrosa, F., Rodriguez-
1932 Mendez, M.L. (2015) The advantages of disposable screen-printed biosensors in a

1933 bioelectronic tongue for the analysis of grapes. *LWT - Food Science and Technology*
1934 **62**, 940 – 947.
1935 Mednova, O., Kirsanov, D., Rudnitskaya, A., Kilmartin, P., Legin, A. (2009)
1936 Application Of A Potentiometric Electronic Tongue For The Determination Of Free
1937 SO_2 And Other Analytical Parameters In White Wines From New Zealand. *AIP*
1938 *Conference Proceedings* **1137**, 263. doi: http://dx.doi.org/10.1063/1.3156521
1939 Mehrotra, P. (2016) Biosensors and their applications – A review. *Journal of Oral*
1940 *Biology and Craniofacial Research* **6**, 153 – 159.
1941 Mello, L. D., Kubota, L. T. (2002) Review of the use of biosensors as analytical tools
1942 in the food and drink industries. *Food Chemistry* **77**, 237 – 256.
1943 Membre, J-M., Dagnas, S. (2016) Modelling microbial responses: application to food
1944 spoilage. *Modelling in Food Microbiology* **2016**, 33 – 60.
1945 Mikš-Krajnik, M., Yoon, Y.J., Ukuku, D.O.,Yuk, H.G. (2016) Volatile chemical
1946 spoilage indexes of raw Atlantic salmon (Salmo salar) stored under aerobic condition
1947 in relation to microbiological and sensory shelf lives.Food Microbiol. 53(Pt B), 182-
1948 91.
1949 Mimendia, A., Gutiérrez, J. M., Leija, L., Hernández, P. R., Favari, L., Munoz, R., del
1950 Valle, M. (2010) A review of the use of the potentiometric electronic tongue in the
1951 monitoring of environmental systems. *Environmental Modelling & Software* **25**, 1023
1952 – 1030.
1953 Monošík, R., Streďanský, M., Šturdík, E. (2012) Biosensors - classification,
1954 characterization and new trends. *Acta Chimica Slovaca* **5**, 109 - 120.

1955 Mossel, D.A.A., Corry, J.E.L., Struijk, C.B. and Baird, R.M. (1995) Essentials of the
1956 Microbiology of Foods: a textbook for advanced studies. Wiley, England, pp. 175 –
1957 214.

1958 Murugaboopathi, G., Parthasarathy, V., Chellaram, C., Prem Anand, T.,
1959 Vinurajkumar, S. (2013) Applications of Biosensors in Food Industry. *Biosciences*
1960 *Biotechnology Research Asia* **10**, 711 - 714.

1961 Mutlu, M. (2016) *Biosensors in Food Processing, Safety, and Quality Control*. CRC
1962 Press.

1963 Muzaddadi, A.U., Devatkal, S., Oberoi, H.S. (2016) *Seafood Enzymes and Their*
1964 *Application in Food Processing* – Chapter 9. Agro-Industrial Wastes as Feedstock for
1965 Enzyme Production. Apply and Exploit the Emerging and Valuable Use Options of
1966 Waste Biomass, 201 – 232.

1967 Nagle, H. T. J. W. G. T. C. P. S. S. S. (2006). Handbook of machine olfaction:
1968 electronic nose technology. Aging (Vol. 7). http://doi.org/10.1002/3527601597.

1969 Naila, A., Flint, S., Fletcher, G., Bremer, P., Meerdink, G. (2010) Control of Biogenic
1970 Amines in Food—Existing and Emerging Approaches. *Journal of Food Science* **75**,
1971 R139 – R150.

1972 Narsaiah, K., Jha, S. N., Bhardwaj, R., Sharma, R., Kumar, R. (2012) Optical
1973 biosensors for food quality and safety assurance—a review. *Journal of Food Science*
1974 *and Technology* **49**, 383 – 406.

1975 Ndagijimana,M., Chaves-Lopez, C., Corsetti, A., Tofalo, R., Sergi, M., Paparella, A.
1976 (2008) Growth and metabolites production by *Penicillium brevicompactum* in
1977 yoghurt, Int. J. Food Microbiol. 127 276–283.

1978 Nelson, D. L., Cox, M. M. (2017) *Lehninger Principles of Biochemistry*, 7th Edition,
1979 Macmillan Higher Education, New York.

1980 Nychas, G.J.E., Skandamis, P.N., Tassou, C.C., Koutsoumanis, K.P., (2008) Meat
1981 spoilage during distribution. *Meat Science* **78**, 77 -89.

1982 Oehlenschlager, J. (2014) Seafood quality assessment. In Boziaris, I.S. (Ed.) Seafood
1983 Processing. Technology, Quality and Safety. *IFST Advances in Food Science Series*,
1984 Wiley Blackwell, 361 – 386.

1985 Otto, M., Thomas, J. D. R. (1985) Model studies on multiple channel analysis of free
1986 magnesium, calcium, sodium, and potassium at physiological concentration levels
1987 with ion-selective electrodes. *Analytical Chemistry* **57**, 2647 – 2651.

1988 Paarup, T., Nieto, J. C., Peláez, C., Reguera, J. I. (1999) Microbiological and physico-
1989 chemical characterisation of deep spoilage in Spanish dry-cured hams and
1990 characterisation of isolated Enterobacteriaceae with regard to salt and temperature
1991 tolerance. *European Food Research and Technology* **209**, 366 – 371.

1992 Paludan-Muller, C., Dalgaard, P., Huss, H.H., Gram, L. (1998) Evaluation of the role
1993 of *Carnobacterium piscicola* in spoilage of vacuum- and modified-atmosphere-
1994 packed cold-smoked salmon stored at 5°C. *International Journal of Food*
1995 *Microbiology*, **39**, 155 – 168.

1996 Panigrahi, S., Balasubramanian, S., Gu, H., Logue, C., Marchello, M., 2006a. Neural-
1997 network-integrated electronic nose system for identification of spoiled beef. LWT 39,
1998 135–145.

1999 Panigrahi, S., Balasubramanian, S., Gu, H., Logue, C., Marchello, M., 2006b. Design
2000 and development of a metal oxide based electronic nose for spoilage classification of
2001 beef. Sensors and Actuators B 119, 2–14

2002 Papadopoulou, O.S., Panagou, E.Z., Mohareb, F.R., Nychas, G.E., 2013. Sensory and
2003 microbiological quality assessment of beef fillets using a portable electronic nose in
2004 tandem with support vector machine analysis. Food Research International 50, 241–
2005 249.

2006 Park, Y. W., Kim, S. M., Lee, J. Y., Jang, W. (2015) Application of biosensors in
2007 smart packaging. *Molecular & Cellular Toxicology* **11**, 277 – 285.

2008 Parlapani, F.F., Mallouchos, A., Haroutounian, S.A., Boziaris, I.S. (2017)
2009 Microbiological spoilage and investigation of volatile profile during storage of sea
2010 bream fillets under various conditions. *International Journal of Food Microbiology*
2011 **189**, 153 – 163.

2012 Parpalani, F.F., Boziaris, I.S. (2016) Monitoring of spoilage and determination of
2013 microbial communities based on 16S rRNA gene sequence analysis of whole sea
2014 bream stored at various temperatures. *LWT Food Science and Technology*, **66**, 553 –
2015 559.

2016 Parpalani, F.F., Haroutounian, S.A., Nychas, G.J., Boziaris, I.S. (2015)
2017 Microbiological spoilage and volatiles production of gutted European sea bass stored
2018 under air and commercial modified atmosphere package at 2°C. *Food Microbiology*
2019 **50**, 44 – 53.

2020 Parpalani, F.F., Meziti, A., Kormas, K.Ar., Boziaris., I.S. (2013) Indigenous and
2021 spoilage microbiota of farmed sea bream stored on ice identified by phenotypic and
2022 16S rRNA gene analysis. Food Microbiology **33**, 85 – 89.

2023 Patel, P. D. (2006) Overview of affinity biosensors in food analysis. *Journal of AOAC*
2024 *International* **89**, 805-818.

2025 Pathange, L. P., Mallikarjunan, P., Marini, R. P., O'Keefe, S., & Vaughan, D. (2006).
2026 Non-destructive evaluation of apple maturity using an electronic nose system. Journal
2027 of Food Engineering, 77(4), 1018–1023.
2028 http://doi.org/10.1016/j.jfoodeng.2005.08.034

2029 Pearce, T. C., Schiffman, S. S., Nagle, H. T., Gardner, J. W. (2006) *Handbook of*
2030 *Machine Olfaction: Electronic Nose Technology*. John Wiley & Sons.

2031 Pein, M., Kirsanov, D., Ciosek, P., del Valle, M., Yaroshenko, I., Wesoły, M.,
2032 Zabadaj, M., Gonzalez-Calabuig, A., Wróblewski, W., Legin, A. (2015) Independent
2033 comparison study of six different electronic tongues applied for pharmaceutical
2034 analysis. *Journal of Pharmaceutical and Biomedical Analysis* **114**, 321-329.

2035 Pennacchia, C., Ercolini, D., Villiani, F. (2011) Spoilage-related microbiota
2036 associated with chilled beef stored in air or vacuum pack. *Food Microbiology* **28,** 84 –
2037 93.

2038 Pérez-López, B., Merkoçi, A. (2011) Nanomaterials based biosensors for food
2039 analysis applications. *Trends in Food Science & Technology* **22**, 625-639.
2040 Peris, M., Escuder-Gilabert, L. (2013) On-line monitoring of food fermentation
2041 processes using electronic noses and electronic tongues: A review. *Analytica Chimica*
2042 *Acta* **804**, 29 – 36.
2043 Peris, M., Escuder-Gilabert, L. (2013). On-line monitoring of food fermentation
2044 processes using electronic noses and electronic tongues: a review. Analytica Chimica
2045 Acta, 804(4), 29-36.

2046 Perry, N. (2012) Dry aging beef. *International Journal of Gastronomy and Food*
2047 *Science* 1, 78 – 80.

2048 Pinu, F., 2016. Early detection of food pathogens and food spoilage microorganisms:
2049 Application of metabolomics. *Trends in Food Science & Technology* 54, 213-215.

2050 Pioggia, G., Di Francesco, F., Marchetti, A., Ferro, M., Leardi, R., Ahluwalia, A.
2051 (2007) A composite sensor array impedentiometric electronic tongue: Part II.
2052 Discrimination of basic tastes. *Biosensors and Bioelectronics* **22**, 2624 – 2628.

2053 Piriya, V. S. A., Joseph, P., Daniel, S. C. G. K., Lakshmanan, S., Kinoshita, T.,
2054 Muthusamy, S. (2017) Colorimetric sensors for rapid detection of various analytes.
2055 *Materials Science & Engineering. C, Materials for Biological Applications* **78**, 1231 -
2056 1245.

2057 Pividori, M. I., Alegret S. (2010) Electrochemical biosensors for food safety.
2058 *Contributions to Science* **6**, 173 – 191.

2059 Poltronieri, P., Mezzolla, V., Primiceri, E., Maruccio G. (2014) Biosensors for the
2060 Detection of Food Pathogens. *Foods* **3**, 511 – 526.

2061 Prodromidis, M. I., Karayannis, M. I. (2002) Enzyme Based Amperometric
2062 Biosensors for Food Analysis. *Electroanalysis* **14**, 241 – 261.

2063 Quigely, L., O'Sullivan, O., Stanton, C., Beresford, T.P., Ross, R.P., Fitzgerals, G.F.,
2064 Cotter, P.D. (2013) The complex microbiota of raw milk. *FEMS Microbiol Rev.* **37**,
2065 664 -698.

2066 Ragazzo-Sanchez, J. A., Chalier, P., Chevalier-Lucia, D., Calderon-Santoyo, M., &
2067 Ghommidh, C. (2009). Off-flavours detection in alcoholic beverages by electronic
2068 nose coupled to GC. Sensors and Actuators, B: Chemical, 140(1), 29–34.
2069 http://doi.org/10.1016/j.snb.2009.02.061

2070 Rajamaki, T., Alakomi, H., Ritvanen, T., Skytta, E., Smolander, M., Ahvenainen, R.,
2071 2006. Application of an electronic nose for quality assessment of modified
2072 atmosphere packaged poultry meat. Food Control 17, 5–13.

2073 Ramirez-Guizar, S., Sykes, H., Perry, J.D., Schwalbe, E.C., Stanforth, S.P., Perez-
2074 Perez, C.I.M., Dean, J.R. (2017) A chromatographic approach to distinguish Gram-
2075 positive from Gram-negative bacteria using exogenous volatile organic compound
2076 metabolites. *Journal of Chromatography A* **1501**, 79-88.

2077 Remenant, B., Jaffres, E., Dousset, X., Pilet, M-F., Zagorec, M. (2015) Bacterial
2078 spoilers of food: Behaviour, fitness and functional properties. *Food Microbiology* **45**,
2079 45 -53.

2080 Riul Jr., A., dos Santos Jr., D. S., Wohnrath, K., Di Tommazo, R., Carvalho, A. C. P.
2081 L. F., Fonseca, F. J., Oliveira Jr., O. N., Taylor, D. M., Mattoso, L. H. C. (2002)
2082 Artificial Taste Sensor: Efficient Combination of Sensors Made from Langmuir-
2083 Blodgett Films of Conducting Polymers and a Ruthenium Complex and Self-
2084 Assembled Films of an Azobenzene-Containing Polymer. *Langmuir* **18**, 239 – 245.
2085 Rodríguez-Delgado, M. M., Alemán-Nava, G. S., Rodríguez-Delgado, J. M., Dieck-
2086 Assad, G., Martínez-Chapa, S. O., Barceló, D., Parra, R. (2015) Laccase-based
2087 biosensors for detection of phenolic compounds. *Trends in Analytical Chemistry* **74**,
2088 21 – 45.
2089 Rodriguez-Méndez, M. L., Medina-Plaza, C., García-Hernández, C., de Saja, J. A.,
2090 Fernández-Escudero J. A., Barajas-Tola, E., Medrano G. (2014) Analysis of grapes
2091 and wines using a voltammetric bioelectronic tongue. Correlation with the phenolic
2092 and sugar content. *IEEE Sensors 2014 Proceedings*, Valencia, 2139 - 2142.

2093 Rodríguez-Méndez, M.L., Apetrei, C., de Saja, J.A. (2008) Evaluation of the
2094 polyphenolic content of extra virgin olive oils using an array of voltammetric sensors.
2095 *Electrochimica Acta* **53**, 5867 – 5872.
2096 Rodríguez-Méndez, M.L., Gay, M., Apetrei, C., de Saja, J.A. (2009) Biogenic amines
2097 and fish freshness assessment using a multisensor system based on voltammetric
2098 electrodes. Comparison between CPE and screen-printed electrodes. *Electrochimica*
2099 *Acta* **54**, 7033 – 7041.
2100 Rogers, K. R. (2000) Principles of affinity-based biosensors. *Molecular*
2101 *Biotechnology* **14**, 109 – 129.
2102 Rotariu, L., Lagarde, F., Jaffrezic-Renault, N., Bala, C. (2016) Electrochemical
2103 biosensors for fast detection of food contaminants –trends and perspective. *TrAC*
2104 *Trends in Analytical Chemistry* **79**, 80 – 87.
2105 Rudnitskaya, A., Polshin, E., Kirsanov, D., Lammertyn, J., Nicolai, B., Saison, D.,
2106 Delvaux, F. R., Delvaux, F., Legin, A. (2009) Instrumental measurement of beer taste
2107 attributes using an electronic tongue. *Analytica Chimica Acta* **646**, 111 – 118.
2108 Rudnitskaya, A., Schmidtke, L. M., Reis, A., Domingues, M. R., Delgadillo, I.,
2109 Debus, B., Kirsanov, D., Legin, A. (2017) Measurements of the effects of wine
2110 maceration with oak chips using an electronic tongue. *Food Chemistry* **229**, 20 - 27.
2111 Ruiz-Rico, M., Fuentes, A., Masot, R., Alcañiz, M., Fernández-Segovia, I., Barat, J.
2112 M. (2013) Use of the voltammetric tongue in fresh cod (*Gadus morhua*) quality
2113 assessment. *Innovative Food Science and Emerging Technologies* **18**, 256 – 263.
2114 Sade, E., Penttinen, K., Bjorkroth, J., Hultman, J. (2017) Exploring lot-to-lot variation
2115 in spoilage bacterial communities on commercial modified atmosphere packaged
2116 beef. *Food Microbiology* **62**, 147 – 152.

2117 Sahu, M., Bala, S. (2017) Food Processing, Food Spoilage and their Prevention: An
2118 Overview. *International Journal of Life-Sciences Scientific Research* **3**, 753 - 759.
2119 Santos, J. P., & Lozano, J. (2015). Real time detection of beer defects with a hand
2120 held electronic nose. In Proceedings of the 2015 10th Spanish Conference on Electron
2121 Devices, CDE 2015. Institute of Electrical and Electronics Engineers Inc.

2122 Santos, J. P., Fernández, M. J., Fontecha, J. L., Lozano, J., Aleixandre, M., García,
2123 M., et al., Horrillo, M. C. (2005). SAW sensor array for wine discrimination. Sensors
2124 and Actuators B: Chemical, 107(1), 291–295.
2125 http://doi.org/10.1016/j.snb.2004.10.013.

2126 Santos, J. P., Lozano, J., Aleixandre, M., Arroyo, T., Cabellos, J. M., Gil, M., &
2127 Horrillo, M. del C. (2010). Threshold detection of aromatic compounds in wine with
2128 an electronic nose and a human sensory panel. Talanta, 80(5), 1899–906.
2129 http://doi.org/10.1016/j.talanta.2009.10.041

2130 Sarnoski, P.J., Jahncke, M.L., O'Keefe, S.F., Mallikarjunan, P., & Flick, G.J.
2131 2008.Journal of Aquatic Food Product Technology, 17(3), 234-252.

2132 Schmidt, V.S.J., Kaufmann, V., Kulozik, U., Scherer, S., Wenning, M. (2012)
2133 Microbial biodiversity, quality and shelf life of microfiltered and pasteurized
2134 extended shelf life (ESL) milk from Germany, Austria and Switzerland. *International*
2135 *Journal of Food Microbiology* **154***,* 1-9.

2136 Schmidtke, L. M., Rudnitskaya, A., Saliba, A. J., Blackman, J. W., Scollary, G. R.,
2137 Clark, A. C., Rutledge, D. N., Delgadillo, I., Legin A. (2010) Sensory, Chemical, and
2138 Electronic Tongue Assessment of Micro-oxygenated Wines and Oak Chip
2139 Maceration: Assessing the Commonality of Analytical Techniques. *Journal of*
2140 *Agricultural and Food Chemistry* **58**, 5026 – 5033.

2141 Scognamiglio, V., Arduini, F., Palleschi, G., Rea, G. (2014) Biosensing technology
2142 for sustainable food safety. *Trends in Analytical Chemistry* **62**, 1 – 10.
2143 Scognamiglio, V., Rea, G., Arduini, F., Palleschi, G. (Eds.) (2016) *Biosensors for*
2144 *Sustainable Food - New Opportunities and Technical Challenges*. Comprehensive
2145 Analytical Chemistry, Volume 74, 3-432, Elsevier BV.
2146 Sehra, G., Cole, M., Gardner, J. W. (2004) Miniature taste sensing system based on
2147 dual SH-SAW sensor device: an electronic tongue. *Sensors and Actuators B:*
2148 *Chemical* **103**, 233 – 239.
2149 Shah, J. S. (2013) An Electronic tongue for core taste identification based on
2150 conductometry. *International Journal of Engineering Research and Applications* **3**,
2151 961 - 963
2152 Shao, Y., Wang, J., Wu, H., Liu, J., Aksay. I. A., Lina, Y. (2010) Graphene Based
2153 Electrochemical Sensors and Biosensors: A Review. *Electroanalysis* **22**, 1027 – 1036.
2154 Sharma, P., Ghosh, A., Tudu, B., Sabhapondit, S., Baruah, B. D., Tamuly, P., …
2155 Bandyopadhyay, R. (2015). Monitoring the fermentation process of black tea using
2156 QCM sensor based electronic nose. Sensors and Actuators, B: Chemical, 219, 146–
2157 157. http://doi.org/10.1016/j.snb.2015.05.013

2158 Si, R. W., Zhai, D. D., Liao, Z. H., Gao, L., Yong, Y. C. (2015) A whole-cell
2159 electrochemical biosensing system based on bacterial inward electron flow for
2160 fumarate quantification. *Biosensors and Bioelectronics* **68**, 34 – 40.
2161 Śliwinska, M., Wisniewska, P., Dymerski, T., Namiesnik, J., Wardencki, W. (2014)
2162 Food Analysis Using Artificial Senses. *Journal of Agricultural and Food Chemistry*
2163 **62**, 1423 – 1448.

2164 Smyth, H., Cozzolino, D. (2013) Instrumental methods (spectroscopy, electronic nose,
2165 and tongue) as tools to predict taste and aroma in beverages: advantages and
2166 limitations. *Chemical Reviews* **113**, 1429 – 1440.

2167 Song, H. S., Jin, H. J., Ahn, S. R., Kim, D., Lee, S. H., Kim, U. K., Simons, C. T.,
2168 Hong, S., Park, T. H. (2014) Bioelectronic tongue using heterodimeric human taste
2169 receptor for the discrimination of sweeteners with human-like performance. *ACS*
2170 *Nano* **8**, 9781 - 9789.

2171 Song, H. S., Jin, H. J., Ahn, S. R., Kim, D., Lee, S. H., Kim, U. K., Simons, C. T.,
2172 Hong, S., Park, T. H. (2014) Bioelectronic Tongue Using Heterodimeric Human Taste
2173 Receptor for the Discrimination of Sweeteners with Human-like Performance. *ACS*
2174 *Nano* **8**, 9781 – 9789.

2175 Song, X., Xu, S., Chen, L., Wei, Y., Xiong, H. (2014) Recent advances in molecularly
2176 imprinted polymers in food analysis. *Journal of Applied Polymer Science* **131**, 40766.
2177 doi: 10.1002/app.40766

2178 Spadafora, N.D., Paramithiotis, S., Drosinos, E., Cammarisano, L., Rogers, H.J.,
2179 Muller, C.T. (2016) Detection of *Listeria monocytogenes* in cut melon fruit using
2180 analysis of volatile organic compounds. *Food Microbiology* **54**, 52 – 59.

2181 Stadler, R. H., Lineback, D. R. (2008) *Process-Induced Food Toxicants: Occurrence,*
2182 *Formation, Mitigation, and Health Risks*. John Wiley & Sons.

2183 Susiluoto, T., Korkeala, H., Bjorkroth, K.J. (2003) *Leuconostoc gasicomitatum* is the
2184 dominating lactic acid bacterium in retail modified-atmosphere-packaged marinated
2185 broiler meat strips on sell-by-day. *International Journal of Food Microbiology* **80**, 89
2186 – 97.

2187 Suzzia, G., Gardini, F. (2002) Biogenic amines in dry fermented sausages: a review.
2188 International Journal of Food Microbiology 88, 41 -54.

2189 Tahara, Y., Toko, K. (2013) Electronic Tongues–A Review. *IEEE Sensors Journal*
2190 **13**, 3001 - 3011.

2191 Tait, E., Stanforth, S.P., Reed, S., Perry, J.D., Dean, J.R. (2014) Use of volatile
2192 compounds as a diagnostic tool for the detection of pathogenic bacteria. Trends Anal.
2193 Chem. 53, 117 -125.

2194 Technologies, Sensors (Basel) 9, 5099–5148.

2195 Tembe, S., D'Souza, S. F. (2015) Immobilisation strategies for construction of
2196 tyrosinase-based biosensors. *Materials Technology* **30**, B190 - B195.

2197 The, K.H., Flint, S., Palmer, J., Andrewes, P., Bremer, P., Lindsay, D. (2014) Biofilm
2198 − An unrecognised source of spoilage enzymes in dairy products? International Dairy
2199 Journal 34, 32-40.

2200 Thévenot, D. R., Toth, K., Durst, R. A., Wilson, G. S. (2001) Electrochemical
2201 biosensors: recommended definitions and classification. *Biosensors and*
2202 *Bioelectronics* **16**, 121 – 131.

2203 Tian, H., Feng, T., Xiao, Z., Song, S., Li, Z., Liu, Q., Mao, D., Li, F. (2015)
2204 Comparison of intensities and binary interactions of four basic tastes between an
2205 electronic tongue and a human tongue. *Food Science and Biotechnology* **24**, 1711 –
2206 1715.

2207 Tian, X., Cai, Q., & Zhang, Y., 2012. Rapid Classification of Hairtail Fish and Pork
2208 Freshness Using an Electronic Nose Based on the PCA Method. *Sensors*, *12*, 260-277.

2209 Timsorn, K., Thoopboochagorn, T., Lertwattanasakul, N., & Wongchoosuk, C.,
2210 (2016). Evaluation of bacterial population on chicken meats using a briefcase
2211 electronic nose. Biosystems Engineering, 151, 116 -125.
2212 Toko K. (2000) *Biomimetic Sensor Technology*, Cambridge University Press.
2213 Toko, K. (1998) Electronic sensing of tastes. *Sensors Update* **3**, 131 – 160.
2214 Turner, A. P. F. (2013) Biosensors: sense and sensibility. *Chemical Society Reviews*
2215 **42**, 3184 – 3196.
2216 ul Hasan, N., Ejaz, N., Ejaz, W., & Kim, H. S. (2012). Meat and fish freshness
2217 inspection system based on odor sensing. Sensors (Basel, Switzerland), 12(11),
2218 15542–15557.
2219 Upadhyay, L. S. B., Verma, N. (2013) Enzyme Inhibition Based Biosensors: A
2220 Review. *Analytical Letters* **46**, 225 – 241.
2221 Upadhyay, R., Sehwag, S., & Mishra, H. N. (2017). Electronic nose guided
2222 determination of frying disposal time of sunflower oil using fuzzy logic analysis.
2223 Food Chemistry, 221, 379–385. http://doi.org/10.1016/j.foodchem.2016.10.089

2224 Valerio, F., De Bellis, P., Di Biase, M., Lonigro, S.L., Giussani, B., Visconti, A.,
2225 Lavermicocca, P., Sisto, A. (2012) Diversity of spore forming bacteria and
2226 identification of *Bacillus amyloliquefaciences* as a species frequently associated with
2227 the ropy spoilage of bread. *International Journal of Food Microbiology* **156** 278 –
2228 285.

2229 Vasilescu, A., Nunes, G., Hayat, A., Latif, U., Marty, J.-L. (2016) Electrochemical
2230 Affinity Biosensors Based on Disposable Screen-Printed Electrodes for Detection of
2231 Food Allergens. *Sensors* **16**, 1863. doi:10.3390/s16111863
2232 Verma, P., & Yadava, R. D. S. (2015). Polymer selection for SAW sensor array based
2233 electronic noses by fuzzy c-means clustering of partition coefficients: Model studies

on detection of freshness and spoilage of milk and fish. Sensors and Actuators, B: Chemical, 209, 751–769. http://doi.org/10.1016/j.snb.2014.11.149

Vilas, C., Alonso, A.A., Herrera, J.R., García-Blanco, A., García, M.R. (2017) A model for the biochemical degradation of inosine monophosphate in hake (*Merluccius merluccius*). *Journal of Food Engineering* **200**, 95 – 101.

Vlasov, Y., Legin, A., Rudnitskaya, A., Di Natale, C., D'Amico, A. (2005) Nonspecific sensor arrays ("electronic tongue") for chemical analysis of liquids. *Pure and Applied Chemistry* **77**, 1965 – 1983.

von Neubeck, M., Baur, C., Krewinkel, M., Stoeckel, M., Krantz, B., Stressler, T., Jorg, L.F. (2015) Biodiversity of refrigerated raw milk microbiota and their enzyamatic spoilage potential. *International Journal of Food Microbiology*, 211, 57 – 65.

Vytrasova, J., Pribanova, P., Marvanova, L. (2002) Occurrence of xerophilic fungi in bakery gingerbread production. *International Journal of Food Microbiology* **72**, 91-96.

Wackerlig, J., Schirhagl, R. (2016) Applications of Molecularly Imprinted Polymer Nanoparticles and Their Advances toward Industrial Use: A Review. *Analytical Chemistry* **88**, 250 – 261.

Wang, C., Yang, J., Zhu, X., Lu, Y., Xue, Y., Lu, Z., 2017. Effects of Salmonella bacteriophage, nisin and potassium sorbate and their combination on safety and shelf life of fresh chilled pork. Food Control, 73, 869-877.

Wang, G-y., Wang, H-h., Han, Y-w., Xing, T., Ye, K-p., Xu, X-l., Zhou, G-h. (2017) Evaluation of the spoilage potential of bacteria isolated from chilled chicken in vitro and in situ. *Food Microbiology* **63**, 139 – 146.

2258 Wang, H., Hu, Z., Long, F., Guo, C., Yuan, Y., Yue, T (2016) Early detection of
2259 Zygosaccharomyces rouxii—spawned spoilage in apple juice by electronic nose
2260 combined with chemometrics. Int. J. Food Microbiol. 217, 68 -78.

2261 Wang, J. C. (2000). *Analytical electrochemistry*, John Wiley & Sons, Chichester.

2262 Wang, Y., Li, Y., Yang, J., Ruan, J., & Sun, C., 2016. Microbial volatile organic
2263 compounds and their application in microorganism identification in foodstuff. Trends
2264 in Analytical Chemistry, 78, 1–16.

2265 Wang, Y., Li, Y., Yang, J., Ruan, J., Sun, C. (2016) Microbial volatile organic
2266 compounds and their application in microorganism identification in foodstuff. *Trends*
2267 *in Analytical Chemistry* **78**, 1-16.

2268 Weber, W., Luzi, S., Karlsson, M., Fussenegger, M. (2009) A novel hybrid dual-
2269 channel catalytic-biological sensor system for assessment of fruit quality. *Journal of*
2270 *Biotechnology* **139**, 314 – 317.

2271 Wilson, A.D., Bauietto, M. (2009) Applications and Advances in Electronic-Nose

2272 Winquist F. (2008) Voltammetric electronic tongues – basic principles and
2273 applications. *Microchimica Acta* **163**, 3 – 10.

2274 Winquist, F., Holmin, S., Krantz-Rückler, C., Wide, P., Lündström, I. (2000) A
2275 hybrid electronic tongue. *Analytica Chimica Acta* **406**, 147 − 157.

2276 Winquist, F., Olsson, J., Eriksson, M. (2011) Multicomponent analysis of drinking
2277 water by a voltammetric electronic tongue. *Analytica Chimica Acta* **683**, 192 – 197.

2278 Wojnowski, W., Majchrzak, T., Dymerski, T., Gębicki, J., Namieśnik, J., 2017.
2279 Electronic noses: Powerful tools in meat quality assessment. Meat Science 131, 119–
2280 131

2281 Yang, M., Soga, T., Pollard, P. J., Adam, J. (2012) The emerging role of fumarate as
2282 an oncometabolite. *Frontiers in Oncology* **2**, 85. doi: 10.3389/fonc.2012.00085

2283 Yang, S.P., Xie, J., Qiang, Y-F (2017) Determination of Spoilage Microbiota of
2284 Pacific White Shrimp During Ambient and Cold Storage Using Next-Generation
2285 Sequencing and Culture-Dependent Method. Journal of Food Science 82, 1178 –
2286 1183.

2287 Yang, X., Badoni, M. (2013) Substrate utilization during incubation in meat juice
2288 medium of psychrotolerant clostridia associated with blown pack spoilage. *Food*
2289 *Microbiology* **34**, 400 -405.

2290 Yano, Y., Yokoyama, K., Tamiya, E., Karube, I. (1996) Direct evaluation of meat
2291 spoilage and the progress of aging using biosensors. *Analytica Chimica Acta* **320**, 269
2292 – 276.

2293 Yongwei, W., Wang, J., Zhou, B., & Lu, Q. (2009). Monitoring storage time and
2294 quality attribute of egg based on electronic nose. Analytica Chimica Acta, 650(2),
2295 183–188. http://doi.org/10.1016/j.aca.2009.07.049.

2296 Yu, K., Thomas, R., Hamilton-Kemp, T.R., Archbold, D.D., Collins, R.W., Newman,
2297 M.C. (2000) Volatile compounds from *Escherichia coli* O157:H7 and their absorption
2298 by strawberry fruit. Journal of Agriculture and Food Chemistry, 48, 413 - 417.

2299 Zeravik, J., Hlavacek, A., Lacina, K., Skládal P. (2009) State of the Art in the Field of
2300 Electronic and Bioelectronic Tongues – Towards the Analysis of Wines.
2301 *Electroanalysis* **21**, 2509 – 2520.

2302 Zhang, F., Keasling, J. (2011) Biosensors and their applications in microbial
2303 metabolic engineering. *Trends in Microbiology* **19**, 323 – 329.

Zhou, G.H., Xu, X.L., Liu, Y. (2010) Preservative technologies for fresh meat – A review. *Meat Science* **86**, 119 – 128.

Zoski C. (ed) (2007). *Handbook of Electrochemistry*, 1st Edition, Elsevier Science, New York.

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		Preservative	Spoilage organism(s)	Reference
	Temperature		Atmospheric conditions		pH				
	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.

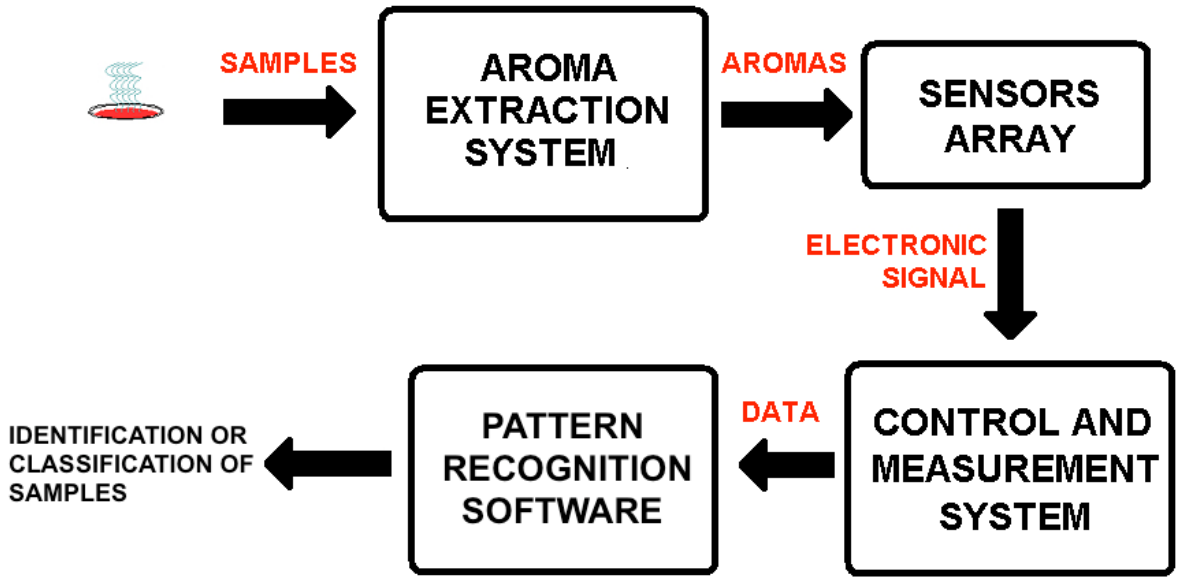

Fig. 1. Block diagram of an electronic nose system.

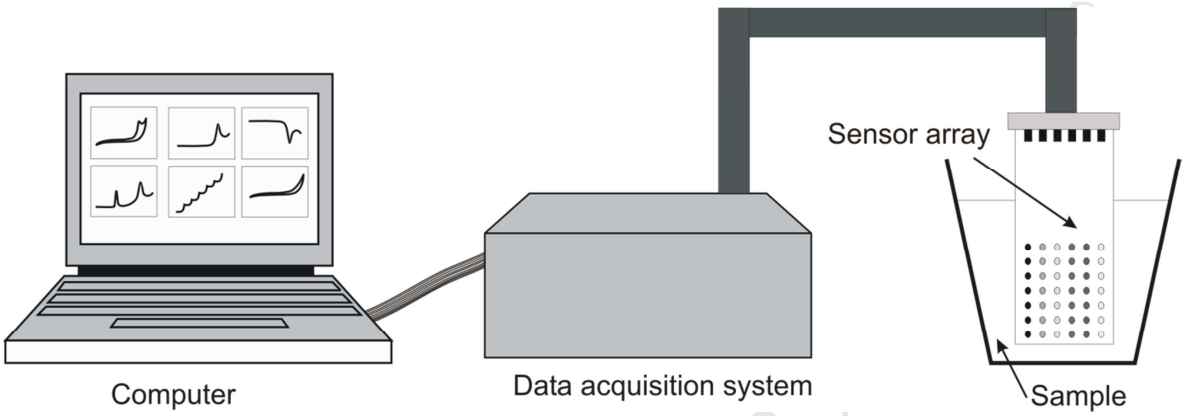

Fig. 2. General scheme of an electronic tongue system

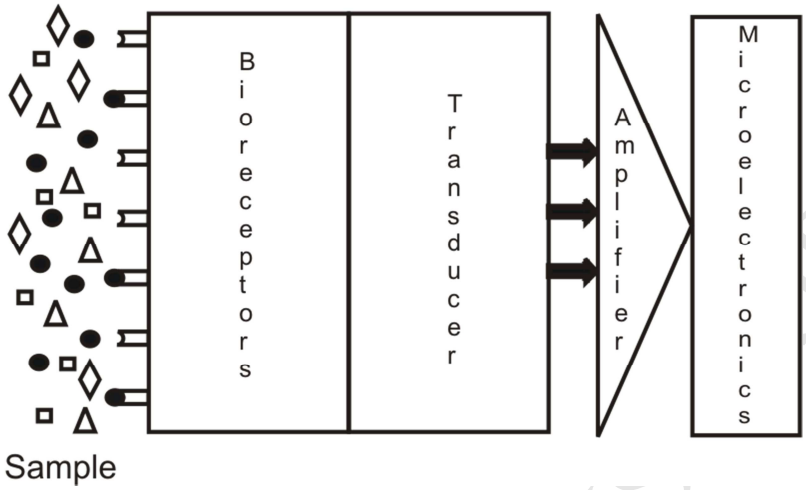

Fig. 3. Biosensor detection scheme

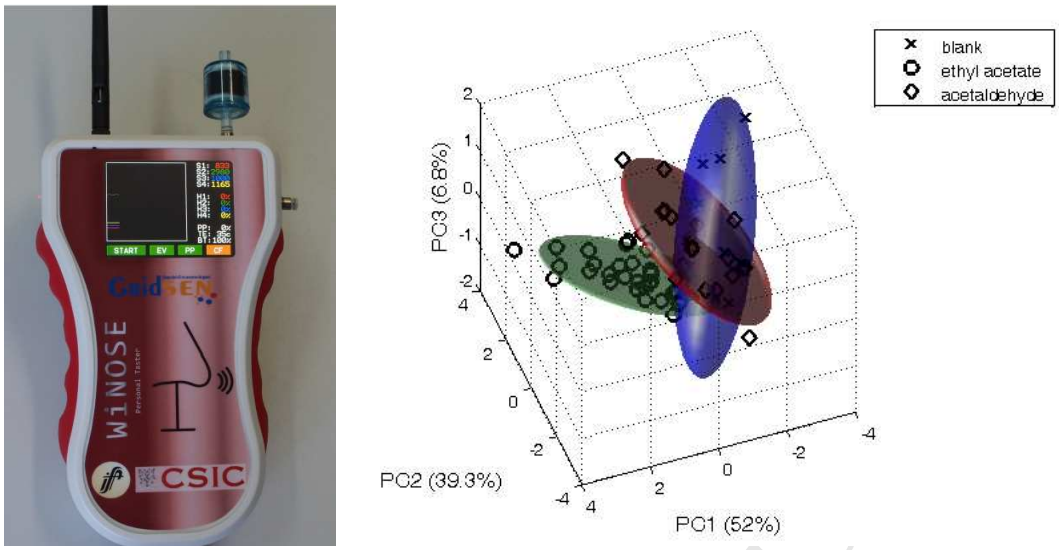

Fig. 4. Portable electronic nose system for the defect discrimination in beer and PCA score plot of measurements of beer defects.

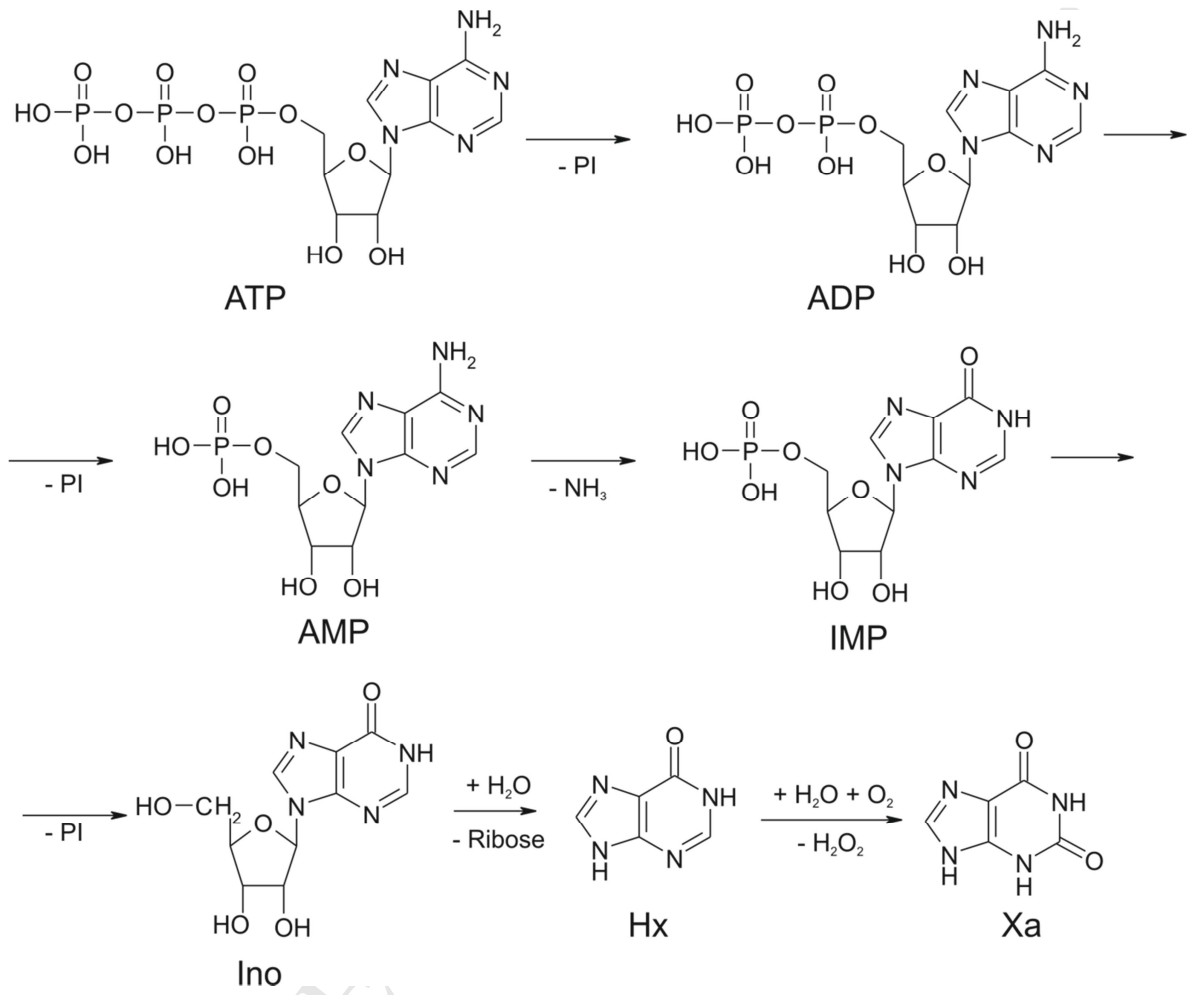

Fig. 5. Decomposition of ATP in the muscles (Nelson & Cox, 2017)

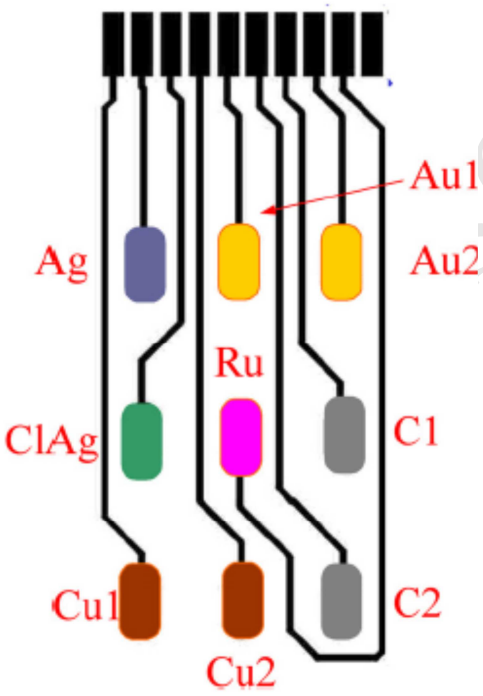

Fig. 6. The sensor array used for the potentiometric electronic tongue (Gil-Sánchez, Soto, Martínez-Máñez, Garcia-Breijo, Ibáñez, & Llobet, 2011).

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.