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Application of E-NOSE technology for ultra-high temperature processed partly skimmed milk production batches monitoring

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In our work we present a case study of the capability of one electronic nose (P.E.N. 2 sensor array by Airsense Analytics, Germany) in discriminating different qualities of milk samples by sensing their aroma. All the analyzed milk samples, belonging both to different production batches and to different brands, were ultra-high temperature (UHT) processed, partly skimmed, and commercially available at retailers. Milk samples showing off-flavors were compared with other samples of the same kind of milk belonging to the same brand (but to different production batches) and to different brands. The comparison was performed by comparing the smell of the samples just after opening of the packaging and again two hours later.
In all cases, principal component analysis carried out on sensor's output was able to discriminate samples into two different groups characterized by normal and anomalous odour. Moreover, the analysis of the olfactory fingerprints showed that two hours after the opening of the packaging, the flavor of anomalous samples evolved in a different way from that of the normal ones. With reference to this last scenario, the classification of milk odour carried out on sensors' output by Linear Discriminant Analysis (LDA) exhibit 98.8 % correct assignation and 98.61% correct prediction.
The obtained results confirm the utility of the e-nose approach in monitoring the quality of UHT partly skimmed milk production batches, especially if combined with chemical, physical, and sensory techniques).

Introduction

Smell and flavor are two key factors determining consumers' acceptance of food whose perception is a multi-component process governed by the properties of the flavor compounds, the nature of the food matrix and, last but not least, the physiological conditions of mouth, nose, and throat during food consumption. In particular, odor is one of the primary factors (together with the senses of touch, sight, and taste) used by people to evaluate food quality, and it is of critical importance in consumer's decision-making as it greatly affects the food attractiveness.

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Within the agro-industrial sector, the use of sensor arrays whose signals are processed by pattern recognition software is actually growing as it allows efficient and rapid monitoring of the foodstuffs available in the market (Deinsingh et al., 2004; Ciosek and Wróbleski, 2006; Yu et al., 2007). That's why e-nose food aroma analysis, offering a fast and non-destructive alternative for sensing aroma, can be an important support for classical quantitative chemical analysis, being advantageously used as a screening device during food processing and production.

Many studies have been published about electronic sensing for rapid characterization and discrimination of the aromas of common raw and processed foods (e.g., meat, fish, milk and cheese, vegetables, as well as soft and alcoholic drinks) focusing the attention on the evaluation of food's shelf-life (Riva and Mannino, 2004; Labreche et al., 2005). In addition, among the possible applications of e-nose monitoring techniques in the food industry are: evaluation of the proper maturing of some cheeses (Patrick et al., 2003; Trihaas et al., 2005), olive oil and milk production zone discrimination (Cosio et al., 2006; Falchero et al., 2009), recognition of the proper ripening stage of fruits and post-harvest quality control monitoring (Di Natale et al., 2001; Pathange et al., 2006; Hernández Gómez et al., 2006a, 2006b), and inspection of the degree of fungal contamination of cereals (Magan and Evans, 2000). With reference to milk, headspace analysis by means of a sensor array has been carried out to track rancidity of different kinds of milk during aging (Capone et al., 2001), to determine shelf-life (Labreche et al., 2005), to differentiate between mastitic and healthy quarter milk samples within dairy cows (Eriksson et al., 2005), and to identify seasonal changes in whole milk powder odor (Biolatto et al., 2007).

Our work is focused on studying the application of a commercial e-nose to monitor the quality of ultra-high temperature (UHT) processed milk sold by an Italian dairy company in order to test the capability of the method to identify production lots that, despite complying with both the chemical and biological standards required by Italian law, show substantial differences in odor.

Material and Methods

UHT partly skimmed milk samples belonging to production batches showing anomalous smell and flavor when opened were compared both to different production batches of the same brand and to production batches of different brands available at retailers in the same period. All the studied samples were commercially available in sealed Tetra Pak bottles equipped with screw caps. All the bottles, after being stored in laboratory at the ambient temperature of 20°C for three days, were thoroughly shaken before opening. By means of a pipette, we then extracted three 20 mL samples of milk from each bottle and put these samples in 40 mL vials, which were promptly sealed with rubber caps. Before performing headspace analysis, all vials were held at 20°C for 30 min (1800 s) to let the volatile fraction of the milk samples saturate the vial's headspace. To carry out the test, 34 partly skimmed UHT milk samples with three replicates each, for a total of 102 acquisitions, were set up. Milk sampling was repeated 2 hours after opening of the packages.

1.1 Odor analysis

Milk odor was analyzed by means of a PEN 2 electronic nose (WMA Airsense, Schwerin, Germany), which consists of a sampling unit, a sensor array made up of ten metal oxide semiconductor (MOS) chemical sensors, and software for data storage and multivariate statistical processing (pattern recognition system). During sampling, two hypodermic needles were inserted through the rubber cap of the vial into the headspace. The first needle was connected to the sampling unit, while the second was connected to a charcoal filter by means of a polytetrafluoroethylene (PTFE, Teflon) hose. Odor analysis was performed in a two step way: measurement and standby. Electro-valves, controlled by a computer program, guided the air through different circuits depending on the stage of the analysis. Irrespective of the phase, airflow in the measurement chamber was kept constant (table 1). During the measurement phase, the sampling unit "inhaled" the volatile gases present in the headspace of the vial and sent them at a constant rate (6.67 mL s^{-1}) to the measurement chamber causing changes in sensor's conductance: this phase lasted 80 s, which was enough time for the sensor signals to reach a stable value. When a measurement was completed, a standby phase of 160 s was activated. Its purpose was to clean the circuit, and the measurement chamber in particular, in order to return the sensor signals to their baselines. During this phase, clean air entered the circuit, crossing the measurement chamber first and pushing the remaining volatiles out of the circuit itself.

The ten MOS chemical sensors comprising the sensor array operated by transduction of the chemical compounds in the milk aroma into electric signals (Yuwono and Lammers, 2004). At the end of the measurement, these signals were recorded and stored, to be analyzed either by the software of the pattern recognition system or by statistical analysis software. One pattern comprises the signals from all ten sensors taken during the measurement of a sample

Table 1: Summary of the operating conditions of the e-nose during headspace analysis of milk odor)

Operating condition	
Transport gas	Ambient air (cleaned by charcoal filter)
Sampling rate	10 mL s^{-1}
Amount of sample/vial	6.67 mL s^{-1}
Vial volume	20 mL
Data acquisition	
Headspace generation time	1800 s
Sampling time	80 s
Flushing time	160 s
Total measurement time	240 s
Acquisition rate	1 signal s^{-1}

The software records the variations occurring in the ratio (G/G_0) between the conductance of each sensor, G (Ω^{-1}), at each second of measurement and the reference, G_0 (Ω^{-1}), which is the conductance that the sensor shows when clean charcoal-filtered air enters the measurement chamber.

1.2 PCA and Discriminant analysis

To increase the knowledge attained from the considered variables and, according to them, trying to discriminate as much as differences as possible during the milk monitoring, data underwent principal component analysis (PCA) followed by discrimnant analysis. Principal component analysis (PCA) is a linear, unsupervised pattern-recognition technique very useful for analyzing, classifying, and reducing the dimensionality of numerical datasets in multivariate problems (Todeschini, 1998). Linear Discriminant Analysis (LDA) (Meloun et al., 1992) is one of the mostly used classification procedure which maximizes the variance between categories and minimizes the variance within categories. The dataset was made of the signals recorded during the last 5 s of measurement when sensor signals were stable meaning that an equilibrium between their sensitivity and the volatile compounds of the milk sample was achieved. Statistical analysis was carried out using SPSS 13.0 for Windows

Results

Figure 1 is the score plot in the two-dimensional plane resulting from principal component 1 (PC1, horizontal axis) and principal component 2 (PC2, vertical axis) and it shows the good performance operated by the PCA in discriminating milks belonging to anomalous samples (both of the same batch and of different batch of production) from the commercial samples used as control.

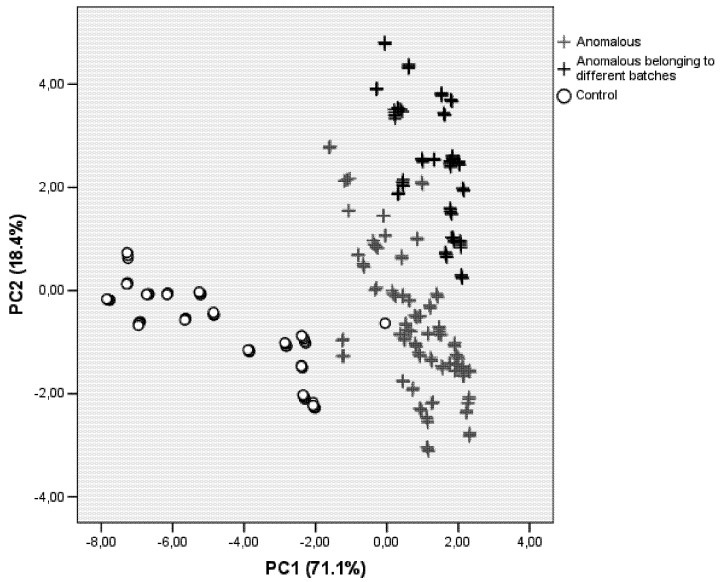

Figure 1: score plot of the analyzed samples in a two-dimensional plane identified by the first two principal components together with the percentages of the variance explained by each component (71.1% for PC1 and 18.4% for PC2).

Figure 2 shows the scatter plot of the groups identified by PCA and discriminated by LDA. With reference to this scenario, the classification of milk samples carried out on

all sensors' output by LDA exhibit 98.8 % correct assignation and 98.61% correct prediction

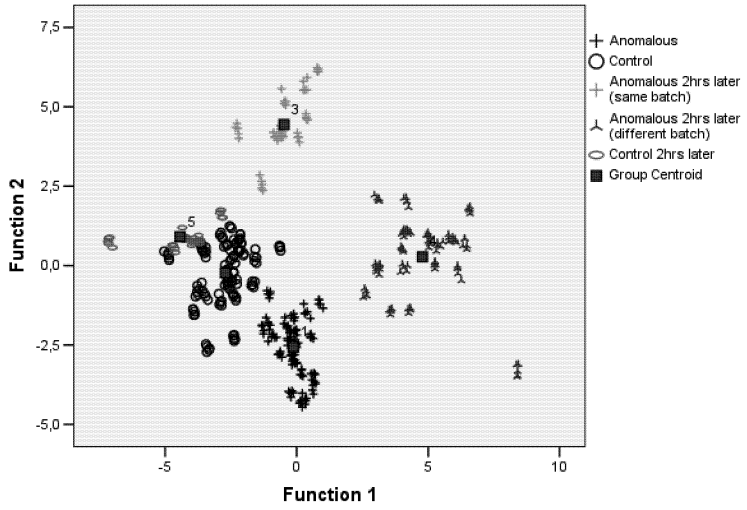

Figure 2: samples classification operated by LDA with the two canonical functions. LDF 1 (55.2% of explained variance): 2.28MOS1 -0.041MOS2 -1.3MOS3 -0.17MOS4 +4.07MOS6 +1.03MOS7 -2.26MOS8 -2.09MOS9 +0.87MOS10; LDF 2 (28.2% of explained variance): -10.6MOS1 +1.76MOS2 +10.7MOS3 +0.59MOS4 -6.11MOS6 -1.99MOS7 +3.05MOS8 +2.66MOS9 +0.90MOS10

The obtained results confirm the utility of the e-nose approach in monitoring the quality of UHT partly skimmed milk production batches, especially if combined with chemical, physical, and sensory techniques).

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