Materials Science and Engineering C 45 (2014) 348–358

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Aging time and brand determination of pasteurized milk using a multisensor e-nose combined with a voltammetric e-tongue

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ARTICLE INFO

Article history:
Received 3 May 2014
Received in revised form 26 August 2014
Accepted 15 September 2014
Available online 18 September 2014

Keywords:
E-nose
E-tongue
Data fusion
Pasteurized milk
Storage days
Chemometrics analysis

ABSTRACT

A combined approach based on a multisensor system to get additional chemical information from liquid samples through the analysis of the solution and its headspace is illustrated and commented. In the present work, innovative analytical techniques, such as a hybrid e-nose and a voltammetric e-tongue were elaborated to differentiate between different pasteurized milk brands and for the exact recognition of their storage days through the data fusion technique of the combined system. The Principal Component Analysis (PCA) has shown an acceptable discrimination of the pasteurized milk brands on the first day of storage, when the two instruments were used independently. Contrariwise, PCA indicated that no clear storage day's discrimination can be drawn when the two instruments are applied separately. *Mid-level of abstraction* data fusion approach has demonstrated that results obtained by the data fusion approach outperformed the classification results of the e-nose and e-tongue taken individually. Furthermore, the Support Vector Machine (SVM) supervised method was applied to the new subset and confirmed that all storage days were correctly identified. This study can be generalized to several beverage and food products where their quality is based on the perception of odor and flavor.

1. Introduction

Milk and dairy products have high nutritional values and excellent flavor characteristics. They play an important role in a healthy human diet since they are good sources of bio available calcium and proteins. The world consumption of pasteurized milk has been steadily increasing in the last years. The quality control of milk after the production steps is still a subject of great interest for industrials and the scientific community. Nevertheless, the chemical analysis of flavors in dairy products is complicated due to the heterogeneous nature of milk. In fact, significant levels of lipids, proteins and carbohydrates in milk make difficult to separate milk compounds. The profile of the chemical components in milk and dairy products can be performed employing instrumental techniques such as gas chromatography–mass spectrometry (GC–MS) [1,2], Near Infrared (NIR) or Mid Infrared (MIR) spectroscopy, Front Face Fluorescence Spectroscopy (FFFS), Nuclear Magnetic Resonance (NMR) [3] and High Performance Liquid Chromatography (HPLC) [4], only to cite a few. These methods can give very detailed information about the chemical compounds present in milk and dairy products. However, they suffer from a number of drawbacks, such as being time consuming, very expensive, requiring of a highly trained staff for correct operation and not giving information that can be easily correlated to human perception of smell and taste. Therefore, early and rapid pattern screening of dairy products, especially those with a short shelf-life, might confer significant benefits not only for dairy producers but also for consumer protection agencies and food security organizations. In that sense, e-noses and e-tongues are good candidates to successfully meet the industry demands of uncomplicated sample preparation, fast response enabling a continuous monitoring, portability for in-field measurements and reduced cost (as opposed to bulky and expensive equipment often needed in instrumental techniques).

Milk has been the subject of several research works employing e-noses. E-noses have been used to recognize different types of milk [5], to discriminate among UHT and pasteurized milk, to control rancidity during shelf life [6], to distinguish among six kinds of milk flavorings with similar odor profile [7], to differentiate between unspoiled, medium spoiled and spoiled milk due to the activity of bacteria and yeasts, and to discern between bacterial and yeast contamination by analyzing the patterns of volatiles resulting from such contamination [8]. The e-noses have been employed also, yet with limited success, to recognize the number of cold-storage days underwent by milk samples [9]. In addition to e-noses, the literature shows that also different e-tongues have been used in the aim of discrimination, classification, quality evaluation,

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http://dx.doi.org/10.1016/j.msec.2014.09.030
0928-4931/

process monitoring and quantitative analysis of various food products in general and milk in particular. This is the case of fruit juices [10], and water samples [11]. E-tongues have been widely used for milk recognition and for the determination of bacterial counts in fresh milk during storage [12], the discrimination between milk and yogurt samples, and also between cultured and non-cultured dairy products [13]. They have been also used for the detection of adulteration of raw caprine skimmed milk with raw bovine skimmed milk [14], or to follow different sources of milk coming into the process and to monitor the cleaning processes employed by the dairy industry [15]. Similarly to the results reported for an e-nose, the prediction of the number of days under cold storage for pasteurized milk samples was not exact when an e-tongue device was employed [16].

Recently, emerging strategies, namely, multisensor data fusion techniques have been proved to efficiently overcome some of the problems. In a previous paper, we reported on the enhanced classification between beer samples, where two e-tongues were combined using a data fusion method [17]. An e-nose and e-tongue were combined for reaching a superior classification of tea samples [18]. Also the characterization of olive oils with different degrees of bitterness was performed with superior results by combining three instruments: e-nose, e-tongue and e-eye [19].

The main aim of this work was to build up fast and efficient techniques devoted to differentiate among different pasteurized milk brands using e-nose and e-tongue, and to show how data fusion of combining e-nose and e-tongue with feature selection and pattern recognition methods was used to rapid pattern screening of cold storage days of pasteurized milk without the issue of sample composition. The data that are produced by the artificial systems are considered as an overall fingerprint, which can be interpreted with the use of appropriate mathematical techniques, such as Principal Component Analysis (PCA) or Support Vector Machines (SVMs). Despite the similarity of the smell and taste of the five pasteurized milk brands, both the hybrid e-nose and the voltammetric e-tongue enabled a perfect classification of the different pasteurized milk brands. To the best knowledge of the authors, this is the first time that a data fusion technique is applied for a rapid pattern screening in view of accurately classifying milk samples according to the number of days they have undergone cold storage. Our approach based on a data fusion technique for a rapid pattern screening in view of accurately classifying milk samples according to the number of days they have undergone cold storage has shown a great enhancement in the discrimination of the number of days they have undergone cold storage, as the PCA results show a perfect discrimination between all the storage days and no mistake has been found when we performed the SVM model evaluated using a leave-one-out cross-validation method.

2. Materials and methods

2.1. Sample preparation

Five different, locally available brands of pasteurized cow's milk were studied: Centrale, Colaimo, Jawda, Jibal, and Saiss. After milk reception, samples of each milk brand were transferred into flask and stored in the refrigerator at a constant temperature of 4 °C. Six samples of each milk brand were analyzed at days 1, 2, 3, 4, and 5 of storage, giving a total of 150 samples. Before performing measurements, the milk samples were allowed to reach ambient temperature and, afterwards, were analyzed for training and evaluating the multi-sensor system (e-nose and e-tongue) capacity to identify the milk according to their origin brand and to classify samples according to the number of storage days. All the e-nose and e-tongue measurements have been carried out using the same sample pre-treatment. Measurements of the pasteurized milk samples were carried out first by means of e-nose and then by the e-tongue.

2.2. Hybrid e-nose setup and measurement

The hybrid e-nose system consisted of two sensor arrays. The first one comprised four micro-machined gas sensors. The micro-sensor substrates consisted of a $SiO_2/Si_3N_4/SiO_2$ membrane with isolated platinum heaters and platinum electrodes. The design and thermal characterization of the membrane have been described previously [20]. The sensing films, namely, 1% Au-doped and 1% Pt-doped SnO_2, and 1% Au-doped and 1% Pt-doped WO_3 were deposited on the micro-sensor substrate using drop coating and sputtering techniques. The four-element micro-hotplate array was mounted on a standard TO-8 package. The details can be found elsewhere [21]. The second array consisted of four commercial tin-dioxide gas sensors: TGS 8xx (with xx = 15, 22, 24 and 42) obtained from Figaro Engineering, Inc. (Osaka, Japan) plus a temperature sensor (LM 335Z) and a relative humidity sensor (HIH4000-01) from National Semiconductor in order to monitor the temperature and the hygrometry into the sensor chambers. Fig. 1 shows a schematic representation of the experimental set-up used in the measurements. The variation of sensor conductivity was acquired and then digitized using a data acquisition board (PCL 812PG, Advantech). For the measurement, a volume of 20 mL of milk was put in a 50 mL vial, heated to 35 °C. The sampling system consists of a dynamic headspace sampling, which means that the nitrogen carrier gas insures volatile transfer continually into the sensor chamber. The e-nose response was registered each 2 s for a time interval of 10 min [22,23]. Each time that a new set of milk was analyzed, new glass vials were used.

A program in LabView was developed to control the data acquisition process. To analyze the response of the hybrid e-nose data, two parameters were extracted from each sensor conductance transient: the steady-state conductance (G_S), calculated from the average value of the conductance during the last minute of the measurement and the dynamic slope of the conductance (dG/dt), calculated between 2 and 7 min of the exposure time to the milk samples. This choice was based on our previous work related to dairy products [24]. Since there were 8 gas sensors within the two arrays, each measurement was described by 16 features.

2.3. Voltammetric e-tongue setup measurement

The voltammetric e-tongue used for this study consisted of four working electrodes (Platinum, Gold, Glassy Carbon and Silver), a reference electrode (Ag/AgCl) and Platinum electrode as the auxiliary. In Fig. 2, the electrodes were assembled in stainless steel tubing. The wires from the electrodes were connected via a relay box to a portable potentiostat PalmSens (PalmSens BV, The Netherlands). The cyclic voltammetry is applied as the measurement principle in the e-tongue. The measurements were carried out at a temperature of 35 °C. Several tests were carried out on pasteurized milk samples in order to optimize the electrochemical window range for each working electrode. An electrochemical cleaning step was also performed to prevent the accumulative effect of impurities on electrode surface. Thus, the electrodes are rinsed with distilled water after each reading [17]. Several strategies have been previously reported for the variable extraction [25–28]. Basically, these consist of either choosing directly among the signal points [29–31] or to compute new variables by performing Fast Fourier Transform (FFT), Discrete Wavelet Transform (DWT), Kernel functions, etc. [32,18]. In this paper, we opted for the first option which consisted to extract specific variables from the obtained voltammograms. Being simple, fast and facile in the computation, this approach aims to retrieve explicitly the most discriminative features and removing non-informative and noisy ones. Thus, three features were extracted from the sensor signals in view of retaining the most important information contained in each voltammogram. The complete list of these features is as follows. $\Delta I = I_{max} - I_{min}$: the current change calculated as the difference between maximum and minimum values of the current (where I_{min} is