Electronic Nose Based on Metal Oxide Semiconductor Sensors as an Alternative Technique for the Spoilage Classification of Red Meat

Keywords: Red meat analysis; Spoilage classification; Microbiological analysis; Electronic nose.

ABSTRACT

The aim of the present study was to develop an electronic nose application for red meat quality control. An electronic nose and bacteriological measurements are performed to analyze beef and sheep meats stored at 4 °C for up to 15 days. Two datasets corresponding to beef and sheep meats are elaborated for electronic nose system. A support vector machines (SVM) with leave-one-out cross validation, based classification technique is used to investigate the performance of an electronic nose system to spoilage classification of red meats. The classification models classify meat samples based on the total microbial population into "unspoiled" (microbial counts < 6 $\log_{10}$ cfu/g) and "spoiled" (microbial counts ≥ 6 $\log_{10}$ cfu/g). The preliminary results obtained by the total count of bacteria shows that the shelf-life of beef and sheep meats stored at 4 °C are 7 and 5 days, respectively. The electronic nose system coupled to SVM could classify into unspoiled/ spoiled beef or sheep meat with a success rate of 98.81 %.

1. INTRODUCTION

Quality evaluation of red meat products is needed because of the wide range of quality of these products on the market [1]. The shelf-life of meat may be defined as the time elapsing between production and the time of spoilage. The spoilage of meat is a sensorial quality and may consist of off-odours and off-flavours or discoloration [2, 3].

The method currently used for determining the status of meat, with respect to spoilage, is analysis of the total count of bacteria and/ or specific spoilage bacteria. An obvious drawback with a bacteriological method is the incubation period of 1–2 days that is required for colony formation and, additionally, the lack of correlation between the degree of spoilage and the total count of bacteria [3, 4].

Quality control of red meats may also be performed using an electronic nose. According to Gardner and Bartlett [5], the electronic nose is an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours. In order to classify samples, an electronic nose combines the response profiles of the various sensors, which react to different types of volatile compounds in the sample gas.

2. EXPERIMENTAL

2.1 SAMPLE PREPARATION AND SAMPLING

Two different types of meat species, representative of Moroccan production and purchased from a local market, are analysed. The samples from different animal species (beef and sheep) were cut into pieces of the same weights (mass of 10 g ± 1 g) immediately after receiving and then the pieces are placed in plastic boxes and introduced in a refrigerator kept at a constant temperature of 4 ± 1 °C. For each measurement, a meat sample was taken from the refrigerator and put inside a 500 mL glass bottle before every experiment. The bottles are sealed and held at room temperature (22 °C ± 2 °C) for 50 min in order to reach a stable headspace composition. The measurements were performed each day for 2 weeks. At each sampling time two replicates were withdrawn for microbiological analysis and six replicates for electronic nose analysis.

2.2 MICROBIOLOGICAL POPULATION ENUMERATION

A 25 g sample of each product was taken aseptically and placed in a sterile stomacher bag containing 225 mL of 0.1 % (wt/vol) peptone water (PW, Oxoid Ltd., Hampshire. England). The sample and the PW were stomached for 2 min. Decimal dilutions were prepared using the same diluent. These dilutions were next plated out on the surface of Plate Count Agar (PCA, Oxoid Ltd.). The plates were incubated at 30 °C for 2 or 3 days. The total viable counts (TVC) were obtained by enumerating colonies present, and calculated as $\log_{10}$ colony forming units (cfu)/g of the sample.

2.3 ELECTRONIC NOSE SYSTEM DEVELOPMENT

An electronic nose system has been developed to obtain the smell patterns from the headspace of meat samples [6]. This electronic nose system contains an array of six tin oxide based Taguchi gas sensors obtained from Figaro Engineering TGS 8XX (with XX= 23, 25, 26, 31, 32 and 82), a temperature sensor (National Semiconductors LM35DZ), and humidity sensor (Philips H1).

The headspace from meat sample is fluxed into the electronic nose sensor chamber at a flow of 500 sccm. Pure nitrogen is used as the carrier gas. The nose response is registered each 1 second for a time interval of 50 minutes. After the 50 min vapour exposure nitrogen are flushed again until steady state baseline was reached.

The variation of the TGS sensors conductivity was acquired and then digitised using a data acquisition board (PCL 812PG, Advantech). A sampling rate of 1 sample/s was used. A program in Labview was developed to control the data acquisition.

The performance of the designed electronic nose system is evaluated by its ability to classify the meat samples into unspoiled/ spoiled. Data processing and pattern recognition are decisive factors in order to obtain a versatile instrument able to reliably recognize a wide variety of odors. Pattern recognition was performed using a Support Vector Machine (SVM) paradigm. Since SVMs make binary classification a one vs. one approach was used to identify any category from the rest. The kernel used was an order 2 polynomial.

3. RESULTS AND DISCUSSION

3.1 RESPONSES OF THE GAS SENSOR-ARRAY

This initial analysis consists of studying the influence of the volatile gases emanating from beef, and sheep meats on the conductance of the sensors. Fig. 1 shows for the six sensors the evolution in their response to the two red meats at days 3 (sub-plots in figure 1 (a, c)) and 9 (sub-plots in figure 1 (b, d)). The intensities of the conductance of the six sensors increase according to exposure time. It can be derived also that the intensities of the conductance of the six sensors increase according to the number of days that meats have undergone cold storage. This behaviour can be justified by an increase in the concentration of volatile gases given out by meats as a function of storage time, or the occurrence of new species in the headspace of meats.

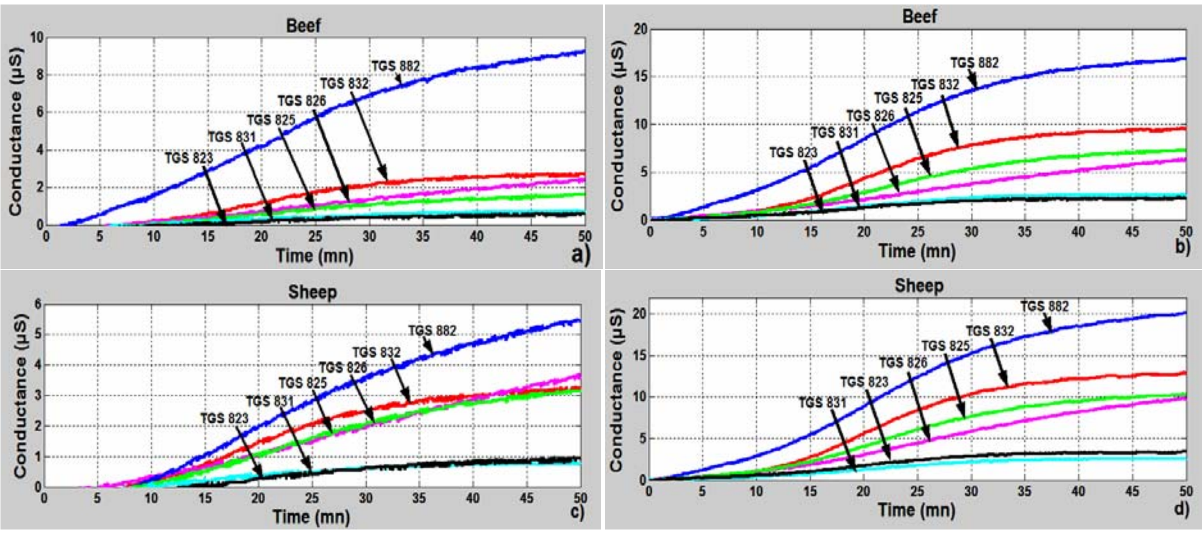

Figure 1: Time responses of an array of the six gas sensors at day 3 ((a) beef, (c) sheep) and day 9 ((b) beef, (d) sheep)

3.2 BACTERIAL ANALYSIS

The bacterial growth on the meat used in the development of the electronic nose classification models is presented in Fig. 2 witch present the evolution of $\log_{10}$ cfu/g developed in the two types of meat according to storage days. A similar behavior has been observed for the two types of analyzed meat. A slight variation in the first five days followed with a very fast increase between the days five and ten, and finally in the last days of conservations the curves have the tendency to stabilize. In addition, we notices that the number of cfu increases with a slightly superior speed in sheep meat then that in the beef meat. We also notices that the threshold of accepting to the consumption (microbial counts < 6 $\log_{10}$ cfu/g) [7] is marked on the day seven for beef meat and the day five for sheep meat.

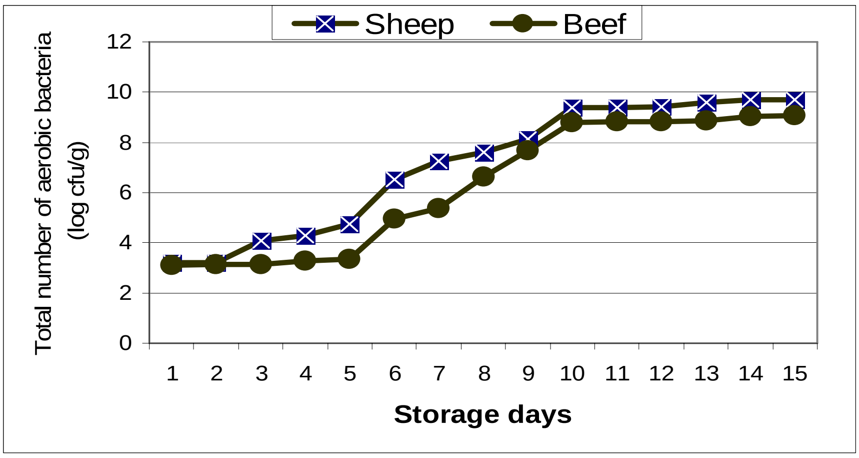

Figure 2: Changes in the count of aerobic bacteria

3.3 MATHEMATICAL MODELS FOR THE RELATIONSHIP BETWEEN THE DEGREE OF SPOILAGE AND THE SENSOR SIGNALS

In parallel to the bacteriological analysis, an analysis of the volatile compounds by the electronic nose has been made. For every type of meat a dataset has been elaborated. In the first time the principal components analysis was performed for beef dataset and for sheep dataset. Fig. 3 shows the evolution of the scores on first principal component PC1 as a function of storage time and polynomial fitting for beef and sheep meats. These scores show a monotonic decrease during the period of storage. A slight variation in the five storage days followed by a very fast decrease of the scores on PC1 in the last storage days. It's observed that the PC1 mainly describe the change in the degree of meat spoilage [8]. We noted that the spoilage of sheep meat is fast then that of beef meat.

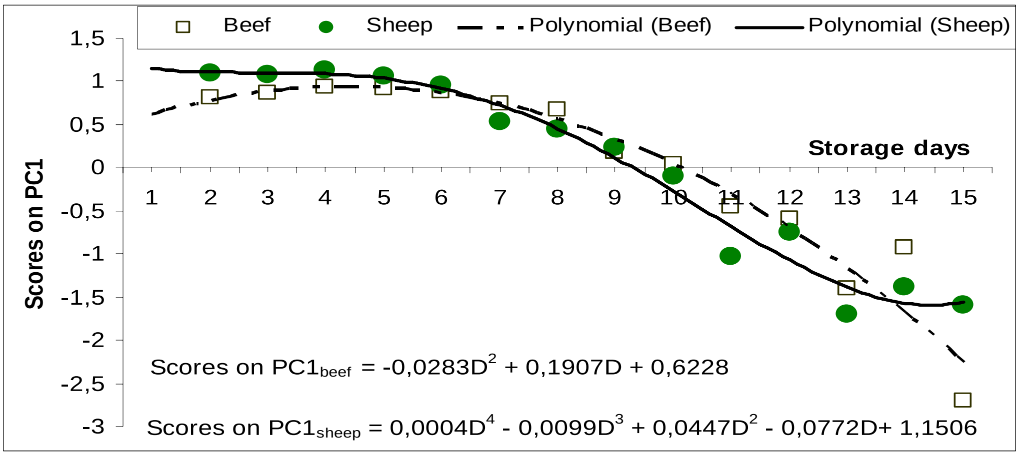

Figure 3: Evolution of the scores on the first principal component with the period of storage and polynomial fitting for beef and sheep meats

In the second time supervised pattern recognition method like Support Vector Machine was called for dataset analysis. As taking as a basis to the bacteriological analysis we divided the dataset in two observations defined as spoiled and unspoiled. SVM with the approach multi classes one against one has been used to develop a rule of decision to classify the observations of the dataset in spoiled/ unspoiled samples. A leave one out technique was used to model classification validation. A very good percentage of classification of 98.81 % has been gotten for spoilage classification of the two type of meats experimented.

4. CONCLUSION

In the present investigation, a bacterial analysis was used as a complementary method to develop a simple and rapid alternative technique for the spoilage classification for red meat. The electronic nose technique has the advantage to be objective on opposite of the bacteriological method since it makes the identification of the sample according to a dataset. The bacterial analysis could be define the shelf-life for beef or sheep meat. However, an obvious drawback with this method is the incubation period 2–3 days that is required for colony formation, what is some is longer. The electronic nose coupled to SVMs showed a very good success rate for spoilage classification. The electronic nose could be used as a rapid and reliable method for red meat quality control.

5. REFERENCES

[1] N. El Barbri. B. Bouchikhi. E. Llobet. N. El Bari. X. Correig. Differentiation of red meat using an electronic nose based on metal oxide semiconductor sensors and support vector machines, International Symposium on Olfaction and Electronic Nose ISOEN'07, Saint-Petersburg, 3-5 May 2007, Russia 2007.

[2] R.H. Dainty. B.M. Mackey. The relationship between the phenotypic properties of bacteria from chill-stored meat and spoilage processes, J. Appl. Bacteriol. 73 (1992). p. 103S–114S

[3] E. Borch. M.-L. Kant-Muermans. Y. Blixt. Bacterial spoilage of meat and cured meat products, Int. J. Food of Microbiol. 33 (1996). p. 103–120

[4] C.O. Gill. Meat spoilage and evaluation of the potential storage life of fresh meat, J. Food Prot. 46 (1983). p. 444–452

[5] J. W. Gardner. P. N. Bartlett. A Brief History of Electronic Noses, Sensors and Actuators B, 18 (1994). P. 211–220

[6] A. Amari. N. El Barbri. E. Llobet. N. El Bari. X. Correig. B. Bouchikhi. Monitoring the Freshness of Moroccan Sardines with a Neural-Network Based Electronic Nose, Sensors 6 (2006). p. 1209-1223,

[7] S. Panigrahi. S. Balasubramanian. H. Gu. C.M. Logue. M. Marchello. Design and development of a metal oxide based electronic nose for spoilage classification of beef, Sensors and Actuators B 119 (2006). p. 2–14

[8] Y. Blixt. E. Borch. Using an electronic nose for determining the spoilage of vacuum packaged beef, International Journal of Food Microbiology 46 (1999). p. 123–134