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

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Abstract

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

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

46 1. Introduction

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

57 Microbiological quality and safety of foodstuff should be monitored and checked to
 58 ensure the consumption security of foods to human beings. Therefore, the originating
 59 factors and detection of spoilage in any microbiological stage across the entire food
 60 supply chain is of particular importance. The identification of microbial species in
 61 foodstuff are still routinely carried out by conventional methods such as biochemical
 62 and culturing approaches which have the disadvantages of being labour-intensive and
 63 time-consuming. Additionally, some analytical techniques enabling identification of
 64 spoilage indicators have been reported in the literature. They include purge and trap
 65 (PT), Proton transfer reaction mass Spectrometry (PRT-MS), Secondary Electrospray
 66 Ionization Mass Spectrometry (SESI-MS), Solid Phase Microextraction (SPME),
 67 Selected Ion Flow Tube Mass Spectrometry (SIFT-MS), Gas Chromatography Mass
 68 Spectrometry (GC-MS), Gas Chromatography Time of Flight Mass Spectrometry
 69 (GC-TOFMS). Apart from the fact that most of these methods require specific
 70 analytical skills and the cost of the sample preparation is relatively expensive, they are

71 also not appropriate for continuous monitoring in food industry (Ghasemi-
72 Varnamkhasti et al., 2012). Moreover some techniques mentioned above, for instance
73 PTR-MS, are not readily available to be used in the food industry. Hence, there is a
74 necessity for the development and use of innovative instrumental techniques as fast,
75 reliable, non-expensive devices for the purpose of food spoilage characterization.

76 Spoilage can occurs in either stages of slaughtering or harvesting, cleaning, blanching,
77 processing, packaging and storage, handling and distribution (Wang, Li, Yang, Ruan,
78 & Sun, 2016). It is worth mentioning the nature of spoilage and the constituents
79 produced during this phenomenon are enormously complicated because the food
80 matrix including fat, carbohydrate, and protein can support microbial growth and the
81 exponential acceleration of spoilage. Awareness of such issues is necessary while
82 developing and using instrumental systems. Since the changes are created either in
83 aroma profile or food body, therefore more efficient monitoring of both mediums
84 could result in better judgment of spoilage (Kiani, Minaei, & Ghasemi-Varnamkhasti,
85 2016).

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

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

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

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

111 Food spoilage describes a variety of cumulative undesirable changes in a food product
112 that renders it unacceptable to consumers (Huis in’t Veld., 1996). Food spoilage is a
113 complex process and loss of quality is associated with two main events; changes in
114 the physical and chemical characteristics of the food product and the microbial
115 activity of a wide range of microorganisms (Dalgaard et al., 2006; Ercolini et al.,
116 2006). It should be noted that the distinction between both processes is not always
117 clear. For instance, undesirable enzymes in milk are responsible for producing the
118 rancidity and bitterness associated with spoilage. These enzymes can either be

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

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

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

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

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

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

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

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

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

239 The development of more rapid and efficient identification methods continues to be
240 the focus of intensive research. While traditional methods are for the most part cost
241 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 catalysed 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 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

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

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

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

335 The aroma extraction system or sampling method carries the volatile compounds from
336 the samples to the sensor chamber and it significantly contributes to the capability and
337 reliability in an odour sensing system. Various techniques of the sample flow, static

338 and preconcentrator systems are available for using with an electronic nose and the
339 most appropriate aroma extraction system should be selected for the project taking
340 into account the type of samples, the application and the portability of the system.

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

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

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

378 Semiconductor chemical sensors detect gases and aromas in samples by a chemical
379 reaction that takes place when the gas comes in direct contact with the sensor surface.
380 This chemical reaction and the presence of the gases can be detected since the
381 electrical resistance in the sensor is modified when it is exposed to the monitored gas.
382 This change in resistance is measured and can be used to identify the presence of a
383 gas, to predict the the gas concentration or other tasks. Tin dioxide in different
384 structures (thin or thick film, nanostructures, nanowires, etc.) is the most common
385 material used in semiconductor sensors, that are commonly used to detect hydrogen,

386 oxygen, alcohol vapor, and harmful gases such as carbon monoxide in different
387 applications related with environment, health, food quality, etc. Operating the device
388 at different temperatures and varying the type and thickness of the material, the
389 sensitivity and selectivity can be optimized.

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

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

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

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

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

430 The main goal of an electronic nose is to identify an odorant sample and perhaps to
431 estimate its concentration. The multivariate information obtained by the sensor array
432 can be sent to a display so a human can read that information and do an action or an
433 analysis. Also, that information, that is an electronic fingerprint of the volatile
434 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, typically 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.

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

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

476

477 5.2. *Electronic tongue*

478 The analysis of the substances dissolved in liquid samples with multisensor systems
479 was firstly developed in mid-1980s (Otto & Thomas, 1985). In the beginning of the
480 1990s, the first taste sensor was built, based on ion-selective electrodes (Hayashi,
481 Yamanaka, Toko, & Yamafuji, 1990; Iiyama, Miyazaki, Hayashi, Toko, Yamafuji,
482 Ikezaki, & Sato, 1992). The sensitive membrane was made of various lipid

483 membranes immobilized onto polyvinyl chloride (Toko, 2000). Later, in 1995, the
484 concept of electronic tongue was introduced. It was based on inorganic chalcogenide
485 glass sensors, being used for both qualitative and quantitative determinations (Legin,
486 Rudnitskaya, Di Natale, Mazzone, & D'Amico, 2000; Vlasov, Legin, Rudnitskaya, Di
487 Natale, & D'Amico, 2005).

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

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

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

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

536 Most electronic tongue systems reported in the specialized literature are based on
537 potentiometric sensors (Mimendia, Gutiérrez, Leija, Hernández, Favari, Muñoz, & del
538 Valle, 2010; Ciosek & Wróblewski, 2011; Cuartero, Carretero, Garcia, & Ortuño,
539 2015). By using the potentiometric methods, one measures the potential between two
540 electrodes in the absence of an external flow of current. The value of potential
541 measured under these circumstances is used for the quantitative determination of the
542 analytical species of interest in the multicomponent liquid solution (Bard & Faulkner,
543 2001; Zoski, 2007; Wang, 2000).

544 Potentiometric sensors present a number of advantages, such as: their functioning
545 principle is well-known, there is a possibility to obtain selective sensors, low cost,
546 high possibility of industrial production, and the detection is very similar to the
547 principle of molecular recognition, i.e., with the principle of biologic detection of the
548 substances responsible of taste. Their disadvantages are their being temperature
549 dependant and the fact that the adsorption of the solution compounds in the sensitive
550 element modifies the value of the measured potential (Bratov, Abramova, & Ipatov,
551 2010; Bobacka, Ivaska, & Lewenstam, 2008).

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

556 & Escuder-Gilabert, 2013; Dias, Veloso, Sousa, Estevinho, Machado, & Peres, 2015;
557 Schmidtke, Rudnitskaya, Saliba, Blackman, Scollary, Clark, Rutledge, Delgadillo, &
558 Legin, 2010; Mednova, Kirsanov, Rudnitskaya, Kilmartin, & Legin, 2009; Gutiérrez-
559 Capitán, Vila-Planas, Llobera, Jiménez-Jorquera, Capdevila, Domingo, & Puig-Pujol,
560 2014).

561 Another category of sensors which has been widely used for the development of
562 electronic tongues are the voltammetric sensors (Bard & Faulkner, 2001; Zoski, 2007;
563 Wang, 2000). In this case, a potential, either fix or, most often, variable, is introduced
564 into the system, and the electroactive compounds present in the sample are oxidized
565 or reduced, which leads to the generation of a flow of anodic or cathodic current.
566 When the sample to be analyzed is a complex one, containing more chemical species
567 with redox properties, the selectivity of this type of sensors is limited for a specific
568 analyte present in the sample. The greatest disadvantage of this type of sensors is their
569 reduced selectivity, but this aspect can be improved by using nanomaterials or by
570 employing pulse techniques (differential pulse voltammetry and square-wave
571 voltammetry) or by optimization of the experimental conditions (Brett & Fungaro,
572 2000; Gupta, Jain, Radhapyari, Jadon, Agarwal, 2011; Reza Ganjali, Garkani Nejad,
573 Beitollahi, Jahani, Rezapour, & Larijani, 2017; Rodríguez-Méndez, Apetrei, & de
574 Saja, 2008).

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

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

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

590 The detection principle of the conductimetric sensors is based on the change in the
591 conductivity of the sensible material as a result of the interaction with various
592 chemical species present in the solution to be analysed. There are only a few studies
593 in the literature which tackle the use of conductimetric sensors in the development of
594 electronic tongues (Winqvist, Holmin, Krantz-Rückler, Wide, Lündström, 2000; Sha,
595 2013).

596 The measurement principle of impedance sensors is based on measuring the
597 impedance at a certain frequency value or for a range of frequencies with the help of
598 impedance spectroscopy. This type of sensors, based on various materials, has been
599 largely used in the development of electronic tongues with various applications
600 (Cabral, Bergamo, Dantas, Riul Jr, & Giacometti, 2009; Guo, Chen, Yang, & Wang,
601 2005).

602 The detection principle of piezoelectric sensors is based on the piezoelectric
603 phenomenon. The result of the exposure of these sensors to various substances is the

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

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

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

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

Fig. 3. Biosensor detection scheme

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

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

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 contaminants, 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, Stred'anský, 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, &

723 Vinurajkumar, 2013). Enzymes in the class of oxidoreductases (laccase, tyrosinase,
 724 peroxidase, dehydrogenases) are used for substrate detection, and the main
 725 electroactive compounds detected by these biosensors are o-quinone derivatives,
 726 hydrogen peroxide or reduced forms of nicotinamide adenine dinucleotide (Amine,
 727 Mohammadi, Bourais, & Palleschi, 2006; Mello & Kubota, 2002; Tembe & D'Souza,
 728 2015). The enzyme sources can be purified enzymes commercially available, but also
 729 organelles, cells, tissues, microorganisms, etc. (Apetrei & Apetrei, 2016; Rodríguez-
 730 Delgado, Alemán-Nava, Rodríguez-Delgado, Dieck-Assad, Martínez-Chapa, Barceló,
 731 Parra, 2015; Gul, Sheeraz Ahmad, Saqlan Naqvi, Hussain, Wali, Farooqi, & Ahmed,
 732 2017; Liu, Wu, Cai, Hu, Zhou, & Wang, 2014; Hasan, Nurunnabi, Morshed, Paul,
 733 Polini, Kuila, Al Hariri, Lee, & Jaffa, 2014; Lim, Ha, Lee, Lee, & Kim, 2015). For the
 734 detection of inhibitors of enzymatic activity, the activity of the enzyme is determined
 735 in the absence and in the presence of the inhibitor, determining the inhibition degree
 736 based on inhibitor concentration. The detection of target compounds does not involve
 737 its transformation (Upadhyay & Nishant, 2013; Murugaboopathi, Parthasarathy,
 738 Chellaram, Prem Anand, & Vinurajkumar, 2013).

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

745 Nano biosensors are emerging as a promising tools for the applications in the food
 746 analysis. They are integrating knowledge of physical sciences, biology, chemistry,
 747 biotechnology, molecular engineering, and nanotechnology offering important

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

6. Literature evidence multisensor systems to food spoilage detection

6.1. Electronic nose

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

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

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

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

787

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

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

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-phenylethanol), 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.

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

862

863 6.2. *Electronic tongue*

864 Electronic tongues have been successfully used for qualitative and quantitative
865 determinations of the spoilage of many foods of interest (Haddi, El Barbri, Tahri,
866 Bougrini, El Bari, Llobet, & B. Bouchikhi, 2015; Śliwinska, Wisniewska, Dymerski,
867 Namiesnik, & Wardencki, 2014). As it is well-known, the foods spoilage is a complex
868 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.

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

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

906 For data validation and for establishing the correlation with the results of classical
907 analytical methods, a number of physical-chemical, microbial and biochemical
908 parameters were analysed. These analyses consisted in pH determination, microbial
909 count, concentrations of inosine 5'-monophosphate, inosine and hypoxanthine. Using
910 the PLS regression method, a very good correlation was found between pH and the
911 data obtained from potentiometric sensors, as well as between K-index
912 (simultaneously measures the variation in the adenosine triphosphate) and the data
913 obtained with the electronic tongue. The conclusion of the study was that the
914 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 Ag₂S) 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

987 potentiostat through a relay box. The responses of the array of sensors in the presence
988 of the samples to be analyzed were recorded by cyclic voltammetry.

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

998 A number of studies reported in the literature relied on the use of voltammetric
999 electronic tongues based on sensors modified with electroactive substances
1000 (phthalocyanines or conducting polymers), both regular and screen-printed electrodes.

1001 A study reported the use of a novel array of voltammetric sensors used for the
1002 detection of the principal biogenic amines resulted from the spoilage process of Tench
1003 fish (Rodríguez-Méndez, Gay, Apetrei, & de Saja, 2009). The array of sensors
1004 consisted of screen-printed electrodes modified with phthalocyanines. The method
1005 conveyed in this study entailed the global detection of the chemical products resulted
1006 from the process of spoilage of fish, including the biogenic amines.

1007 The sensors proved very good sensitivity to biogenic amines present in the solution to
1008 be analysed (ammonia, dimethylamine, trimethylamine, cadaverine and histamine). It
1009 was observed that biogenic amines have great influence on the chemical behaviour of
1010 the sensors, due to the fact that some biogenic amines are electroactive and that all

1011 biogenic amines have basic and nucleophilic properties. The developed sensors are
1012 very sensitive, reproducible, and present good stability on long term.

1013 The array of sensors was used for the determination of the freshness degree of fish
1014 kept at 4°C in the refrigerator for 12 days. The responses recorded by cyclic
1015 voltammetry were successfully used for assessing freshness and for determining the
1016 post-mortem period. The voltammetric signals displayed increasing intensity with the
1017 increasing of storage time.

1018 The ability of discriminating fish samples based on their freshness was demonstrated
1019 by principal component analysis. The ability of classifying the fish samples according
1020 to their freshness, as well as the prediction of freshness of some samples was
1021 calculated by partial least squares-discriminant Analysis (PLS-DA). The results
1022 proved that voltammetric electronic tongue is able for determining the degree of fish
1023 freshness by monitoring the production of spoilage products. In addition, this method
1024 is able to determine the stage of the spoilage process, which comprises 4 states.

1025 Another paper reported the use of a voltammetric electronic tongue for monitoring the
1026 freshness of Pontic shad fish samples (Apetrei, Rodriguez-Mendez, Apetrei, de Saja,
1027 2013). The samples were Pontic shad (*Alosa Pontica*), a species living in the north-
1028 western part of the Black Sea. Pontic shad migrates in the Danube River for
1029 spawning. The array of sensors was made up of a series of sensors based on carbon
1030 screen printed electrodes modified with polypyrrole doped with different doping
1031 agents. The electrochemical signals are complex and present redox processes related
1032 to the electrochemical activity of the amines, and redox peaks associated to the
1033 electrochemical activity of the electroactive material. The viability of the
1034 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).

1081 Yano et al. (1996) developed a direct sensing method in order to determine the quality
1082 of beef (Yano, Yokoyama, Tamiya, & Karube, 1996). The biosensor was made of an
1083 Ag/AgCl electrode and a platinum electrode onto which two enzymes were
1084 immobilized, namely putrescine oxidase or xanthine oxidase. The detection method
1085 used was potential-step chronoamperometry, the potential was stepped in the range
1086 from 0.3 V to 0.6 V. The experimental conditions, such as pH and selectivity, were
1087 adequate and the target compounds could be analysed on the beef surface. Sensitivity,
1088 selectivity and stability of the biosensor were very good in detecting putrescine,
1089 cadaverine and hypoxanthine. The experimental results demonstrated that the method
1090 of direct determination with this biosensor could be successfully used in the non-
1091 destructive assessment of beef quality.

1092 Kress-Rogers et al. (1993) developed a prototype biosensor (in the form of an array of
1093 biosensors) in view of ultra-fast assessment of pork meat freshness (Kress-Rogers,
1094 D'Costa, Sollars, Gibbs, & Turner, 1993). The biosensors array allows the
1095 measurement of glucose concentration at 2 and 4 mm depth under the meat surface.
1096 The array of biosensors was used to monitor the spoilage process of refrigerated pork
1097 carrying a slaughterhouse flora. The assessment of meat freshness was pursued based
1098 on the three-dimensional profile of glucose near the meat surface. This method can be
1099 applied as a marker for the fast evaluation of complex foods, in what concerns the
1100 microbial and oxidative spoilage, maturation and the fermentation process.

1101 Fish and fish products spoilage is also of great interest in food industry, as fish is
1102 susceptible to spoilage due to storage conditions. Fish spoilage under refrigeration
1103 conditions is attributed to the metabolic degradation of trimethylamine N-oxide
1104 (TMAO) to trimethylamine (TMA) by psychrophilic bacteria. TMA accumulation in
1105 tissues is responsible for the specific smell of degrading fish, while the TMA

1106 concentration depends on the stage of the spoilage process (Barrett & Kwan, 1985;
1107 Muzaddadi, Devatkal, & Oberoi, 2016).

1108 Gamati et al. (1991) developed a biosensor for monitoring the trimethylamine
1109 concentration, based on the difference in the oxygen uptake response of two microbial
1110 electrodes (Gamati, Luong & Mulchandani, 1991). One of the electrodes was
1111 produced using *Pseudomonas aminovorans* grown on TMA. It was particularly
1112 sensitive to TMA, trimethylamine N-oxide, dimethylamine and monomethylamine.
1113 The other electrode was produced using *Pseudomonas aminovorans* grown on
1114 TMAO, and it was sensitive to TMA, trimethylamine N-oxide, dimethylamine and
1115 monomethylamine. The response of biosensor is linear with TMA concentration and
1116 the limit of detection is in pM domain. Besides, the relative standard deviation of the
1117 biosensor response is low, the response is stable and reproducible. The results
1118 obtained with the help of this sensor were validated by HPLC. The biosensor is useful
1119 for TMA determination in fish tissue extracts.

1120 Another biosensor for the TMA detection was developed by Bourigua et al. (2011). It
1121 was based on polypyrrole–flavin-containing monooxygenase (FMO3) and ferrocene.
1122 The detection techniques employed were amperometry and impedance spectroscopy.
1123 The biosensor presents high selectivity and sensitivity to TMA in real samples. The
1124 validation of the biosensor was carried out using GC/SM and the real sample was fish
1125 extract after deterioration during storage (Bourigua, El Ichi, Korri-Youssoufi, Maaref,
1126 Dzyadevych, & Jaffrezic Renault, 2011).

1127 In food industry, fish processing is difficult because of its low commercial life and
1128 high variability of the raw material, starting from the biologic species and ending with
1129 fishing and storage. An important biomarker of fish spoilage is the level of xanthine:

1130 above certain values, it is certain that the spoilage process has begun (Costa &
1131 Miertus, 1993).

1132 Fish freshness is the most important feature of this raw material for its processing in
1133 food industry under safe, qualitative conditions. After the fish's death, breathing and
1134 biosynthesis of adenosine triphosphate (ATP) nucleotide cease. Consequently, the
1135 ATP in the muscles is degraded, according to the scheme presented in Fig. 5.

1136 Among the spoilage products, IMP is the main factor which contributes to fish
1137 freshness flavour, and the spoilage product hypoxanthine is what gives the fish meat
1138 its specific bitter taste. Dervisevic et al. (2015) produced a biosensor based on a host
1139 matrix nanocomposite for immobilization of xanthine oxidase made up of MWCNT
1140 incorporate in poly (GMA-co-VFc) copolymer film (Dervisevic, Custiuc, Çevik, &
1141 Senel, 2015). The inclusion of MWCNT in the polymer matrix resulted in a
1142 substantial growth of the sensitivity of the biosensor. The fabrication process of the
1143 sensitive layer of the biosensor was characterized by scanning electron microscopy.
1144 The electrochemical behaviour of the biosensor was studied by cyclic voltammetry
1145 and electrochemical impedance spectroscopy. The biosensor presents maximum
1146 response to xanthine at pH 7.0 and 45°C, when +0.35 V is applied. The biosensor
1147 reaches 95% of steady-state current in approximately 4 seconds. The limit of
1148 detection of the biosensor to xanthine detection is of 0.12 μM , positive results being
1149 obtained for the measurement of xanthine concentration in fish meat. The response of
1150 the biosensor is stable and the interferences are very low.

1151 Dervisevic et al. (2015) studied the detection of xanthine molecules, which is an
1152 indicator of meat spoilage (Dervisevic, Custiuc, Çevik, Durmus, Senel, Durmus,
1153 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-co-vinylferrocene) 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 $0.17 \mu\text{M}$ 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 soured 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.

1177 Histamine is a biogenic amine of low molecular weight, with biologic activity.
1178 Histamine intoxication is also known as “scombroid fish poisoning”. Histamine
1179 concentration is used as an indicator of fish spoilage (Luten, 2006; Feng, Teuber, &
1180 Gershwin, 2016).

1181 Histamine is accumulated in seafood after the beginning of bacterial spoilage and
1182 causes histamine poisoning even though the fish may not be altered in what the visual
1183 aspect and smell is concerned (Luten, 2006; Feng, Teuber, & Gershwin, 2016).

1184 Keow et al. (2007) developed a biosensor based on diaminoxidase for the detection of
1185 histamine in tiger prawn (*Penaeus monodon*) (Keow, Bakar, Salleh, Heng, Wagiran,
1186 & Bean, 2007). The response time of the biosensor is below 1 minute under optimal
1187 pH conditions of 7.4. The limit of detection is in the sub-ppm domain (under 50 ppm,
1188 the level established by FDA USA), which recommends it for practical usage.

1189 For the validation of the biosensor on real samples, the variation of histamine
1190 concentration was studied on tiger prawn samples after a 5-hour exposure at $30 \pm 2^\circ\text{C}$
1191 temperature. The results obtained were comparable to the results determined by
1192 HPLC. There is good linear correlation between the two methods, with the
1193 determination coefficient higher than 0.95. The biosensor is reusable and may be used
1194 for the determination and quantification of histamine without further sample
1195 processing, being appropriate for the analysis of histamine in tiger prawn and also for
1196 spoilage monitoring.

1197 Bóka et al. (2012) developed a novel amperometric biosensor based on putrescine
1198 oxidase for the selective detection and quantification of putrescine, a characteristic
1199 which may function as an indicator of microbial spoilage (Bóka, Adányi, Szamos,
1200 Virág, & Kiss, 2012). Putrescine oxidase was isolated from *Kocuria rosea*

1201 (*Micrococcus rubens*). The purified enzyme was immobilized onto the surface of a
1202 graphite electrode in a hydrogel containing horseradish peroxidase, as a mediator of
1203 electron transfer and poly (ethylene glycol) (400) diglycidyl ether as a reticular agent.

1204 This biosensor was used in an amperometric electrochemical cell in flow together
1205 with the reference electrode Ag/AgCl (0.1 M KCl) and a platinum wire as an auxiliary
1206 electrode. Under optimal conditions of pH, flow rate and applied potential, a vast
1207 linearity domain was obtained between the response of the biosensor and the
1208 putrescine concentration, with a detection limit appropriate for applications in foods
1209 analysis. The validation of the biosensor was pursued by analysing beer samples and
1210 comparing the results obtained with the results of the reference method HPLC.

1211 The formation of volatile compounds, such as acetaldehyde and ethylene in plants and
1212 fruits is related to the state of their metabolism. For example, the synthesis speed of
1213 ethylene in apples increases with the time spent after harvest, while the acetaldehyde
1214 production is related to the anaerobic metabolism which grows in fruits after
1215 harvesting. The quantity of ethylene and acetaldehyde is related to the metabolic state
1216 and to the quality of fruit (Chen, Zhang, Hao, Chen, & Cheng, 2015; Maffei, 2010).

1217 Weber et al. (2009) developed and implemented a hybrid dual-channel catalytic-
1218 biological sensor system, able to quantify the two volatile substances in situ (Weber,
1219 Luzi, Karlsson, & Fussenegger, 2009). This biosensor is based on a mammalian cell
1220 line engineered for constitutive expression of an *Aspergillus nidulans*, which triggers
1221 quantitative reporter gene expression in the presence of acetaldehyde. Ethylene
1222 oxidized to acetaldehyde through Wacker process can be quantified with the same
1223 biosensor. The quantification of metabolites allowed the accurate assessment of the

1224 quality of fruits, the fresh apples being clearly differentiated from the old and rotten
1225 apples.

1226 By placing in relation the catalytic processes and the detection technology of the
1227 biosensors, it was possible to determine the metabolic state of food. Consequently,
1228 this could be used in the assessment of foods which suffer biochemical
1229 transformations, as well as in control processes for detecting and preventing food
1230 spoilage (Zhang & Keasling, 2011).

1231 Fumarate is a very important intermediary in Krebs cycle (the tricarboxylic acid
1232 cycle) and has a key role in the fundamental processes which produce energy, as well
1233 as in the biosynthesis of amino acids and lipids (Nelson & Cox, 2017).

1234 The accumulation of fumarate in organism above a certain limit, due to fumarate
1235 hydratase mutation, is one of the main causes of hereditary leiomyomatosis and renal
1236 cell cancer, being considered an oncometabolite (Yang, Soga, Pollard, & Adam,
1237 2012)

1238 On the other hand, fumarate is present in beverages, baking powders and candy, as a
1239 result of the microbial activity which leads to spoilage. Another source of
1240 contamination is represented by the impurities present in certain synthetic additives.
1241 Accordingly, fumarate is an important and relevant indicator of food quality, which
1242 can be used as a biomarker of food freshness (Hurrell, 2010; Kvasničk & Voldřich,
1243 2000). Nevertheless, a cost-effective and fast analytical method for the detection and
1244 quantification of fumarate is desired. Si et al. (2015) produced an electrochemical
1245 whole-cell biosensing system for the quantification of fumarate in foods (apple juice)
1246 (Si, Zhai, Liao, Gao, & Yong, 2015). A sensitive inwards electric output (electron
1247 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.

1256

1257 **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

1297 include the miniaturization of the systems able to measure in-flow in real-time
1298 analysis, coupled with wireless signal transmitters, expert systems for data analysis
1299 and feed-back action. These multisensory systems will assure a rapid and accurate
1300 control of food spoilage, important for the producers and for the consumers.

1301

1302 **8. Conclusion**

1303 In this paper, we have outlined the major contributions of electronic nose, biosensors,
1304 and electronic tongue technologies related with food spoilage. There is a great interest
1305 for handheld instruments that respond to simple questions related with food spoilage
1306 posed by producers, food inspectors and general consumers. A great number of
1307 references can be found with different applications of food spoilage detection,
1308 including wine spoilage monitoring and detection of off-flavors, beer defects,
1309 microbial contamination in tomatoes, egg quality detection, grain spoilage,
1310 enterobacteriaceae in vegetable soups, spoilage of bakery products, contamination of
1311 soft drinks, apple defects, milk spoilage and olive oil defects, fish freshness
1312 monitoring, meats freshness, seafood spoilage, apple juice spoilage, among others.
1313 Electronic noses and gas sensors have shown in the last years an important
1314 enhancement in the time response and time life as well as a decrease in the size and
1315 consumption. The latest works about the electronic tongue systems for detection of
1316 food spoilage demonstrates one significant progress in the terms of high sensitive
1317 sensor arrays based on different methods of detection and the use of improved data
1318 analyses. The biosensors were used in the detection of target analytes related to food
1319 spoilage with high sensitivity, improved selectivity, and low detection limit. These
1320 superior analytical characteristics are principally related to the use of nanomaterials
1321 and nanotechnologies in the development of biosensors.

1322

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1328

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2315 **Captions of Figures**

2316 **Fig. 1.** Block diagram of an electronic nose system.

2317 **Fig. 2.** General scheme of an electronic tongue system

2318 **Fig. 3.** Biosensor detection scheme

2319 **Fig. 4.** Portable electronic nose system for the defect discrimination in beer

2320 **Fig. 5.** Decomposition of ATP in the muscles (Nelson & Cox, 2017)

2321 **Fig. 6.** The sensor array used for the potentiometric electronic tongue (Gil-Sánchez,

2322 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 inosinate, Disodium guanylate
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, Chaliér, 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, Damberg, 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,

	(Cyanose 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, Sehwal, & 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 <i>Salmonella</i> 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 <i>R. aquatilis</i>	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 (<i>Callinectes sapidus</i>) meat	CP (Cyranose) TM	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				Preservative	Spoilage organism(s)	Reference
	Temperature		Atmospheric conditions		pH				
	Low	High	Aerobic	Anaerobic	Low	High			
Baked products		x	x			(x)		<i>Bacillus</i> spp. Moulds	Valerio et al., (2012); Vytrasova et al., 2002
Meat	x			x		x		Lactic acid bacteria, Enterobacteriaceae, <i>Clostridium</i> , <i>Shewanella</i>	Cavill et al., 2011; Doulgeracki et al., (2010); Hernandez- Macedo et al., 2012;
Meat	x		x			x		<i>Pseudomonas</i> , <i>Brochothrix</i> <i>thermosphacta</i> , <i>Photobacterium</i> ,	Ercolini et al., 2006; Nychas et al., 2008; Pennachia et al., 2011
Meat		x	x			x		Enterobacteriaceae, <i>Pseudomonas</i> , <i>Acinetobacter</i>	Gill and Newton, 1979
Meat	x			x		x	Nisin	Enterobacteriaceae, <i>Pseudomonas</i>	Ferrocino et al., 2013
Marinated broiler	x			x		x	Spices	<i>Leuconostoc</i> <i>gasicomaticum</i>	Susuiluito et al., (2003)
Raw milk (refrigeration)	x		x			Neutral		<i>Pseudomonas</i> , <i>Lactococcus</i> , <i>Acinetobacter</i>	von Neubeck et al., (2015)
Minimally processed vegetable	x		x			(x)		<i>Pseudomonas</i> , <i>Enterobacteriaceae</i> , <i>Cryptococcus</i>	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			<i>Acinetobacter</i> , <i>Chryseobacterium</i> , <i>Psychrobacter</i> , <i>Sphingomonas</i> , <i>Paenibacillus</i> , <i>Bacillus</i>	Schmidt et al., 2012
Fish	x			x		x	Essential oil	<i>Aeromonas</i> , <i>Lactococcus</i>	Zhang et al., 2017
Fish		x	x			x		<i>Pseudomonas</i> , H ₂ S producing bacteria, Enterobacteriaceae	Parpalani et al., 2014
Fish	x			x		x		<i>Pseudomonas</i> , <i>Photobacterium</i> , <i>Lactococcus</i> , <i>Brocothrix</i> <i>thermosphacta</i>	Koutsoumanis et al., (2000); Mace et al., 2012
Smoked fish	x			x		x		Lactic acid bacteria, <i>Phospobacterium</i> , psychotrophic Enterobacteriaceae	Lovdal, 2015
Seafood		x	x			x		<i>Proteus</i> , <i>Vibrio</i>	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	<i>Lactobacillus</i> spp., <i>Pediococcus</i> spp., <i>Pectinatus</i> spp., <i>Megaspaera</i> 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, ethyloctanoate, ethyldecanoate ethyl butanoate hexanal	glucose	air stored beef	Ercolini et al. 2010
		ethanol	meat	La Stora et al. (2012)
		lipids	fish	Leduc et al. (2012)
Pungent/alcoholic/ fermented	3-methyl-1-butanol, 2- butanol, ethanol 1-pentanol acetic acid	sugars	fish	Miks-Krajnik et al. (2016); Parpalani et al. (2017)
		sugars	RTE salads	Dias-Lula et al. (2017)
		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 Butanoic acid 2,3-heptanedione	glucose triglycerides/amino acids	fish meat	Miks-Krajnik et al. (2016) Ercolini et al. (2011)
Sulphide off-odour	H ₂ S	sulphur containing amino acids	shrimps fish	Jaffres et al. (2011) Fonnechbech Vogel et al. (2005)
	Dimethyl sulfoxide	sulphur containing amino acids	baby spinach	Dias-Lula et al. (2017)

^aThe 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)

^aThe combination of acrolein with polyphenols leads to the production of bitter compounds.

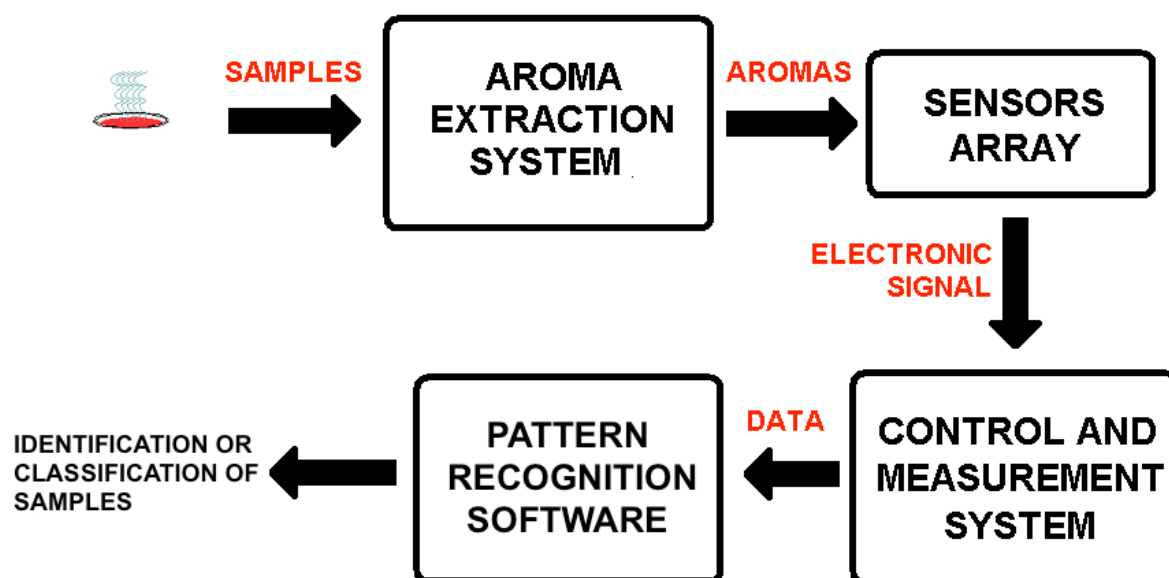


Fig. 1. Block diagram of an electronic nose system.

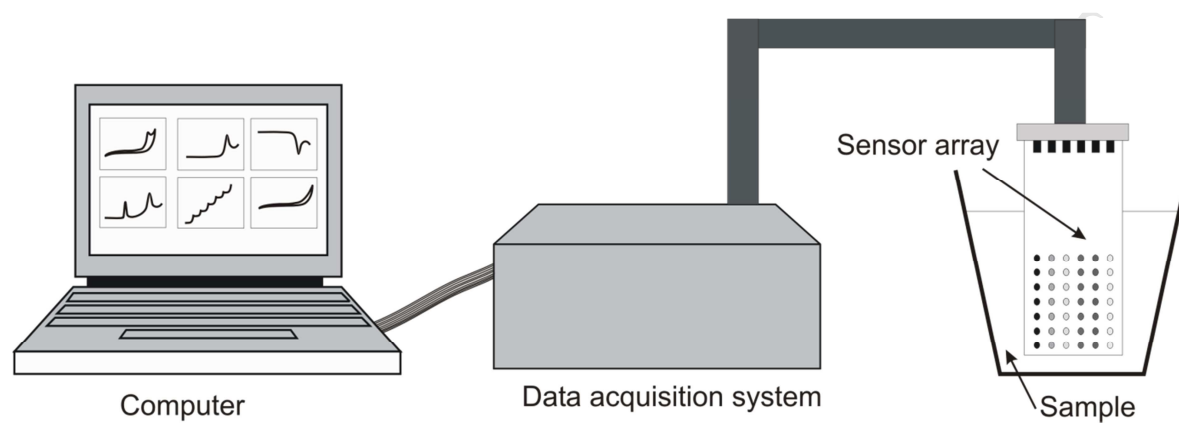


Fig. 2. General scheme of an electronic tongue system

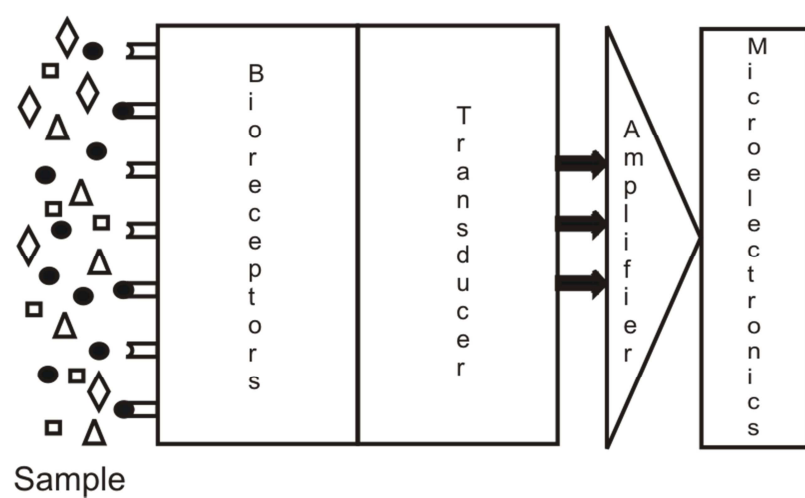


Fig. 3. Biosensor detection scheme

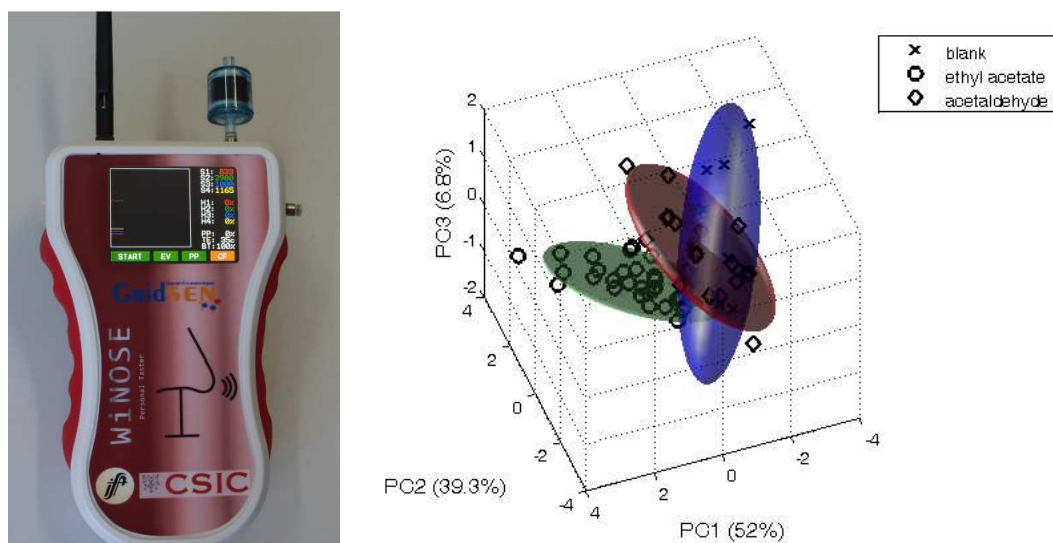


Fig. 4. Portable electronic nose system for the defect discrimination in beer and PCA score plot of measurements of beer defects.

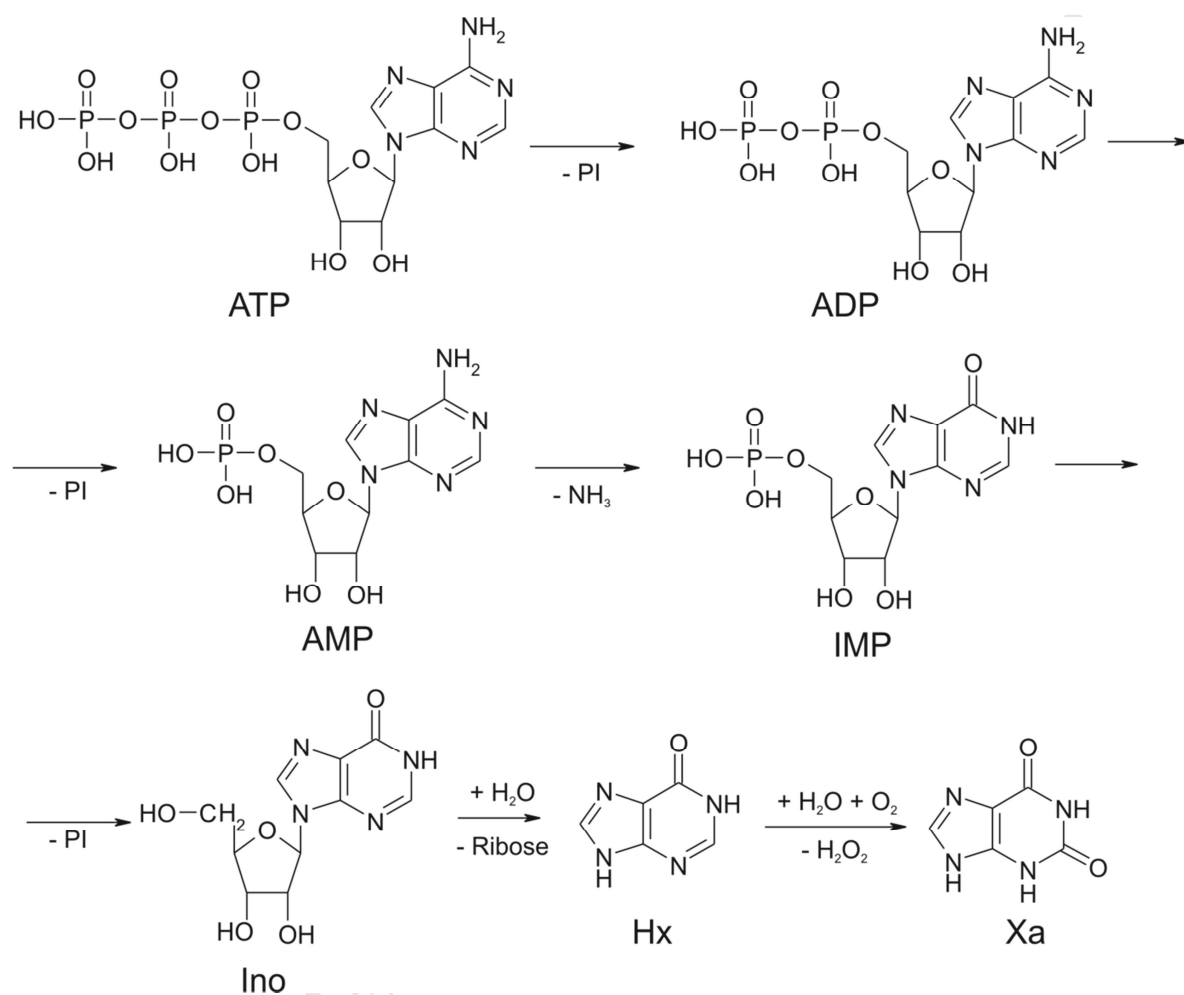


Fig. 5. Decomposition of ATP in the muscles (Nelson & Cox, 2017)

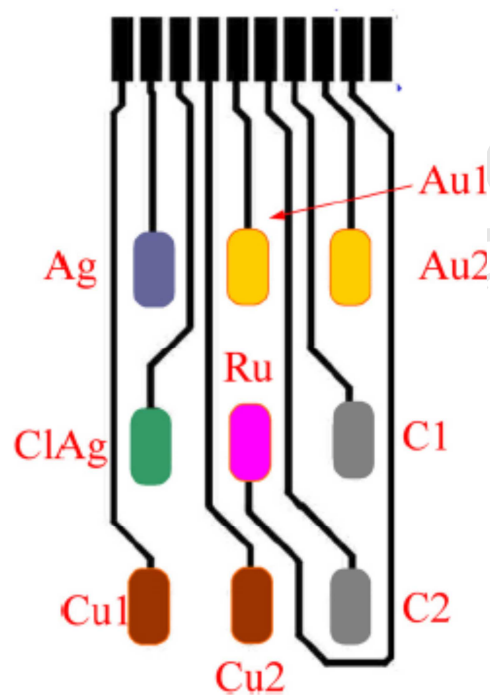


Fig. 6. The sensor array used for the potentiometric electronic tongue (Gil-Sánchez, Soto, Martínez-Máñez, García-Breijo, Ibáñez, & Llobet, 2011).

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.