

Analytical Methods

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1 Instrumental assessment of red meat origins and their
2 storage time using electronic sensing systems

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13 Abstract

14 Objective and rapid electronic sensing systems for distinguishing among meat species and
15 identifying the degree of spoilage have been developed. A metal oxide sensor-based electronic
16 nose system consisting of six sensors is designed and used to analyze the headspace emanating
17 from beef, goat and sheep meats stored at 4 °C. A rapid, non-destructive technique based on
18 electronic tongue system formed by seven working electrodes is also applied and used to
19 analyse the fingerprint of the electrochemical compounds of the three meat samples. Data
20 analysis is performed by two pattern recognition methods: Principal Component Analysis (PCA)
21 and Support Vector Machines (SVMs). Discrimination and classification function analyses are
22 performed on the response of the electronic nose and electronic tongue systems to each of the
23 three red meats. The obtained results show that the three red meats can be distinguished and the
24 number of days spent in cold storage days can be identified.

25
26 **Keywords:** Electronic nose; Electronic tongue; PCA; SVMs; Red meat discrimination;
27 Spoilage.

1. Introduction

In 2013, the meat scandal made headline news across Europe and even further afield. The evidence gathered did not point to a public health issue, but rather an issue of food quality and especially a fraudulent labelling.¹ The control of the origin of red meat is not only a major concern for the consumers but also for producers and distributors as well. It is, therefore, critical to ensure the supply of high quality and safe meat products. Furthermore, the quantitative determination of the degree of spoilage of beef, goat and sheep meat requires the development of reliable and simple tools, which would facilitate routine control assessments to be implemented. The degree of spoilage of a red meat sample is related to the number of days this sample has underwent cold storage at a given constant temperature.² It depends also on numerous factors, and particularly on the quantity of microorganisms presents in the raw sample at day zero.^{3,4} On the other hand, the distinction between goat and sheep meat deserves special attention due to their similar visual aspect. Consumers demand higher protection from falsely labelled meat products for a variety of economic and health reasons. In this context, important progress on the development of robust techniques for meat freshness and species identification is being carried out.^{5,6} The use of electronic noses and/or tongues for sensing the quality of food products as a means of non-destructive sensing is becoming widespread, fast and reliable.⁷⁻¹⁰ Electronic noses or tongues are inspired by the way in which mammals recognize samples via their olfaction and taste senses.¹¹ In these approaches, gas and liquid sensors do not have to be selective but to respond unspecifically to a group of related chemical species. The sensors are then integrated in an array and their response is analyzed by suitable pattern recognition procedures.

These electronic nose/tongue systems do not give any information about the compounds causing the aroma/flavour nor about their identity.^{12,13} However, with the help of appropriate mathematical techniques, like neural networks or statistical methods, the electronic nose/tongue

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3 53 is able to recognize the aroma/flavour pattern from a particular sample and to distinguish it
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5 54 from other samples.^{14,15}
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8 55 The smell and taste pattern signatures obtained from the electronic nose/tongue sensors are
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10 56 complex and need to be analyzed using appropriate pattern recognition techniques. Pattern
11
12 57 recognition techniques like Principal Component Analysis (PCA), Partial Least Squares (PLS),
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14 58 Discriminant Factor Analysis (DFA), Artificial Neural Network (ANN) and Support Vector
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16 59 Machines (SVMs) have been used for data analysis in electronic nose or tongue applications.¹⁶
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19 60 Electronic nose has been applied for beef freshness detection,¹⁷ discrimination of chicken and
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21 61 pork adulteration in minced mutton^{18,19} to assess meat quality at different temperatures,²⁰ to
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23 62 predict chilled pork shelf-life,²¹ to classify meat spoilage markers using nanostructured ZnO
24
25 63 thin films,²² etc.²³ However, meats were not examined enough by electronic tongues. Only
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27 64 some investigations in literature can be found, especially for monitoring physical–chemical and
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29 65 microbiological changes²⁴ and prediction of NaCl, nitrate and nitrite contents.^{25,26} To our
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31 66 knowledge, no studies have been performed on meat discrimination and spoilage analysis for
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33 67 beef, goat and sheep meats using electronic tongues. Thus, the objective of this paper is to
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35 68 evaluate the performance of an electronic nose and tongue system for the distinction among
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37 69 meat from beef, goat and sheep by developing analytical methods for acquiring aroma/taste
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39 70 signatures from the three types of meat samples and then to determine the number of days that
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41 71 meat products have undergone cold storage, which is an indirect estimation of the degree of
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43 72 spoilage of such products.
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48 49 **2. Material and methods**

50 51 52 **2.1 Electronic nose set-up**

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55 75 An electronic nose system has been developed to analyse the smell patterns from the headspace
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57 76 of meat samples. The sensor array contained 6 heated metal oxide gas sensors Figaro TGS 8XX
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3 77 (with XX= 23, 25, 26, 31, 32 and 82). In the literature, many studies have stated that the
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5 78 temperature of the sample, sensor chamber, and sensors must be kept constant to achieve
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7 79 repeatable performance of the electronic nose system. This is because a modification of the
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9
10 80 environmental temperature value can induce a variation of the sensor operating temperature,
11
12 81 modifying the sensor sensitivity and then the steady-state conductance value.²⁷⁻²⁹ As a direct
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14 82 cause, a temperature sensor (LM35DZ) and a relative humidity sensor (Phillips H1) were used
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16 83 for constantly monitoring the inner sensor chamber temperature and relative humidity. A
17
18 84 schematic diagram of the electronic–nose measurements is shown in Fig. 1. Every TGS sensor
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20 85 was heated by applying 5 Volts to its heating resistor and its conductance was measured in a
21
22 86 half-bridge configuration using 10 Volts as supply voltage (V_C) according to Figaro
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24 87 Engineering operating data sheets for measurement of the sensors conductance variation. The
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26 88 relationship between the sensor conductance and the V_C is expressed by the following equation:
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$$G = \frac{1}{R_L} \cdot \left(\frac{V_{RL}}{V_C - V_{RL}} \right) \quad (1)$$

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31 89
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33 90 Where: G is the sensor conductance, R_L is the load resistance, V_C is the supply voltage, and V_{RL}
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35 91 is the output voltage.
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39 92 The electronic nose sensor cell consists of a cylindrical chamber connected to a line of gases.
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41 93 The variation of the sensors conductivity was acquired and then digitised using a data
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43 94 acquisition board Advantech (PCL 812PG). A sampling rate of 1 sample/s was used. A program
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45 95 in Labview was developed to control the data acquisition. Additionally, this program was in
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47 96 charge of keeping constant the temperature inside the sensor cell via the temperature sensor and
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49 97 some digital outputs of the data acquisition card, which actuated the heating coil or the cooling
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51 98 system and the fan when needed.
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54 99 **2.2 Electronic tongue set-up**

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3 100 The voltammetric electronic tongue has been developed using an array of seven working
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5 101 electrodes, a platinum counter electrode as an auxiliary (length 5 mm, diameter 2 mm), and an
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7 102 Ag/AgCl reference electrode (1M saturated KCl, diameter 2mm). The working electrodes,
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9 103 made up of platinum, gold, silver and glassy carbon, (purity 99.9%, length 5 mm, and diameter
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11 104 2 mm) were purchased from CH Instruments, Texas, USA; and those made up of palladium,
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13 105 copper and nickel (purity 99.9%, length 6 mm, and diameter 1.6 mm) were purchased from
14
15 106 BAS Inc., Tokyo, Japan. In Fig. 2, the electrodes were assembled in stainless steel tubing. The
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17 107 wires from the electrodes were connected via a relay box to a portable potentiostat PalmSens
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19 108 (PalmSens BV, The Netherlands). The responses of the array to the samples in all experiments
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21 109 were measured by means of cyclic voltammetry (CV).
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26 110 **2.3 Sample preparation**

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29 111 Three different types of meat species, representative of Moroccan production were purchased
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31 112 from a local market and were analyzed. Immediately after getting meat from different animal
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33 113 species (beef, goat and sheep) with no break in the chain of refrigeration, the samples were cut
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35 114 into pieces of the same weights (mass of $25 \text{ g} \pm 1 \text{ g}$) without being chopped, and these were
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37 115 placed in plastic boxes and kept at a constant temperature of $4 \pm 1 \text{ }^\circ\text{C}$ for up to 2 weeks. The 4
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39 116 $^\circ\text{C}$ storage temperature is chosen to represent the typical storage temperature of meat in grocery
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41 117 stores.³
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45 118 **2.4 Sampling procedure**

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48 119 The responses of the electronic nose and tongue to the meat samples are acquired daily starting
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50 120 from day 3 to day 15 at an interval of 3 days (i.e., samples were measured at days 3, 6, 9, 12
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52 121 and 15). At $4 \text{ }^\circ\text{C}$, meat spoilage occurs at a much slower rate than at ambient temperature.³⁰ For
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54 122 this reason, we have chosen a 3-day sampling interval and examined spoilage over a long
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3 123 period of time. At each sampling time, 15 measurements are performed, which correspond to 5
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5 124 sample measurements for each type of meat.
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8 9 125 **2.5 Experiment methodology**

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11 126 The experimental procedures implemented to measure with the e-nose and e-tongue instruments
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13 127 are as follows:
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15 16 128 **2.5.1 Electronic nose**

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19 129 For each measurement, a meat sample is taken from the refrigerator and put inside a 500 ml
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21 130 glass bottle. The bottle is sealed and held at room temperature ($26\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$) for 20 minutes in
22
23 131 order to reach a stable headspace composition. The headspace from meat sample is fluxed into
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25 132 the electronic nose sensor chamber at a flow of 500 sccm (standard centimetre cube per minute).
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28 133 Pure nitrogen is used as the carrier gas. The electronic nose response is registered every second
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30 134 for a time interval of 50 minutes. After this stage, we open the sensor chamber to expose
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32 135 sensors to the laboratory air until steady state baseline is achieved. The process is repeated 5
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34 136 times for each meat product to check the repeatability of the measurements.
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37 137 **2.5.2 Electronic tongue**

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40 138 The electrochemical measurements with the voltammetric electronic tongue are carried out
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42 139 directly in the solid form of the three different types of meat species. The set of the electrodes is
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44 140 inserted uniformly into the meat. The electrodes were pressed inside the meat sample at a depth
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46 141 of ~ 2 mm in order to ensure a complete contact between the sample and the electrodes. After
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48 142 each reading, the electrodes spend 2 minutes in a solution of 50 mM KOH and 25% H_2O_2
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50 143 before rinsing with distilled water in order to remove possible products that may accumulate on
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52 144 electrode surface. CV was carried out using conditions as follows: scan rate: 20 mVs^{-1} and step
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55 145 potential: 2 mV. It is worth noting that several tests were carried out on meat samples for each
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3 146 working electrode, separately, in order to optimize the electrochemical window range. This is
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5 147 the reason behind the difference between the window ranges of the electrodes.
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8 148 **2.6 System performance evaluation and development of classification models**

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10 149 The performance of the designed electronic instruments is evaluated by their ability to
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12 150 discriminate the meat samples into three groups (beef, goat and sheep) and to identify the
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14 151 number of days of cold storage the different meat samples have undergone. Data processing and
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16 152 pattern recognition are decisive factors to obtain a versatile instrument able to reliably
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18 153 recognize a wide variety of odours/flavour.
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21 154 **2.6.1 Feature extraction**

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24 155 Several strategies have been previously reported in the literature for the feature extraction.
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26 156 Basically, these consist of either choosing directly amongst the features (signal points)
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28 157 available³¹ or to compute new variables (e.g. by performing Fast Fourier Transform or Discrete
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30 158 Wavelet Transform, etc.).³² The approach developed in this paper consists of choosing directly
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32 159 amongst the variables available. Based on previous works reported on electronic nose³³ and
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34 160 electronic tongue,³⁴ we have shown that a combination between the initial conductance, the
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36 161 steady-state conductance, the dynamic slope of the conductance, and the area below the
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38 162 conductance curve is often well correlated with the type of pattern and in many cases drives the
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40 163 main part of the information for electronic nose systems. By following the same strategy for the
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42 164 electronic tongue, already adopted for several purposes, only three features were directly
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44 165 extracted from the cyclic voltammogram that initially contains hundreds of measures with
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46 166 usually overlapping regions and non-stationary characteristics.
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52 167 In the case of electronic nose system, the dataset comprised the following set of features:
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55 168 • G_0 : the initial conductance of a sensor calculated as the average value of its conductance
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57 169 during the first 15 minutes of a measurement.
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3 170 • G_s : the steady-state conductance calculated as the average value of its conductance during
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5 171 the last 5 minutes of a measurement.
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7 172 • dG/dt : the dynamic slope of the conductance calculated between minute 15 and 35 of a
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9 173 measurement. This corresponds to a phase of where a fast increase of sensor conductance is
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11 174 observed.
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14 175 • A : the area below the conductance curve in a time interval defined between 15 and 40 min
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16 176 of a measurement. This area is estimated by the trapeze method.
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19 177 Three datasets were elaborated corresponding to beef, goat and sheep meat. The size for each e-
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21 178 nose dataset is 25 (5 sampling days \times 5 replicates) \times 24 (6 sensors \times 4 features).
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24 179 In the case of electronic tongue system, the dataset comprised the following set of features:
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- 27 180 • S_{ox} : the maximum slope of the current curve in the oxidation shape.
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29 181 • S_{rd} : the maximum slope of the current curve in the reduction shape.
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31 182 • $\Delta I = I_{max} - I_{min}$: the current change calculated as the difference between maximum and
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33 183 minimum values of the current; I_{max} : the maximum value of the current measured in the
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35 184 final potential range and I_{min} : the minimal value of the current measured in the initial
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37 185 potential.
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41 186 As there are 7 working electrodes within the array, each voltammetric measurement is
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43 187 described by 21 variables. Three datasets were elaborated corresponding to beef, goat and sheep
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45 188 meat. The size for each e-tongue dataset is 25 (5 sampling days \times 5 replicates) \times 21 (7
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47 189 electrodes \times 3 features).
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50 51 190 **2.6.2 Data pre-processing**

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54 191 The choice of the data pre-processing algorithm has been shown to affect the performance of
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56 192 the pattern recognition stage. The choice should depend upon the underlying sensor principle
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3 193 and the nature of interfering signals. The common pre-processing techniques applied to the
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5 194 acquired data prior to the use of any multivariate data analysis technique are mean-centring or
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7 195 auto-scaling.³⁵ By performing auto-scaling, the bias due to the domination of high sensor
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9 196 responses in the analysis could be prevented. In all data analysis, the datasets were normalized
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11 197 to set their range to [0, 1] when PCA or SVMs were used.

14 198 **2.6.3 Data Analysis**

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17 199 The fingerprint spectra obtained with both the electronic nose and electronic tongue are
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19 200 gathered in a dataset and used to build a model to identify the origin of meat and the number of
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21 201 cold storage days the different red meat samples have undergone. PCA and a SVMs multiclass
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23 202 are developed to classify the stored meat samples into three categories: beef, sheep and goat;
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25 203 based upon the origin animals, and to identify the storage days for each meat.

26
27 204 The use of PCA to assess clustering within the datasets is discussed bellow. PCA is a powerful,
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29 205 linear, and ‘unsupervised’ pattern recognition technique that has been shown to be effective for
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31 206 the classification of electronic nose and tongue datasets.^{36,37} PCA decomposes the primary data
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33 207 matrix by projecting the multidimensional data onto a new coordinate base formed by the
34
35 208 orthogonal directions with data maximum variance. The eigenvectors of the data matrix are
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37 209 called Principal Components (PC) and they are uncorrelated among them. The principal
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39 210 components are ordered so that the first one displays the greatest amount of variance, followed
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41 211 by the next greatest and so on.

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43 212 SVMs approach was also used, as a supervised learning technique, for identification analysis.
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45 213 SVMs have demonstrated to be a powerful learning method³⁸ and its use in the fields of
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47 214 electronic nose and tongue is gaining more importance every day.^{23,39,40} SVMs were originally
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49 215 designed for binary classification. Currently there are two types of approaches for multi-class
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51 216 SVM. One is by constructing and combining several binary classifiers “one-against-one or one-
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3 217 against-all methods”, while the other is by directly considering all data in one optimization
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5 218 formulation.

6 7 8 219 **3. Results and discussion**

9 10 220 **3.1 Electronic nose response analysis**

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13 221 This initial analysis consists of studying the influence of the volatile gases emanating from beef,
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15 222 goat and sheep meat samples on the conductance of the sensors. Fig. 3 shows the response
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17 223 evolution of the TGS 832 and TGS 825 sensors, as an example, in the presence of the three red
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19 224 meat samples from day 3 to day 15.

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23 225 A similar behaviour is observed for the two sensors. The intensities of the conductance of the
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25 226 two sensors increase according to exposure time. It can be derived also that the intensities of the
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27 227 conductance of the two sensors increase according to the number of days that meat has
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29 228 undergone cold storage. This behaviour, observed for the others TGS sensors, can be justified
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31 229 by an increase in the concentration of volatile gases given out by meat as a function of storage
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33 230 time, or the occurrence of new species in the headspace of meat. It can also be noticed that a
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35 231 saturation of the dynamic response of the sensors appears more distinctly for the last days of
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37 232 conservation. The results showed that the intensities of the conductance for the sensor TGS 832
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39 233 change according to the type of meat samples used (sub-plots in figure 3 (a)). For example at
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41 234 day 9, the maximum conductance value of TGS 832 reaches 45 μS , 13 μS and 97 μS for beef,
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43 235 goat and sheep meat samples respectively. Similar results are shown for sensor TGS 825 (sub-
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45 236 plots in figure 3 (b)). The maximum conductance values of TGS 825 at day nine were close to
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47 237 20 μS , 7 μS and 45 μS for beef, goat and sheep meats, respectively.

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52 238 The difference that exists among the sensor responses is due to change in concentration of
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54 239 volatile gases emanating from each type of meat. It can be due also to the difference in nature
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56 240 of volatiles released from each meat product. The changes in sensor response according to the
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3 241 type of meat samples and to the number of days the samples were kept under cold storage are
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5 242 clearly shown in figure 4. This figure shows in radar plots, the evolution of the steady-state
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7 243 conductance of the sensor array at day 3 (Figure 4 (a)) and day 9 (Figure 4 (b)) for the three red
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9 244 meats. The sensor responses to three red meats are normalized. These polar plots show the
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11 245 differences existing among the meat samples. These radar-like plots with unitary radius were
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13 246 performed also in order to see whether pattern differences developed among meat samples with
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15 247 different storage days. It can be observed that the shape of the sensor array patterns is very
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17 248 different between day 3 and day 9.

249 **3.2 Electronic tongue voltammogram analysis**

250 The voltammetric behaviour of red meat profiles was also investigated using CV. The
251 electrochemical response of a given object depends on the intrinsic chemical nature of both the
252 electrode and the redox behaviour of the product itself. As an example, the voltammograms
253 from the Au and Pd voltammetric sensors immersed in the three types of meats for the five
254 sampling days are shown in Fig. 5.

255 It is observed that the voltammetric electrodes displayed different signals for each type of meat
256 depending on the number of cold storage days it had undergone. As can be seen, different
257 response profiles were obtained depending on the nature of the electrode employed (not only in
258 the voltammogram shape, but also in the obtained currents). Additionally, the presence of clear
259 and poor redox peaks reveals changes in the voltammograms and indicates that different redox
260 species can be present in the meat matrix. For instance, in the case of the Au electrode, the shift
261 in the reduction peak occurred toward the decreasing potentials and related to the evolution of
262 the number of storage days of meat. Indeed, the interval variation, from day 3 to day 15, of the
263 reduction peak was [0.638V 0.534V], [0.573V 0.513V] and [0.595V 0.433V] for beef, goat and
264 sheep meats respectively. In the case of the Pd electrode, some differentiated current intensities
265 could be seen at both extreme potentials in the oxidation and reduction zones. The generation of

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2
3 266 a clear response variability, a good departure point for an electronic tongue approach.

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5 267 The voltammograms of Ag and Ni electrodes immersed in the three types of meats for the 3rd
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7 268 and 9th storage days are shown in Fig. 6. A clear response variability of the three meats was
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10 269 observed in the voltammograms of the two sensors, as well as for the other sensors, for each
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12 270 storage day. This clear response variability represents a good departure point for an electronic
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14 271 tongue approach. Most of voltammograms obtained for the three types of meat have a similar
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16 272 shape. However, the associated current values differ significantly from one another. Probably,
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18 273 this was due to the concentration changes of the electrochemical compounds from the meat to
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20 274 another and/or to the differences in the electrochemical compounds released from each meat
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22 275 product.⁴¹

26 276 **3.3 Degree of spoilage evaluation**

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29 277 In order to test the capability of the electronic sensing systems developed to recognise the
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31 278 storage day of the three red meats, we have analysed all their sensors data by means of PCA.

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33 279 Figure 7 (a-c) reports, in a three-dimensional plot (PC1-PC2-PC3), the electronic nose data
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35 280 coming from the measurements corresponding to beef, goat and sheep meats respectively.

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37 281 Measurements were collected during a period of 15 days. It can be observed that five distinct
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39 282 groups, which correspond to day 3, day 6, day 9, day 12 and day 15, are fairly distinguished.

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41
42 283 We notice that the projection of the measurements performed at day 3 is very close to the one of
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44 284 measurements undertaken at day 6. This can be explained by meat stored at 4°C for 3 to 6 days
45
46 285 is presenting a very similar headspace. It is also noticed that the dispersion of the samples
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48 286 around the barycentre for each group increases according to the storage period. This scattering
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50 287 can be explained by the occurrence of new volatiles in the headspace that reveal the onset of
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52 288 quality deterioration in meats stored at 4 °C.

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56 289 Figure 8 (a-c) illustrates, in a 3D space formed by the first three principal components (PC1-
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58 290 PC2-PC3), the projections of the electronic tongue data corresponding to beef, goat and sheep

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3 291 respectively. It can be seen that a perfect discrimination among all storage days has been
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5 292 obtained. The first three components represent 83.64%, 83.15% and 86.15% of the data
6
7 293 variance for beef, goat and sheep meats respectively. In the electronic tongue PCA plots, the
8
9 294 five distinct groups, corresponding to day 3, day 6, day 9, day 12 and day 15, can be easily
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11 295 identified. Thus, electronic tongue results seem to be very useful for recognising correctly the
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13 296 number of storage days a meat sample had undergone. A fortiori, the physical–chemical and
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15 297 microbiological changes in meats during the storage time are the main responsible of the quality
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17 298 degradation,^{4,23,24,42} enabling thereby the recognition of storage period by the electronic nose
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19 299 and tongue systems. Indeed, in our previous works,⁴ we have shown that electronic nose could
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21 300 be used as a rapid and alternative way for microbial activity prediction in red meats (i.e.,
22
23 301 through the volatile components). On the other hand, L. Gil et al.,²⁴ has already demonstrated a
24
25 302 relatively good correlation between the response of the electronic tongue and certain
26
27 303 degradation indexes such as the pH, microbial count, K-index and nucleoside concentrations in
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29 304 meats.

305 **3.4 Rapid distinction among red meat**

306 PCA is performed in order to provide partial visualization of the dataset in a reduced dimension
307 and to determine the capability of the sensor array to distinguish among beef, goat and sheep
308 meats day by day. Yet, we have chosen to represent the scores on PCA for days in which meats
309 are still fresh. Consequently, the three red meats can be analyzed at days 3 or 6 when they are
310 presenting very similar headspaces.⁴

311 Fig. 9 shows the projection of the electronic nose dataset related to beef, goat and sheep meats
312 measurements on a two-dimensional plane PC1–PC2. The first two components can be used to
313 represent 93.56% of the data variance related to the sixth storage day. Although a notable
314 scattering was observed around the meat group barycentre, a clear discrimination of the three
315 clusters can be obtained. The obtained findings indicated that it is possible to distinguish

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3 316 between goat and sheep meats, which is not obvious by the human eye, unlike between beef
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5 317 and goat meats or beef and sheep meats.

6
7 318 A similar analysis was conducted on electronic tongue dataset. Fig. 10 shows the scores plot in
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9 319 the PC1-PC2 plane for the data of beef, goat and sheep meats. The first two components can be
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11 320 used to represent 86.46% of the data variance. These plots show a high discrimination of the
12
13 321 three groups. PC 1 seemed to discriminate mostly between beef from goat and sheep meats. In
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15 322 the vertical direction (PC 2), there was an evident distinction between goat from sheep meats.

16 323 **3.5 SVM for identifying the number of storage day and the type of red meat**

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19 324 In order to classify meat samples into the three classes and to determine the five storage days
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21 325 for each red meat, a supervised pattern recognition method is applied. SVMs multi-class one-
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23 326 against-one has been trained. Second polynomial Kernel function is used to project the training
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25 327 data to a space that maximise the margin hyperplane.

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28 328 First, we have applied the SVMs model on electronic nose and tongue datasets in order to check
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30 329 the performance of such classifier at estimating meat freshness over a long period of storage (15
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32 330 storage days). Due to the relatively small number of measurements available, *leave-one-out*
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34 331 *cross-validation* method was implemented to better estimate the true success rate that could be
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36 332 reached with the SVMs. This assumes that, with the given n measurements, the model was
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38 333 trained n times using $n-1$ training vectors. The vector left out during the training phase was then
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40 334 used for the test. The performance of the given model was estimated as the average
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42 335 performance over n tests. High success rates in the determination of the number of storage days
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44 336 undergone by meat samples were obtained with the SVM classifier. When the electronic nose
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46 337 system was used, the success rates were 96% for goat meat and 92% for beef and sheep meats.
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48 338 When the electronic tongue system was used, a 100% success rate was achieved for the three
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50 339 types of meats.
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3 340 In the second step, the identification of the type of meats was attempted employing either the
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5 341 electronic nose or tongue. SVMs classifier was built and validated for every day in which
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7 342 measurements had been taken, i.e. 5 SVM models were built for classifying meats sampled at
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9 343 days 3, 6, 9, 12 and 15, respectively. Once more, a *leave one out cross-validation* process was
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11 344 employed. Table 1 summarizes the classification success rates obtained with SVMs. For
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13 345 instance, at days 3 or 12, all meat samples were perfectly identified (success rate reached 100%)
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15 346 when using the electronic nose or the electronic tongue. While the electronic tongue is always
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17 347 able to correctly identify red meats, regardless the particular day in which meat samples were
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19 348 measured, this is not the case of the electronic nose. This can be attributed to the complex
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21 349 nature of the spectrum of volatiles released by red meat along the cold storage process.
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25 350 Another classification analysis was performed on the three types of meats, but this time no
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27 351 information about the date of measurement was used. In fact, this is the most probable situation,
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29 352 because, usually in a butcher shop or supermarket, it is unclear how the meat has spent on the
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31 353 shelf. A new SVM classifier model was trained and validated on a dataset that contained 75
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33 354 measurements (5 samples \times 5 storage days \times 3 types of meats). The obtained classification
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35 355 results were also very promising: 81.33% success rate for the electronic nose and 100% for the
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37 356 electronic tongue. Once more, the voltammetric electronic tongue (in direct contact to the meat
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39 357 matrix) is more suited than the electronic nose (relying on volatiles found in the headspace of
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41 358 meat) to identify the type of meat along the cold storage process. Finally, we have attempted to
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43 359 classify the storage time with no information about meat origin. Table 2.a and 2.b show the
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45 360 confusion matrix of the SVM classifier for electronic nose (94.67%) and tongue (100%)
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47 361 respectively. These findings indicate that only 4 meat samples, among 75, were misclassified
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49 362 for the electronic nose and all storage days were perfectly identified for the electronic tongue
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51 363 independently of the type of meat.
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3 364 It is worth noting that since leave-one-out cross-validation method may provide over-optimistic
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5 365 results, it is better to test other cross-validation techniques and so yield a good generalization of
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7 366 the studied situations.
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10 367 **4. Conclusions**

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13 368 Two electronic sensing systems were home-fabricated for rapid screening of meat species. The
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15 369 electronic nose and voltammetric electronic tongue have been succeeded not only to
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17 370 discriminate red meats coming from different animal origins, but also to identify the number of
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19 371 cold storage days meat samples had undergone.
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22 372 The results showed that PCA analysis of electronic nose data cannot differentiate correctly
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24 373 between the 3rd and 6th day of storage of beef, goat and sheep meats. On the other hand, PCA
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26 374 analysis of electronic tongue data showed a good separation between storage days for the three
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28 375 types of meats. Additionally, a perfect discrimination among beef, goat and sheep meats has
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30 376 been obtained by using a SVMs classifier trained and validated on electronic tongue data. It is
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32 377 important to stress that a 100% success rate was obtained for the discrimination among beef,
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34 378 goat and sheep at day 6 (fresh meat) either using the electronic nose or the electronic tongue
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36 379 systems. Finally, the voltammetric electronic tongue has succeeded in the recognition of meat
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38 380 origin with no information about its storage day; and also in the identification of storage time
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40 381 independently of meat origin. Future work involves further validation of these findings on a
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42 382 larger datasets including horse, pork, poultry meats and their mixture for a good consumer
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44 383 protection and fraudulent labelling detection.
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3 454 **Figure captions**

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6 456 **Fig. 1.** Electronic nose system developed for analysis of meat headspace.

7
8 457 **Fig. 2.** Voltammetric electronic tongue setup for red meat analysis.

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10 458 **Fig. 3.** Dynamic response of two sensors to beef, goat and sheep samples: (a) TGS 832; (b)
11 TGS 825.

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13 459
14 460 **Fig. 4.** Radar plots of the steady-state conductance of the sensor array for beef, goat and sheep
15 meat on (a) day 3 and (b) day 9. Axes: S₁: TGS 823, S₂: TGS 825, S₃: TGS 826, S₄: TGS 831,
16 S₅: TGS 832 and S₆: TGS 882.

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18 461
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20 463 **Fig. 5.** Cyclic Voltammograms of Au & Pd electrodes immersed in samples of 3rd, 6th, 9th, 12th
21 and 15th day of storage of three types of red meat.

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23 464
24 465 **Fig. 6.** Cyclic Voltammograms of Ag & Ni electrodes immersed in the three types of red meat
25 during the 3rd and 9th day of storage.

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27 466
28 467 **Fig. 7.** Scores plot of PCA analysis for the determination of the number of storage days by
29 electronic nose: (a) beef; (b) goat; (c) sheep.

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32 469 **Fig. 8.** Scores plot of a PCA analysis for the determination of storage days employing the
33 electronic tongue: (a) beef; (b) goat; (c) sheep.

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35 470
36 471 **Fig. 9.** Two-dimensional PCA plot performed on the three types of meat at day six gathered
37 using the TGS sensor array.

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39 472
40 473 **Fig. 10.** Two-dimensional PCA plot performed on the three types of meats at day six gathered
41 using the voltammetric sensor array.

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60476 **Table captions**477 **Table 1:** SVM success rate (%) for the electronic nose and electronic tongue. (B) beef, (G) goat
478 and (S) sheep.479 **Table 2:** SVM confusion matrix for the classification of storage days independently of meat
480 origin by means of (a) electronic nose and (b) electronic tongue.

Figure 1

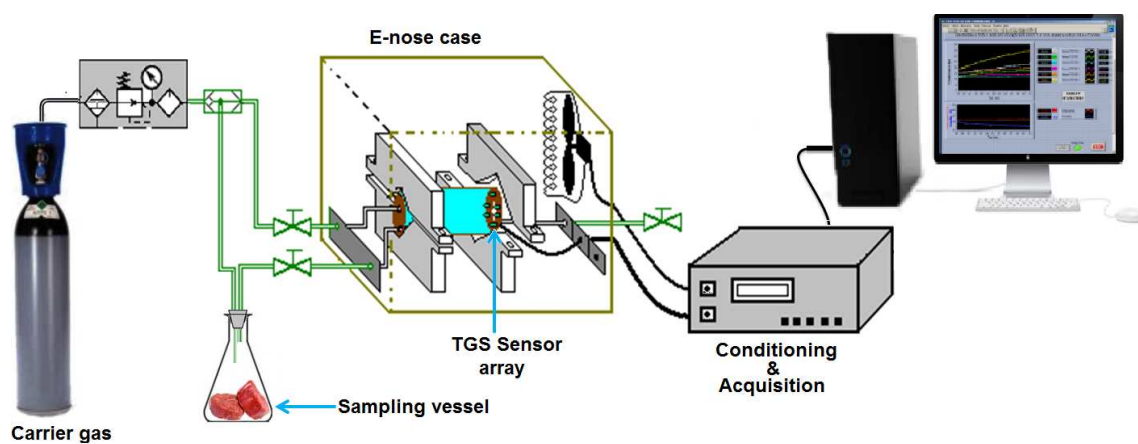
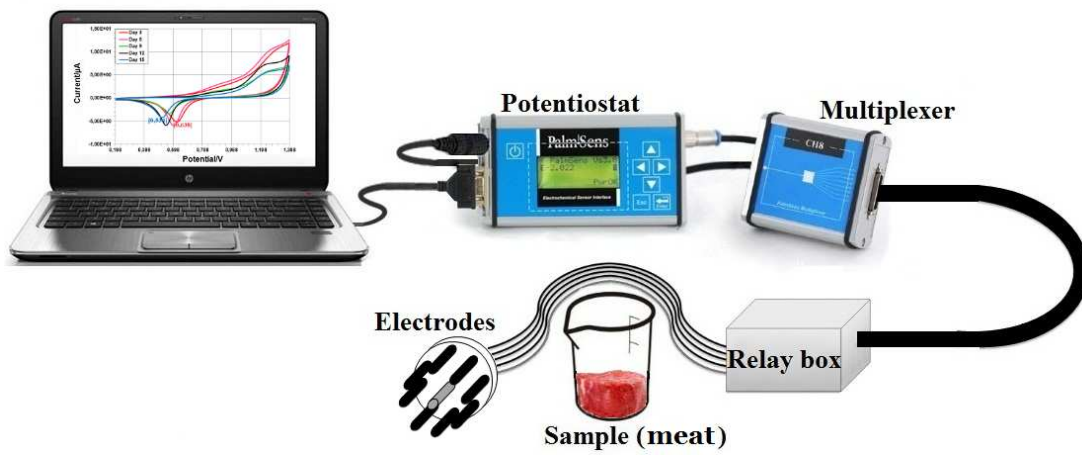
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Figure 2



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Figure 3

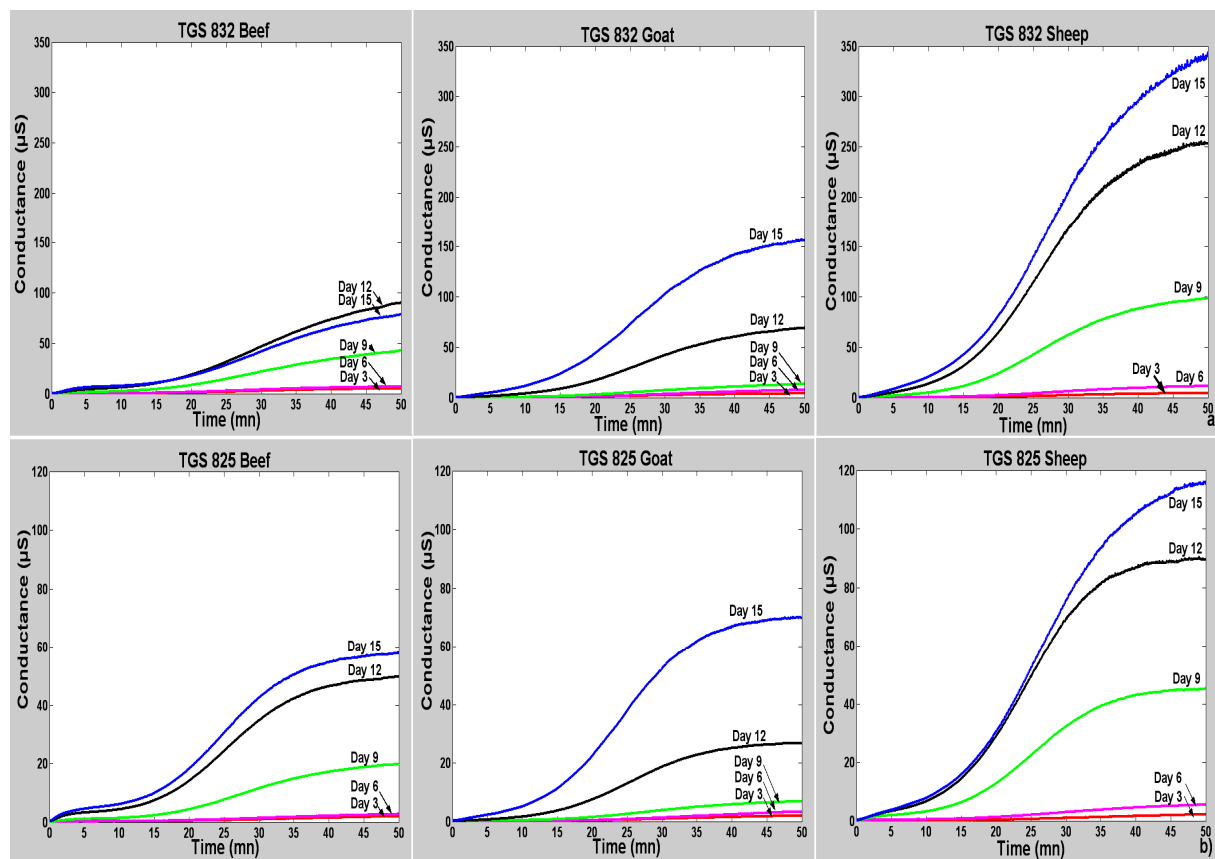
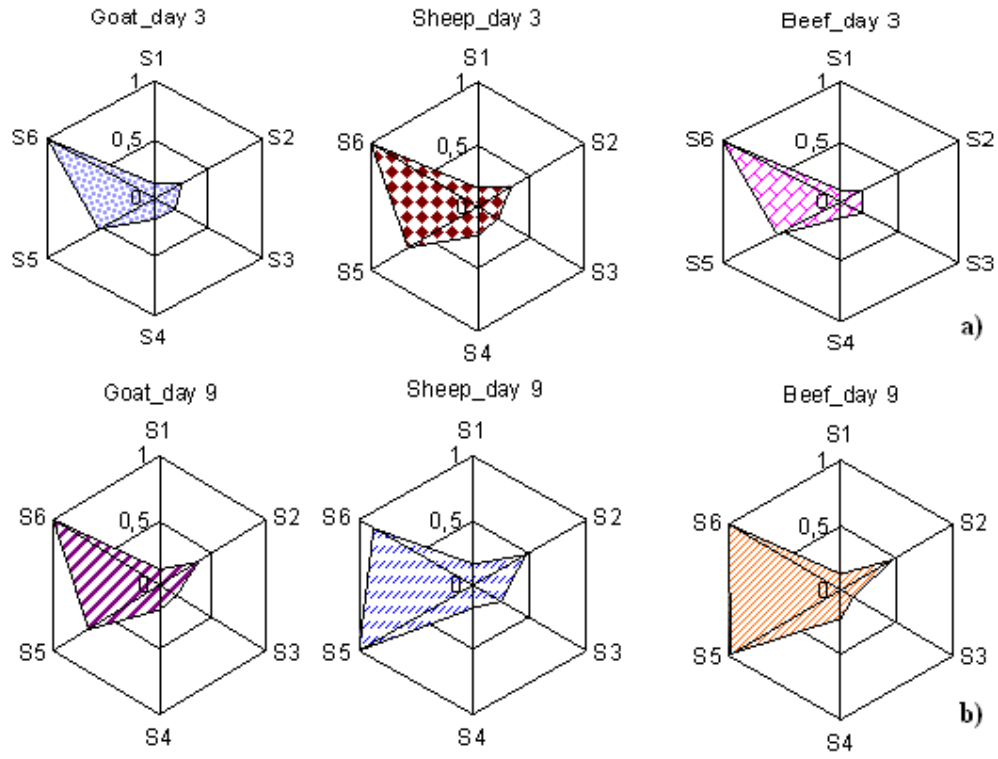


Figure 4



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Figure 5

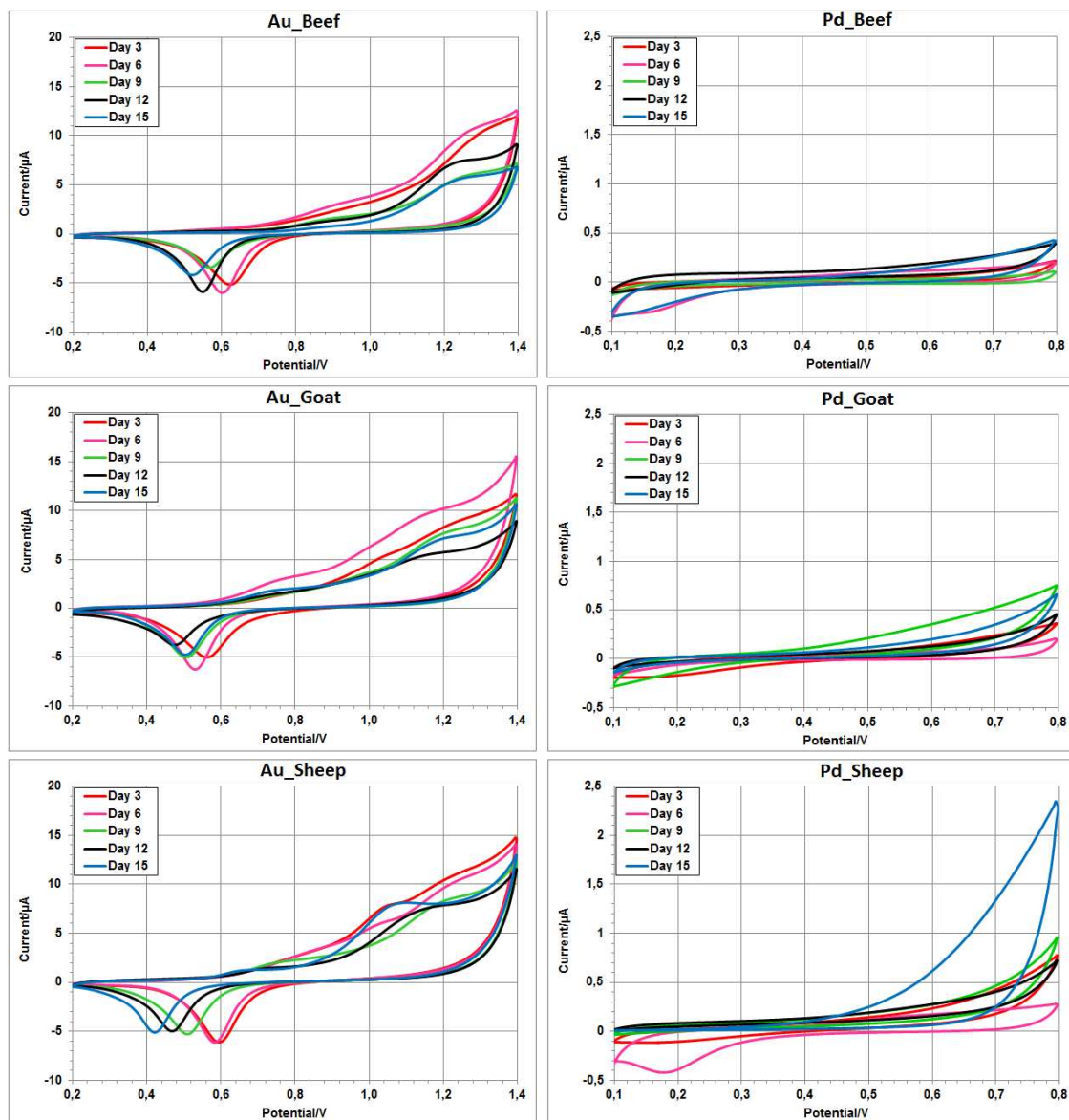
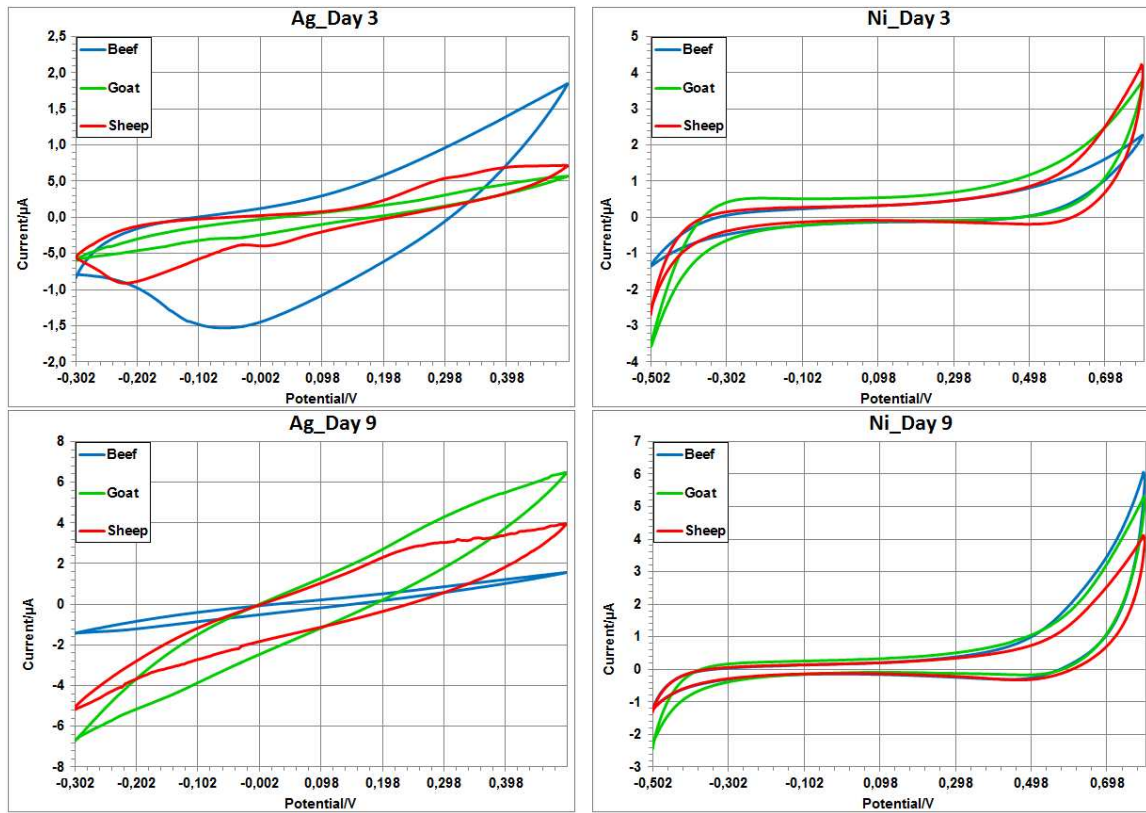


Figure 6



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Figure 7

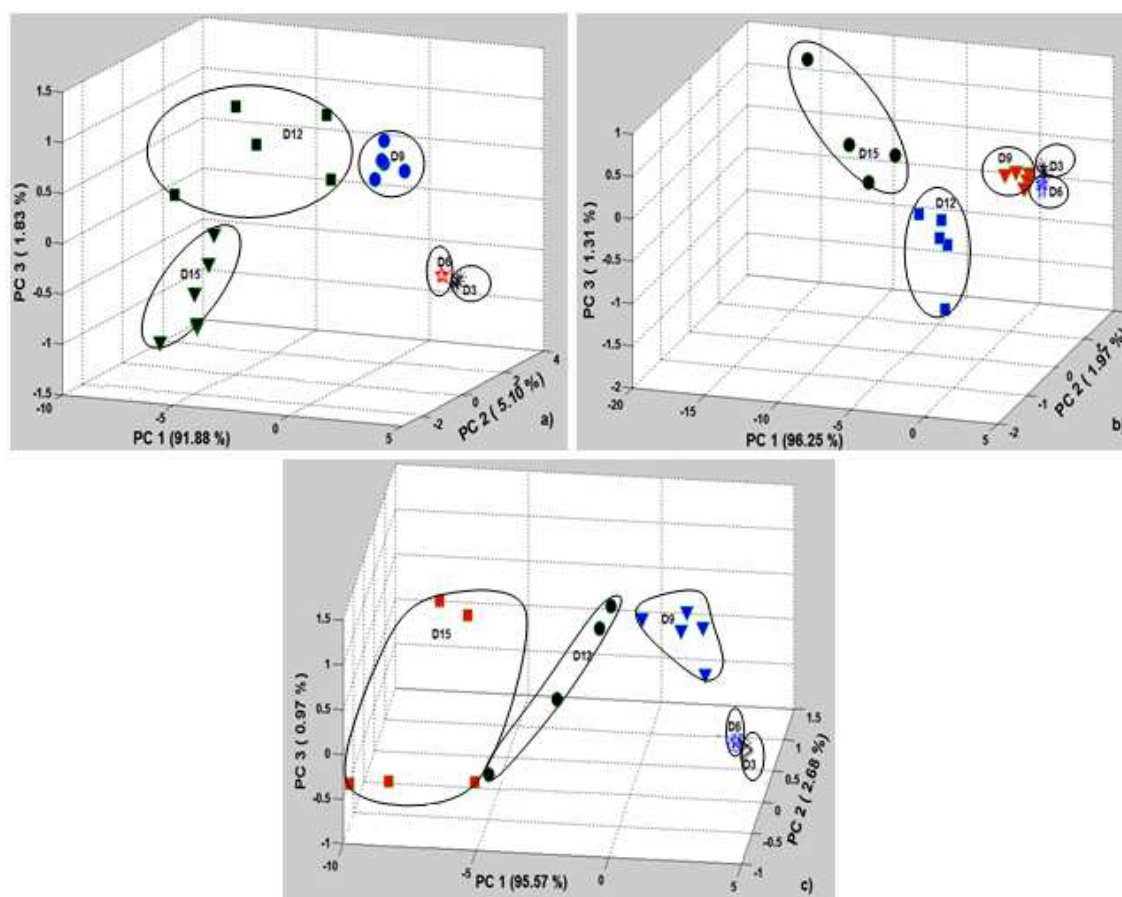
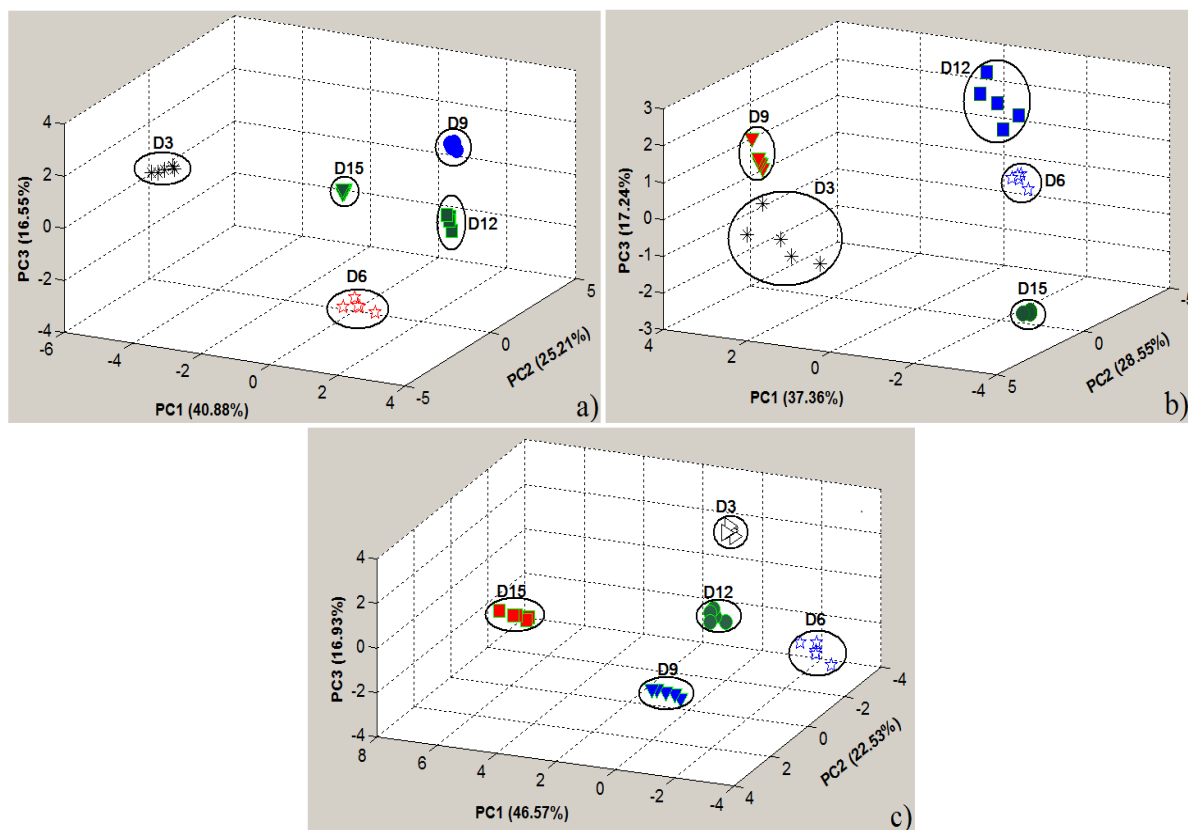
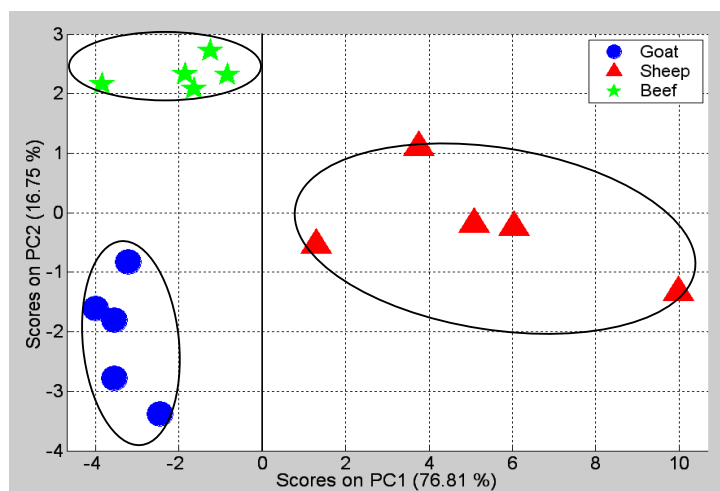
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Figure 8



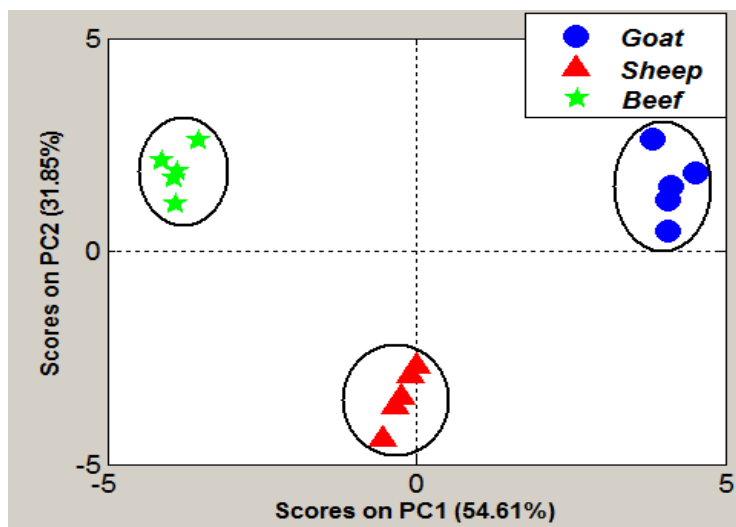
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Figure 9



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Figure 10



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Table 1

	e-nose	e-tongue
Meats	G-S-B	G-S-B
Day 3	100	100
Day 6	93.33	100
Day 9	93.33	100
Day 12	100	100
Day 15	86.67	100
Days 3-15	81.33	100

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Table 2.a

Actual	Predicted				
	Day 3	Day 6	Day 9	Day 12	Day 15
Day 3	15				
Day 6		15			
Day 9			14	1	
Day 12				14	1
Day 15				2	13

Table 2.b

Actual	Predicted				
	Day 3	Day 6	Day 9	Day 12	Day 15
Day 3	15				
Day 6		15			
Day 9			15		
Day 12				15	
Day 15					15