Sensors and Actuators B 242 (2017) 511–521

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

A novel framework for analyzing MOS E-nose data based on voting theory: Application to evaluate the internal quality of Chinese pecans

Shui Jiang, Jun Wang*, Yongwei Wang, Shaoming Cheng

Department of Biosystems Engineering, Zhejiang University, 866 Yuhangtang Road, Hangzhou 310058, PR China

ARTICLE INFO

Article history:
Received 6 July 2016
Received in revised form
10 November 2016
Accepted 14 November 2016
Available online 15 November 2016

Keywords:
Chinese pecans
Electronic nose
Fatty acids
Nondestructive detection
Voting method

ABSTRACT

Metal oxide semiconductor (MOS) gas sensors have been widely used in the field of electronic nose (E-nose) for detecting the simple or complex volatile compounds. The electrical signals of MOS sensor array contain the abundant "fingerprint" information of samples. In this paper, an E-nose equipped with an array of MOS sensors was applied to detect Chinese pecans nondestructively for qualitative discrimination and quantitative prediction. Traditionally, most pattern recognition methods are based on single feature, which loses much useful information. To extract more information, a voting method, which was composed of principle component analysis (PCA) results based on 5 features (i.e., the 10th second values, the 75th second values, the area values, the maximum values and the minimum values of E-nose response curves), was proposed to classify pecan samples with different storage times. For quantitative prediction, six regression models were built on random forest (RF) algorithm to predict the contents of fatty acids in pecans. The analysis results showed that the voting method classified different pecan samples with 96% accuracy rate, and the regression models had satisfying prediction performance ($R^2 > 0.97$ in calibration sets and $R^2 > 0.95$ in validation sets). These results suggest that the voting method and RF algorithm would be promising analysis method for E-nose data.

1. Introduction

Electronic nose (E-nose) is an instrument to detect the simple or complex volatile compounds by simulating the olfactory system of animals. A typical electronic nose consists of sensor array and pattern recognition which are mimics of olfactory cells and the brain respectively [1]. During the detection, the volatile compounds of samples collectively work on each sensor, and signals of each sensor are saved to form the response curves. These response curves are regarded as the unique pattern or "fingerprint" of sample gas. With the help of multivariate statistical techniques and artificial neural networks, these patterns could be recognized to distinguish different samples. As the core component, the sensor array plays a crucially important role for the performance of E-nose. It is the decisive factor for success of E-nose application to select the appropriate sensor type according to the different purposes. Metal oxide semiconductor (MOS) gas sensors, which have the advantages of cross-sensitivity, broad spectrum response and low-cost, have been widely used in E-nose application [2]. Because of the aforementioned advantages, the electrical signal of E-nose based on MOS sensors contains abundant information of complex sample gas.

Currently, many researchers have focused on the application of MOS E-nose on food quality detection [3]. While part of these literatures ([4–6]) just used E-nose to classify different samples, which wasted the potential prediction capacity of E-nose. Though some other literatures ([7–9]) carried out studies on the prediction of indexes, the performances of obtained regression models were unsatisfactory. It could be easily summarized from the aforementioned literatures that most classification analyses were based on principal component analysis (PCA) or linear discriminant analysis (LDA), and prediction analyses were based on partial least squares regression (PLSR). Moreover in these studies, only single feature was extracted from the response curves of E-nose for qualitative discrimination and quantitative prediction. The inappropriate analysis method might loss much useful information for characterizing the internal qualities of samples during the data mining procedure [10].

In order to extract more useful information from the MOS E-nose data, there is an urgent need for E-nose field to introduce novel pattern recognition and prediction methods. In this study, the authors proposed a novel method based on voting theory to classify different samples. Voting theory, as one of the most important research topics in computational social choice, is widely used in

* Corresponding author.
E-mail address: jwang@zju.edu.cn (J. Wang).

http://dx.doi.org/10.1016/j.snb.2016.11.074
0925-4005/

field of artificial intelligence, economics and sociology [11]. While in E-nose field, there is no relevant application about voting theory. The main working principle of voting method is to obtain the optimum results by aggregating the personal preference of every voters. For the application in E-nose field, the voters are different features of response curves. The combination of voting method and the characteristics of MOS sensors could classify different samples more efficiently. Voting theory could also be applied in quantitative prediction in E-nose field. Random forest (RF) proposed by Breiman in 2001 is another typical algorithm based on voting theory [12]. RF is composed of a collection of tree predictors (i.e., decision tree or CART) which are weak classifiers. During the procedure of data analysis, each tree predictor plays a voter role and the final results of classification and regression are performed by aggregating the decisions. As a machine learning strategy, RF avoids the misclassification and accidental error to a certain extent. Furthermore, RF algorithm has many advantages such as strong robustness, high learning speed and accuracy rate, which makes it suitable for many research fields [13]. However to the best of our knowledge, there is very few published literatures about that RF deals with E-nose data. Therein, most literatures just apply RF to classify different samples, which waste the potential capacity of regression [14].

To verify the feasibility of voting method and RF algorithm in E-nose filed, they were applied to analysis the E-nose data of in-shell Chinese pecans. Chinese pecan (*Carya cathayensis*) is an important nut species planted in China and is typically high in fat (60–70%) [15]. Chinese pecans are usually ripe for harvest at the first ten days of September and the harvest time lasts only about 7 days. Because of the short harvest time, the processing enterprises always collect a very large amount of pecans and store them in cold storehouse for subsequent processing. During the storage, the internal quality of pecans continuously deteriorate and some new compounds such as free fatty acids and peroxides are produced. These changed compounds cause the composition changes of sample gas [16–18]. Pecan shell is comprised of materials such as fiber and lignin and the natural microporous channel allows the sample gas out of the pecans [19]. According to the previous study of us, it is proven that the application of E-nose to classify different pecan samples and detect the internal quality is available [20]. In this paper, voting method and RF were applied to do the qualitative discrimination and quantitative prediction of Chinese pecans, respectively. The aims of this paper are: (1) to characterize pecans of different storage times by using E-nose, and to measure contents of pecan fatty acids by GC–MS; (2) to classify different samples by using the voting method and predict the fatty acids profiles of pecans by using RF; (3) to evaluate the performances of RF regression models according to the determination coefficient (R^2) and root mean square error (RMSE).

2. Experimental

2.1. Samples preparation

In this study, Chinese pecans (*Carya cathayensis*), which were supplied by Tuanyuanren Company, were used as the experimental materials. These pecans were harvested in Longgang Town, Linan City of Zhejiang province, China (119.72 E, 30.22 N) and had been stored in a 4 °C cold storehouse for 3 months.

According to the previous study, the internal quality of pecans, which were protected by shells, had little change in short store time. To accelerate the process of whole experiment, the artificial process of pecans was applied. In the process, the in-shell pecans were put into an incubator (STIK (Shanghai) CO., China) with a temperature of 35 °C and relative humidity (RH) of 30%. The published literatures show that pecans stored in this artificial environment for 10 d and 20 d could simulate that stored in 4 °C storehouse for 1 and 2 years respectively [21–23]. The supplied pecans were randomly divided into 5 groups (15 sample sets per group and 20 pecans (about 70 g) in each set). During the experiment, 4 groups were put into the incubator for artificial process and one group of them was taken out every 5 days. The original samples were defined as 0 day, and processed samples were respectively defined as 5 day, 10 day, 15 day and 20 day. In each detection day, the processed samples were taken out from the incubator, and then exposed in the clean air for enough time to ensure the samples were cooled down to room temperature of 20 °C ± 1 °C. Then the E-nose detection was performed immediately. After the E-nose detection, all the pecan samples were cracked carefully and the kernels were taken out. Finally, these pecan kernels were processed into sample oils which were used for the detection of fatty acids profiles.

2.2. Electronic nose detection

In this study, an E-nose (PEN2, Airsense Company, German) equipped with an array of metal oxide semiconductor (MOS) sensors was used to detect sample gas. This sensor array, which is located in a gas chamber, consists of 10 MOS sensors which were sensitive to specific groups of volatile compounds. In the gas chamber, the sample gas is pumped in and works on the MOS sensors. Table 1 lists the 10 MOS sensors equipped in the PEN2 E-nose system and describes the main applications of each sensor briefly.

Before the detection of pecans, the E-nose system working conditions (i.e., sample weight, temperature, beaker volume, and head space generated time) were optimized by a set of experiments to get the best performance. According to the optimized result, 20 pecans (about 70 g) were put into a glass beaker (500 mL) which was subsequently sealed with plastic wrap. Then the beaker was kept for 45 min (headspace generated time) at the room temperature to ensure that enough volatile compounds were emitted from the pecans and get equilibrium. According to the technical manual, the E-nose system was started at least 60 min before the detection to ensure all the sensors were heated up to working temperature (above 200 °C) and the gas path was cleaned by the clean air.

A complete detection of a sample includes cleaning process (70 s) and monitoring process (80 s). Hence, there was 2.5 min interval between two sample detections to guarantee the headspace generated times were same. During the cleaning process, clean air was pumped into the gas path and gas chamber at a flow rate of 600 mL min^{-1} to normalize the sensor signals. In the monitoring process, sample gas was pumped into the sensor chamber at a flow rate of 200 mL min^{-1} and one signal of every sensor was recorded once per second. The output signal of E-nose is G/G0. G0 and G represents the electronic conductivity of sensor when detecting the clean air and sample gas, respectively. The data matrix (10×80) was automatically recorded by the WinMuster software (version 1.6.2, Airsense Analytics, German) as the raw data for the following analysis. During the detection of one sample, 10 response curves of MOS sensors in E-nose were obtained. The typical response curves of E-nose in different sample detections are shown in Fig. 1.

A typical response curve of MOS sensor consists of three stages: the initialization stage, changing stage and stationary stage. After the cleaning process, the response curve is forcibly initialized to value 1 in initialization stage to ensure that all the detections starts at the same level. In the changing stage, the response curve changes rapidly and the maximum slope of curve occurs. The range of changing stage is between 5th second and 35th second. Subsequently, the response curve goes into stationary stage. During the stationary stage, the signals are almost constant, and the curve comes to a steady state. The tendency of response curves could be explained by the interactive principle of the MOS sensors. The reaction of sen-