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# Shelf life determination by electronic nose: application to milk

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**Abstract**

Electronic Nose is mostly used for different applications in food and beverage industries: identification, quantification, quality control. In each application, the principal goal is that this instrument could discriminate different organoleptic properties of different samples. Those properties could be qualities, origins, defects, concentration of pollutants.

One of the usefulness of this instrument is when it induces, on the analyzed products, the same structure as the one induced by a human sensory panel allowing instrumental measurement of sensory properties. In this case, mathematical methods are used to exploit this correlation in order to bring in line the sensory panel capabilities. Sensory panel knowledge and capabilities are transferred to the production shop floor for routine analysis.

In this paper, one presents the results of Electronic Nose used to determine the shelf life of milk. To do this, milk was stored at ambient temperature and at constant temperature of 5 °C. Samples of each of the stored milk have been analyzed by electronic nose at different times. The mathematical method presented here will suggest some interesting time-events, found in the literature on milk shelf life, that correspond to significant ones in the milk evolution or aging.


*Keywords:* Electronic nose; Shelf life; Sensory panel; Bacteria growth

## 1. Introduction

In the recent years, we have seen that electronic nose devices have been successfully used for different applications particularly for the food and beverage industries. To validate the results of this new technology, its results have been compared to those obtained by classical technologies like GC or GC/MS. They have been also compared, for some application, to the results obtained by sensory analysis [1]. For each application or objective, mathematical and statistical methods have been proposed to exploit the relationship or the correlation between the results obtained by the new technology and the others ones.

The freshness of foodstuff, particularly the determination of shelf life, is one application for which electronic nose could be used. Freshness of fish has been studied by different authors [2,3]. Interesting results have been published.

In this paper, the results of using electronic nose to predict the milk shelf life is considered. To do this, samples of milk stored during 52 days at ambient temperature and at 5 °C have been analyzed by the system. In parallel to the instrumental analysis, milk changes have been investigated by estimation of the microbial count by using the 3M™ Petrifilm™ test. The microbial count evolution will be detected by the electronic nose results. This result firstly shows correlation between microbial evaluation and fingerprint sensor measurement. An other part of the results obtained with electronic nose is correlated with the milk shelf life work published by Labuza [4,5] particularly the demonstration of the absence of correlation between shelf-life and the microbial count and also the significant event-times suggested by the analyzes.

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## 2. Materials, instrument and methods

### 2.1.1. *Materials*

The growth of total bacteria in the milk was measured at two temperatures: ambient temperature and 5 °C during 52 days (8 July 2003 to 28 August 2003).

During this period, samples of the milk have been analyzed by electronic nose.

As we know that sensors drift [6] can alter electronic nose results, calibration samples of three pure products (acetone, propanol and isopropanol) are periodically analyzed to be used for correction purposes if required.

### 2.2. *Electronic nose*

The electronic nose used for this study was a Fox 4000 (ALPHA MOS, Toulouse FR) with three Metal Oxide Sensors chambers equipped with 18 sensors (LY2/AA, LY2/G, LY2/gCT, LY2/gCTl, LY2/Gh, LY2/LG, P10/1, P10/2, P30/1,P30/2, P40/1, P40/2, PA2,T30/1, T40/2, T70/2, T40/1, TA2). The carrier gas was TOC grade synthetic air ($P$ = 5 psi). The samples were injected to the Fox system with an autosampler HS100 (Alpha MOS, Toulouse FR) from 10ml sealed vials, the acquisition time and time between subsequent analyses were respectively 120 s and 20 min and the flow rate was kept at 150 ml/min.

*Analytical conditions with FOX system:*

| | |
|---|---|
| Quantity of sample in the vial | 1 ml |
| Total volume of the vial | 10 ml |
| Headspace generation time | 300 s |
| Headspace generation temperature | 50 °C |
| Syringe volume | 2.5 ml |
| Injected volume | 1 ml |
| Injected speed | 1 ml/s |
| Acquisition time | 120 s |
| Runtime | 1200 s |

### 2.3. *Microbial counts*

Total aerobic bacteria were enumerated using 3M Petrifilm [7,8]. Samples were diluted in water, and 1 ml of sample was transferred onto the film. The Petrifilm contained standard method nutrients and a cold water soluble gelling agent, while the top film is coated with the gelling agent (5,6,7) and 2,3,5-triphenylterazoluim chloride (TTC). Colonies appear red and were counted following incubation at 37 °C for 48 h for total aerobic.

### 2.4. *Mathematical method*

Detecting the shelf life of products needs a definition of an appropriate function depending on time. Let $F$ this function, at each time $t$, one compares $F(t)$ to $F(0)$

Table 1
Milk analysis dates

| Label | Date |
|---|---|
| 1 | 15/07/03 |
| 2 | 16/07/03 |
| 3 | 17/07/03 |
| 4 | 18/07/03 |
| 5 | 21/07/03 |
| 6 | 22/07/03 |
| 7 | 23/07/03 |
| 8 | 24/07/03 |
| 9 | 25/07/03 |
| 10 | 28/07/03 |
| 11 | 30/07/03 |
| 12 | 01/08/03 |
| 13 | 04/08/03 |
| 14 | 07/08/03 |
| 15 | 14/08/03 |
| 16 | 21/08/03 |
| 17 | 28/08/03 |

Each significant variation of this function corresponds to significant evolution of the analyzed product.

By using the vector norm for this function, one observes the necessity of fitting this function. In fact, this function is a good global indicator but slow variation on each sensor can induce noise on the global measure. Fit with mobile average has been used.

Table 2
Pure product analysis dates

| Label | Date |
|---|---|
| 1 | 10/07/03 |
| 2 | 11/07/03 |
| 3 | 16/07/03 |
| 4 | 17/07/03 |
| 5 | 21/07/03 |
| 6 | 24/07/03 |
| 7 | 25/07/03 |
| 8 | 28/07/03 |
| 9 | 01/08/03 |
| 10 | 04/08/03 |
| 11 | 05/08/03 |
| 12 | 06/08/03 |
| 13 | 07/08/03 |
| 14 | 08/08/03 |
| 15 | 11/08/03 |
| 16 | 14/08/03 |
| 17 | 19/08/03 |
| 18 | 20/08/03 |
| 19 | 21/08/03 |
| 20 | 28/08/03 |
| 21 | 03/09/03 |
| 22 | 12/09/03 |
| 23 | 18/09/03 |
| 24 | 19/09/03 |
| 25 | 22/09/03 |
| 26 | 23/09/03 |
| 27 | 26/09/03 |

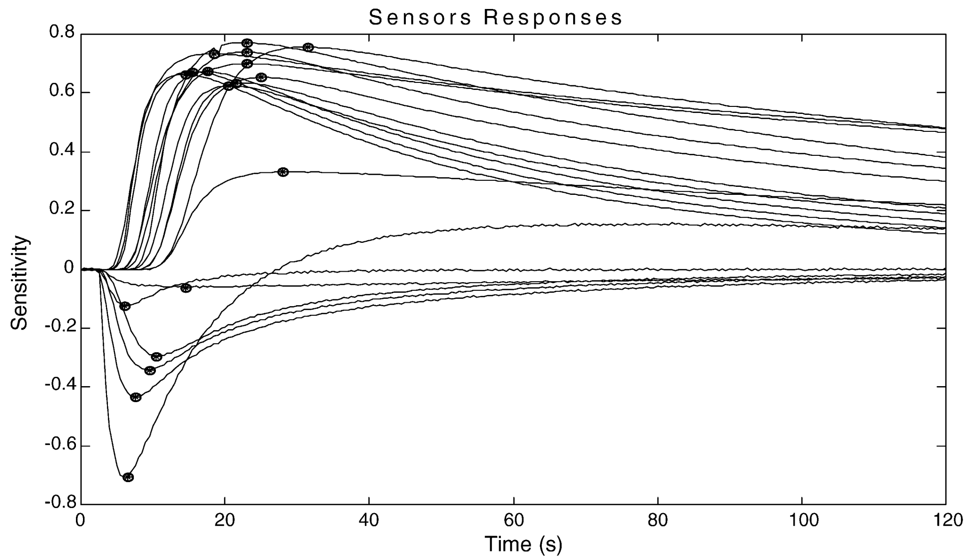


Fig. 1. Typical sensors responses and significant points.

At each time $t$, the system generates a vector $X_t$ of $n$ components $\{X_t(j)$: $j = 1{:}n\}$, where $n$ is the sensor number of the electronic nose. $X_t(j)$ is the resistance of $j$th sensor at time $t$. With this notation, the function $F$ is defined as follows

$$F(t) = \sqrt[n]{\sum_{j=1}^{n}(X_t(j) \times X_t(j))}$$

Interesting time-events would be associated to inflection points of this function or null values of its derivative.

## 3. Results

### 3.1. Analysis dates

Table 1 [resp. 2] summarizes the dates of the milk [resp. pure products] analysis.

These analysis dates have been chosen so that milk's ones could be covered by the ones of the pure products for calibration and correction purposes (Table 2).

### 3.2. System characteristics

In Fig. 1 below, we have represented raw sensitivity values of 18 sensors. The $x$-axis represents the time of the analyze and the y axis represents the sensitivity of the sensors. The

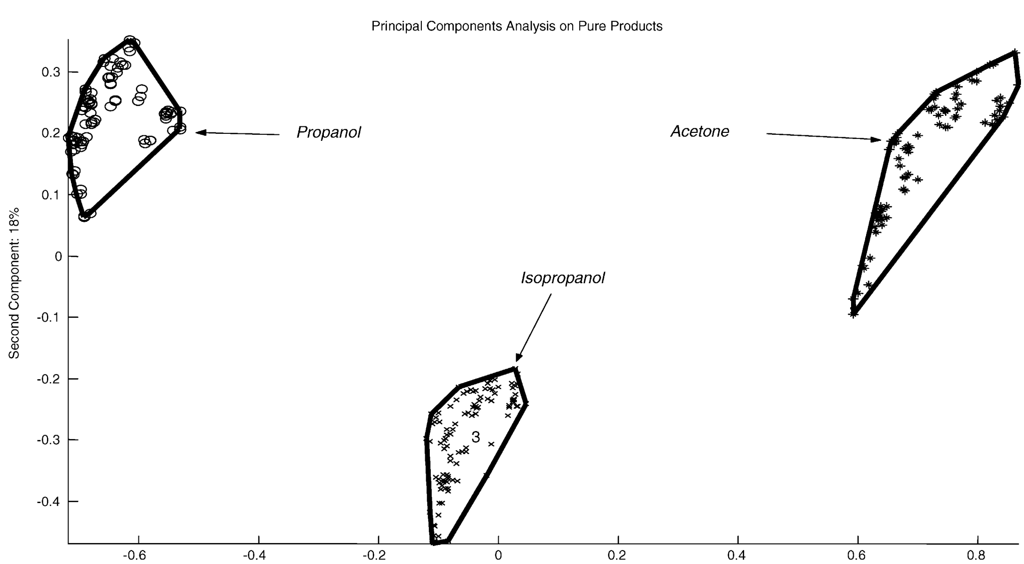


Fig. 2. Projection of all pure products samples on the first principal plane.

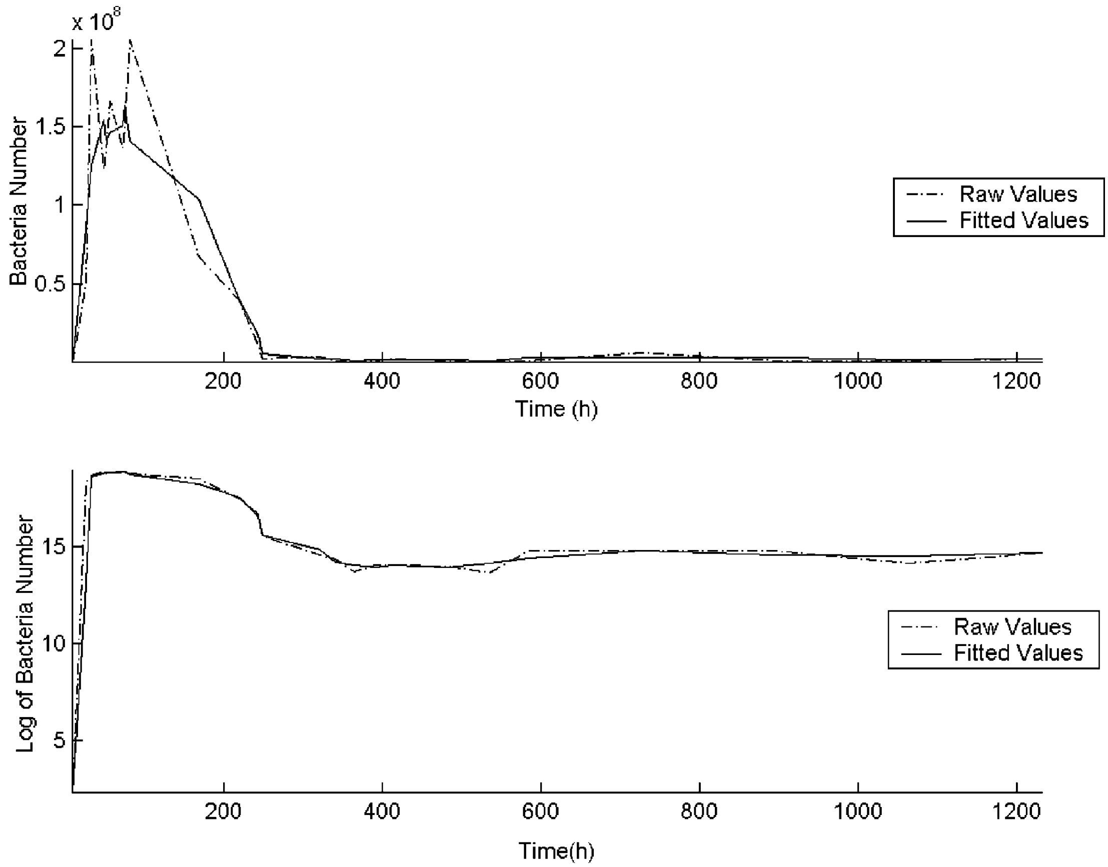


Fig. 3. Microbial growth in milk stored at ambient temperature.

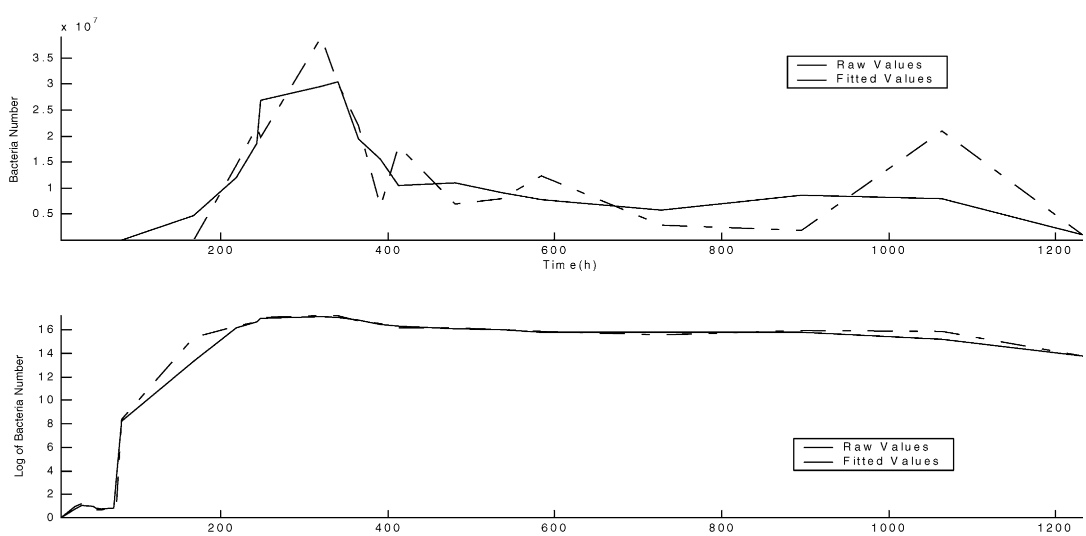


Fig. 4. Microbial growth in milk stored at 5 °C.

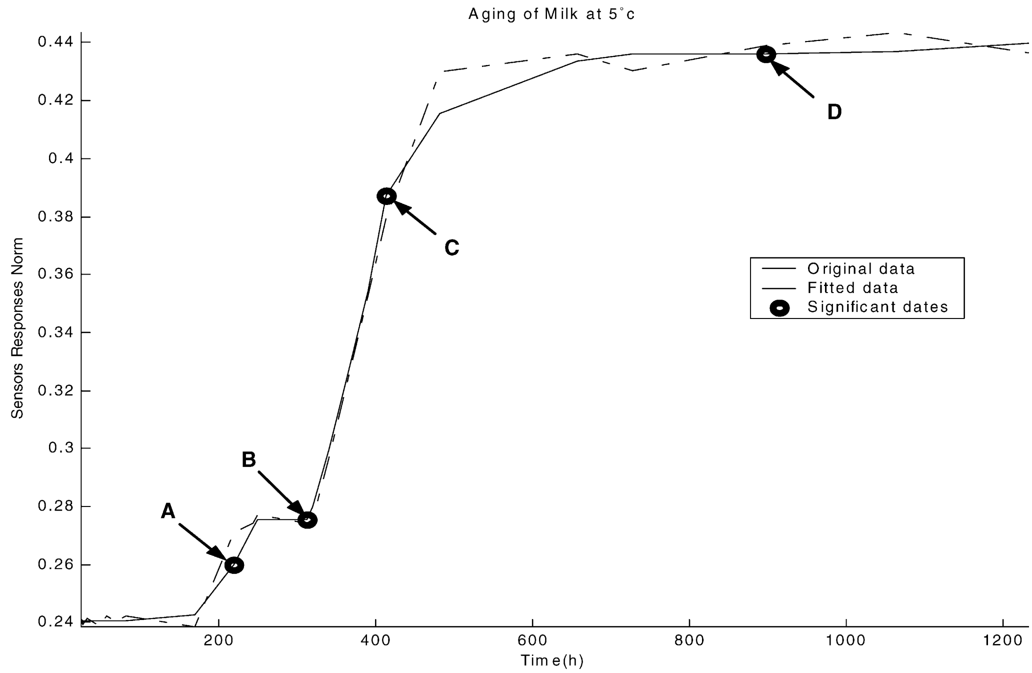


Fig. 5. Significant time-events detected by the method.

last is calculated as follows:

$$\text{Sensivity}(t) = [R(t) - R(0)]/R(0),$$

where $R(t)$ is the sensors resistance at time $t$.

On each curve, one represents the optimum of all the measures. The set of the 18 significant features will represent a line of the database, which will be used in the statistical method.

Before presenting the shelf-life milk results, one summarizes some of the most important characteristics that an electronic nose need to satisfy: reproducibility, long term stability, identification capability and model robustness. To do this, principal components analysis (PCA) is done on the pure

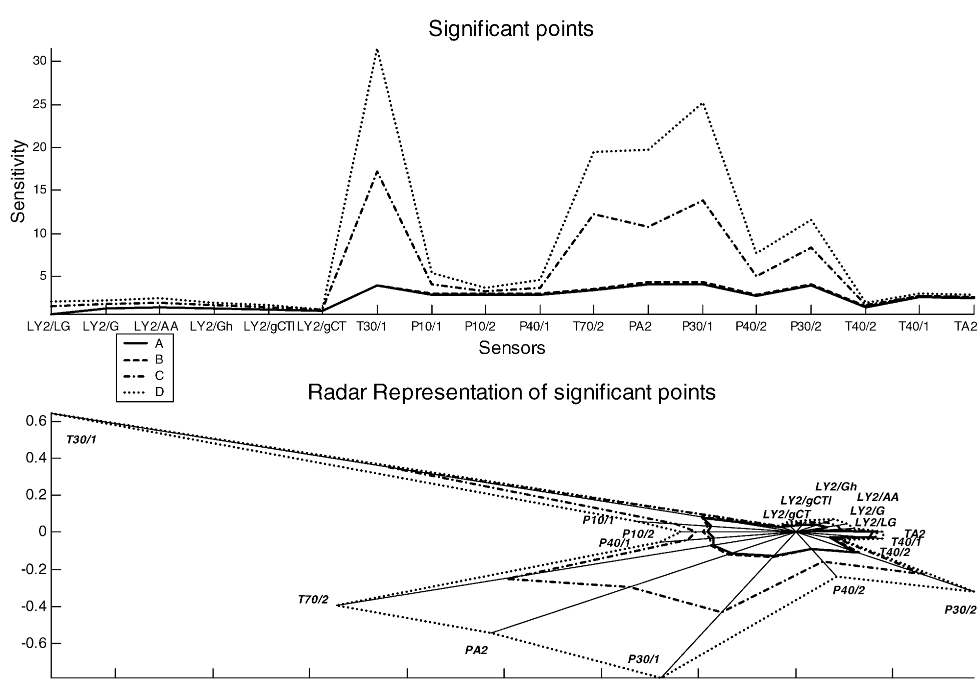


Fig. 6. Sensors sensitivities at significant times.

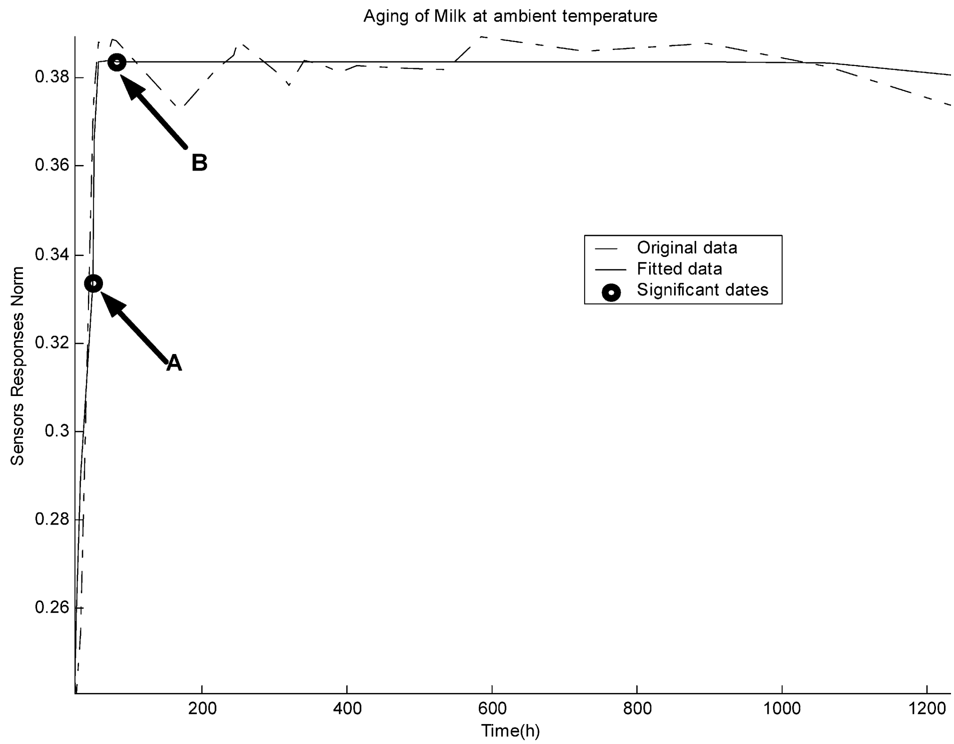


Fig. 7. Significant time-events detected by the method.

products measurements. Results of this method are presented in Fig. 2.

### 3.3. Microbial flora evolution

The bacteria populations have been counted during the milk analysis [7,8]. Growth kinetics are displayed in Figs. 3 and 4. As expected, growth is a lot faster at ambient temperature.

### 3.4. Electronic nose responses

Figs. 5, 6, 7 and 8 show the norms of the sensors responses according to the milk storage time. From this representation,

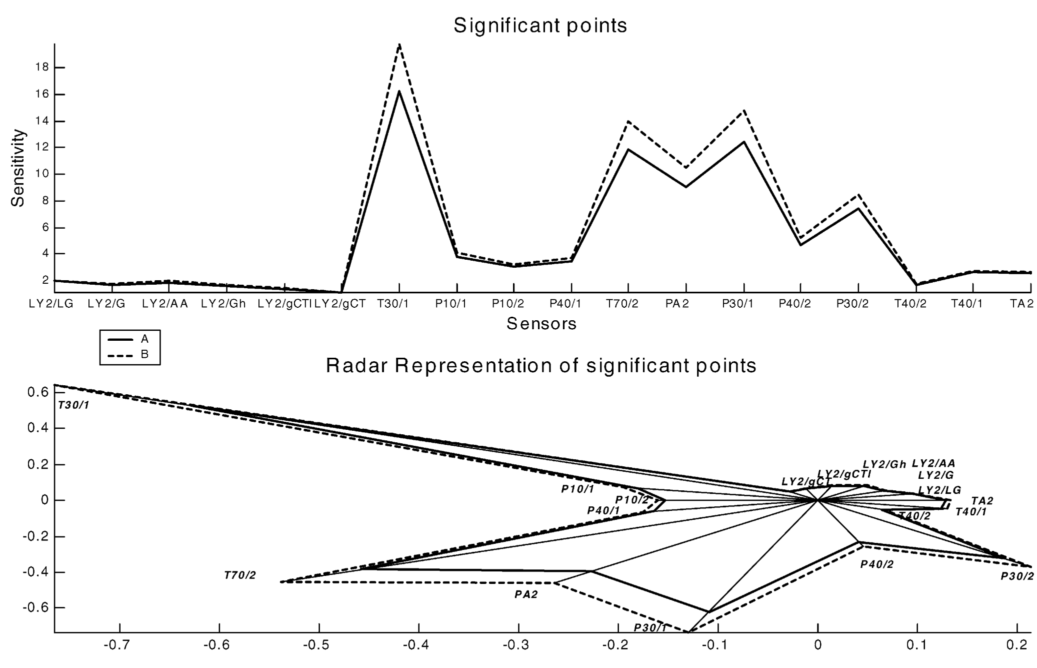


Fig. 8. Sensors sensitivities at significant times.

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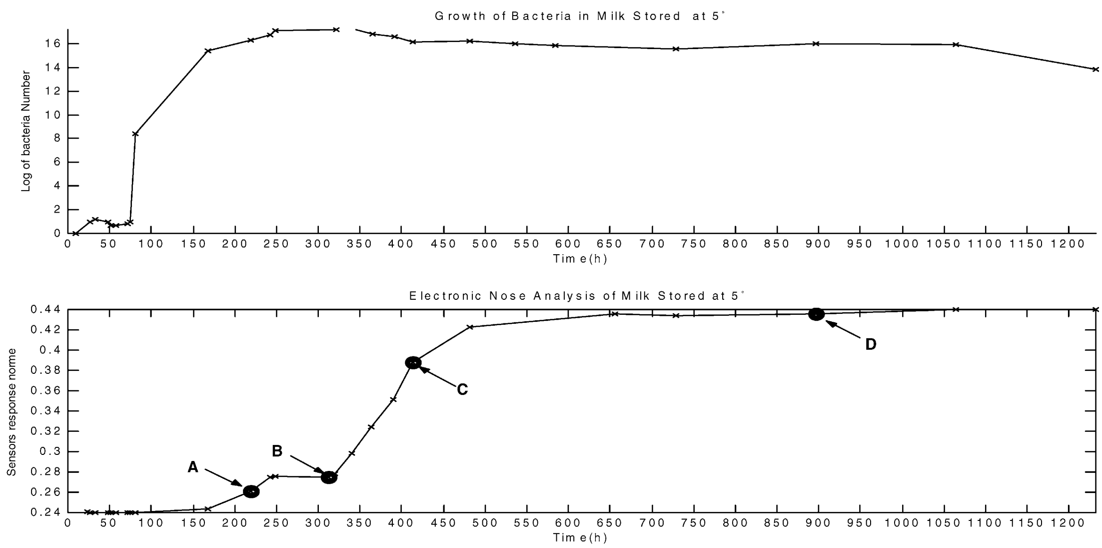


Fig. 9. Correlation between the bacteria growth and sensors response norm.

we have extracted significant points (A–D) that correspond to significant changes in milk evolution.

Four significant times have been found in the analysis of the milk stored at 5 °C. They correspond to the following days: 9.16, 13, 17.21 and 37.34.

For the milk at ambient temperature, only two dates corresponding to day 2 and 3.4 have been found significant.

Gacula introduced in 1975 [9] the use of Weibull Hazard statistical method to test food the shelf life. By using this method, Duyvesteyn et al. [4] have shown that the shelf life for milk stored at 5 °C is about 13.7 days with (12.19–15.34) range for 95% confidence range.

## 4. Correlation and interpretations

To interpret the significant dates in the milk aging suggested by the analysis of vectors norm, we firstly present partial correlation between the analytical results and the ones obtained by bacteria counting (Figs. 9 and 10).

The significant point A, in the two storage conditions, corresponds to the time when the number of bacteria is maximum or near the maximum. Until this time, bacteria count and sensors vector norm increase.

For milk stored at ambient temperature, the vector norm reach its maximum after 3 days and become constant.

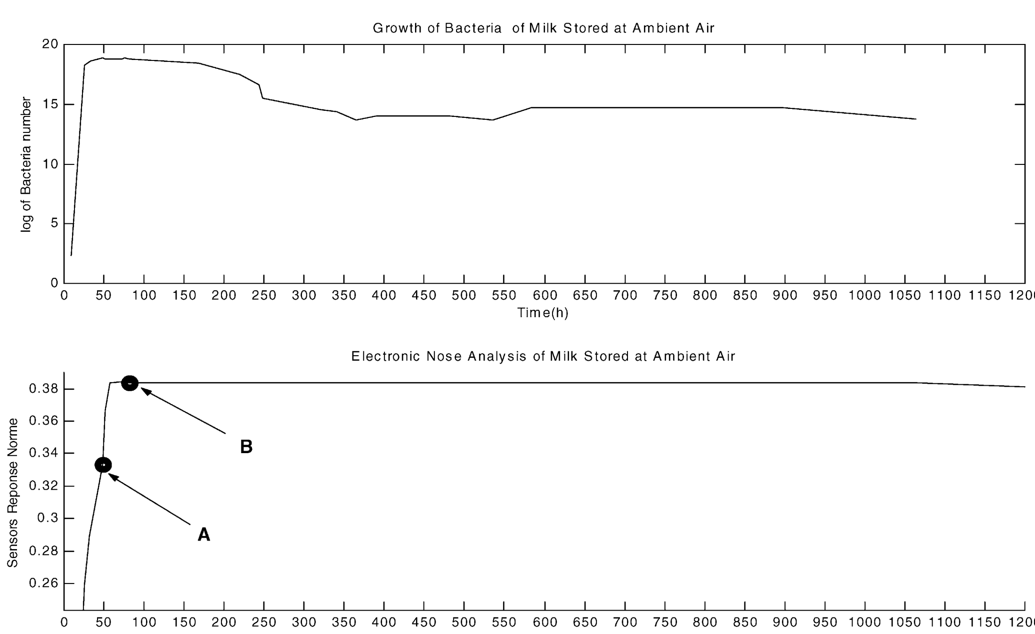


Fig. 10. Correlation between the bacteria growth and sensors response norm.

For milk stored at 5 °C, the vector norm continues to grow until 600 h of storage (25 days). The significant point B suggested by the method is in the interval 12–14 suggested by Lagrange and Hammond [10].

Between this point and the significant point C, one observes a big increment of the norm function. We suppose that an important transformation of the milk happens in this time interval. After point C and until point D, the increment is decreasing. Just before point D until the end of the analysis, the function norm is constant and therefore milk deterioration reaches steady state.

## 5. Conclusion

The results presented in this paper show that measurement generated by the electronic nose can be used to detect both bacteria growth in milk and shelf life. The time-events suggested by the mathematical method can be associated to significant dates in the milk evolution. So this instrument can be easily used to date products and to control their freshness.

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