# **Fuji Apple Storage Time Predictive Method Using Electronic Nose**

Hui Guohua • Wu Yuling • Ye Dandan • Ding Wenwen

Received: 21 December 2011 / Accepted: 3 April 2012 / Published online: 27 April 2012 © Springer Science+Business Media, LLC 2012

Abstract An electronic nose-based Fuji apple storage time prediction method is investigated in this paper. A home-made electronic nose with eight metal oxide semiconductors gas sensor array was used to measure the apples stored at room temperature. Principal component analysis cannot discriminate all samples. Stochastic resonance signal-to-noise ratio spectrum distinguishes fresh, medium, and aged apples successfully. The prediction model is developed based on signalto-noise ratio maximums. In validating experiments, results show that the predicting accuracy of this model is 84.62 %. This method takes some advantages including fast detection, easy operation, high accuracy, and good repeatability.

**Keywords** Electronic nose · Apple storage time analysis · Principal component analysis · Stochastic resonance · Signal-to-noise ratio

# Introduction

The fruit quality determination plays an important role in agro-industries because it influences the choice of consumers to a great deal. Currently, the common methods for fruit quality evaluation include sensory and instrumental studies. For sensory analysis, taste and aroma aspects of fruit samples are assessed by specially trained people. The evaluation result provides unique information about the acceptance degree of fruit samples. This method is widely accepted in overall fruit quality assessment. The most important problems of this method are measurement standardization, stability, and reproducibility. Sometimes, the high costs for people training and use of sensory panels also limit the applications of this technique. Instrumental analysis methods, including gas chromatography (GC), gas chromatography–mass spectrometry (GC-MS), and high-performance liquid chromatography (HPLC), are usually utilized for fruit quality evaluation in lab. However, these methods are high-cost and time-consuming. Moreover, the skilled operators are required to perform the instrumental analytical experiments.

A popular nondestructive method is the employment of electronic nose (E-nose), an instrumentation which consists of an array of some electronic chemical sensors with partial specificity. Appropriate patterns or fingerprints from known odors are employed to construct a database and train a pattern recognition system so that later unknown odors can subsequently be classified and identified (Hammond et al. 2002; Gardner and Bartlett 1999; Peris and Escuder-Gilabert 2009). The E-nose technology has been successfully employed in diverse fields such as agriculture (Zhang and Wang 2007), pharmaceutics (Zhu et al. 2004), environmental controls (Ameer and Adeloju 2005; Canhoto and Magan 2003; Lamagna et al. 2008), and clinical diagnostics (Bernabei et al. 2008; Di Natale et al. 2003). In the past decade, E-nose technique, most notably, has been employed in the recognition and quality analysis of various foods and agro-products, such as beverages (Ragazzo-Sanchez et al. 2008; Reinhard et al. 2008), milk (Wang et al. 2010a), edible oil (Apetrei et al. 2010; Lerma-Garcia et al. 2009), meat (Balasubramanian et al. 2008; Vestergaard et al. 2007), fish (El Barbri et al. 2009), vegetables (Concina et al. 2009; Gomez et al. 2008), and fruits (Gomez et al. 2007; Benady et al. 1995; Sarig 1998; Maul et al. 1999; Oshita et al. 2000; Berna et al. 2004; Saevels et al. 2003; Zhang et al. 2008).

H. Guohua (⊠) · W. Yuling · Y. Dandan · D. Wenwen College of Food Science and Biotechnology, Food Safety Key Laboratory of Zhejiang Province, Zhejiang Gongshang University, Zhejiang Province, Hangzhou 310035, China e-mail: ghui@zjsu.edu.cn

Fig. 1 Schematic diagram of E-nose system



In this paper, a home-made E-nose has been employed to investigate the apple storage time at room temperature. Principal component analysis (PCA) method discriminates fresh and medium apples from aged apples, but it is difficult to implement the discrimination between fresh and medium apples. Signal-tonoise ratio (SNR) spectrum is calculated using stochastic resonance (SR). SNR maximum values successfully distinguish fresh, medium, and aged apple samples. Apple storage time prediction model is developed using SNR maximums (max-SNR). Predicting error of this model is less than 10 %. This method provides a new way for fruit storage time assessment.

## **Materials and Methods**

#### Materials

Sixty "Fuji" apples (Malus domestica Borkh.), purchased from a fruit market in Hangzhou, are taken from the same box and likely harvested at the same time and underwent the same postharvest treatment. The apples approximately have the same weight and curvature radius. Apples are placed in nonhermetic box and stored at room temperature for the whole period of the experiment. Thirty apples are used in E-nose measurement, and the rest 30 apples are utilized in validating experiments. The samples are measured on days 0, 2, 4, 6, 8, and 10.

#### E-nose System

E-nose system is developed by our laboratory, and its structure is shown in Fig. 1. The diagram includes three main parts: data acquisition, modulating, and transmitting unit (U1); sensor array and chamber unit (U2); and power and gas supply unit (U3). The sensor array consists of eight semiconductor gas sensors, whose sensing species is showed in Table 1. Polytetrafluoroethylene material is utilized to fabricate the chamber. Each sensor chamber is separated, which helps to eliminate the cross-influence of the gas flow.

### Methods

The whole apple was put into a 500-ml beaker at room temperature. After 3 h, the E-nose sampling pinhead was put into the headspace of the beaker. Gases within the headspace were sucked into E-nose sensor chamber and reacted with the sensors. Each experiment lasted for 40 s, and the real-time responses to the apples were recorded for further analysis.

# Storage Time Prediction Method

SR plays an important part in signal processing (Benzi et al. 1981; Dutta et al. 2006; Wang et al. 2010b; Gammaitoni et al. 1998). SR has three elements: a bistable system, a coherent input, and a noise source, which can be described as:

$$\frac{dx}{dt} = -\frac{dV(x)}{dx} + MI(t) + C\xi(t) \tag{1}$$

where x is the position of the Brownian particle, t is the time, M and C are adjustable parameters, I(t) = S(t) + N(t)

Table 1         Constitution of gas sensor array	Sensor no.	Sensor type	Sensing species	
	<b>S</b> 1	MQ-2	Propane, liquefied petroleum gas	
	S2	MQ-3	Ethanol	
	S3	MQ-6	Butane, liquefied petroleum gas	
	S4	TGS- 2201	Gasoline and diesel exhaust gas	
	S5	MQ-7	Carbon monoxide	
	S6	MQ-8	Hydrogen	
	S7	TGS- 842	Hydrogen and methane	
	S8	TGS- 825	Hydrogen sulfide	





denotes an input signal S(t) and intrinsic noise N(t),  $\xi(t)$  is the external noise, and V(x) is the simplest double-well potential with the constants *a* and *b*, characterizing the system.

$$V(x) = -\frac{1}{2}ax^2 + \frac{1}{4}bx^4$$
(2)

Equation (1) can be written as

$$\frac{dx}{dt} = ax - bx^3 + MI(t) + C\xi(t)$$
(3)

The minima of V(x) are located at  $\pm x_m$ , where  $x_m = (a/b)^{1/2}$ . A potential barrier separates the minima with the height given by  $\Delta U = a^2/4b$ . The barrier top is located at  $x_b=0$ . When three elements of SR interact coherently, the potential barrier can be reduced, and the Brownian particle may surmount the energy barrier and enter another potential well (Benzi et al. 1981; Gammaitoni et al. 1998). The intensity of signals will increase, which makes it possible that the weak signal can be detected from noise background.

Suppose the input signal is  $I(t) = A \sin(2\pi f t + \phi)$ , where *A* is the signal intensity, *f* is the signal frequency. *D* is the external noise intensity. SNR is the common quantifier for SR and it can be approximately described as (Gammaitoni et al. 1998):

$$SNR = \sqrt{2}\Delta U \left(\frac{A}{D}\right)^2 e^{-AU/D} \tag{4}$$

Noise intensity is just a parameter of SR model. SR model is used as a data processing method in this research. We use  $I(t) = A \sin(2\pi f t + \phi) + E - \operatorname{nose}(t) + N(t)$  as input matrix. It has a sinusoid signal  $A \sin(2\pi f t + \phi)$ , E-nose response data E-nose(t), and intrinsic noise N(t). Noise intensity changes within the range (0–900). SNR between the output and input is calculated. A graphical illustration of SR processing is shown in Fig. 2.

## **Results and Discussion**

### E-nose Analysis Results

E-nose responses to apple samples are shown in Fig. 3a. Most of the E-nose sensors are sensitive to apple samples. Sensors S8, S6, S5, S4, and S1 are more sensitive to apple samples. Their responses increase obviously in the time interval between 2.5 and 25 s, and after that, the responses tend to be saturated. The saturated value of sensor S8 is the maximal, and that of sensor S7 is the minimal. The saturated values related to the average sensor response for each kind of apple, as a function of time, are shown in Fig. 3b. The responses of S8, S3, S1, S2, S4, S5, and S6 fluctuate during the whole experimental procedure, but the responses of S7 remain



Fig. 3 Responses of E-nose to apple samples: (a) sensor array responses and (b) sensor array saturated value as a function of storage time

Fig. 4 PCA analysis on the experimental data with all the sensors: (a) PC2 vs. PC1, (b) PC3 vs. PC1, and (c) loading plot of the first three components (explained variance=92.07 %). The apple samples under different storage times are marked with color



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**Fig. 5** Apple quality prediction model: (**a**) spectrum of apple samples and (**b**) apple quality prediction model

unchanged. The E-nose measurement results indicate that volatile gas type and concentration released by apple samples under different storage times vary a lot.

PCA analysis results were plotted onto the principle components (PCs) in Fig. 4. The first two components, PC1 and PC2, captured 84.80 % of data variance (see Fig. 4a). The figure showed the projections of the experimental results on a two-dimensional plane formed by the first two PCs. Apples can be divided in three categories. Each of three categories corresponds to fresh, medium, and aged apples, respectively. The fresh group corresponds to the samples having undergone up to 2 days of storage. The medium group corresponds to the samples from 4 to 6 days of storage. The aged group corresponds to the samples stored over 8 days. The quality of fresh and medium groups is acceptable for consumers and can be grouped as acceptable group.

The aged group is possible going to bad and can be named as bad group. The acceptable and bad groups appear ordered along the first PC according to the number of storage days, but the fresh and medium groups overlap together and cannot be discriminated. All the samples increase their scattering along PC1 and PC2. The PC3 as function of PC1 was displayed in Fig. 4b, and these two PCs captured 69.91 % of data variance. The samples cannot be totally discriminated. The loading plot of the first three PCs was displayed in Fig. 4c. Samples of days 0 and 4 are more scattered along PC3. Samples of days 2 and 6 show more scattered along PC1. Samples of days 8 and 10 show more scattering along PC2. PCA method can successfully discriminate acceptable (fresh and medium) and bad samples (aged), but the distributions of fresh and medium samples are overlapping, which makes it difficult to discriminate from each other.

#### Quality Prediction Model

SR SNR spectrum is showed in Fig. 5a. As mentioned in Sect. 3.2, PCA analysis cannot discriminate fresh and medium apples. Here, we add noise to the input matrix, passing it through the SR model to get the output and calculate the SNR between input and output. SR is observed at various noise intensities for different apple samples. Max-SNR values of each sample are completely different. Figure 5b shows the individual maximum SNR for apples of different storage times. The maximums of SR SNR increase as the increase of the number of storage days. We use the linear fit of the maximums to predict the apple storage time. The linear fitting regression results are shown as Eq. (4). After the transform, Eq. (5) is used as an apple storage time

$$y = -76.855 + 0.74111x \left( R^2 = 0.99583 \right) \tag{4}$$

$$\text{Time}_{\text{apple}} = \frac{76.855 + \text{Max} - \text{SNR}}{0.74111}$$
(5)

Twenty-six E-nose validating measurement data is randomly selected and processed by SR. The max-SNR values are calculated and used as input of Eq. (5) for storage time prediction. The results are shown in Table 2. The predicting accuracy of this model is 84.62 %. The results demonstrate that this model can predict apple storage time at room temperature successfully.

**Table 2**Quality predictionresults

Prediction sample no.	Predicting value	Storage time	Error (%)	Results
A-sam1	5.767	6	3.883	$\checkmark$
A-sam2	10.382	10	3.820	
A-sam3	7.806	8	2.425	
A-sam4	3.657	4	8.575	
A-sam5	2.085	2	4.250	
A-sam6	8.062	8	0.775	$\checkmark$
A-sam7	0.074	0	/	
A-sam8	2.101	2	5.050	
A-sam9	6.708	6	11.800	х
A-sam10	8.336	8	4.200	$\checkmark$
A-sam11	9.632	10	3.680	$\checkmark$
A-sam12	7.493	8	6.338	$\checkmark$
A-sam13	6.414	6	6.900	$\checkmark$
A-sam14	6.637	6	10.617	х
A-sam15	1.859	2	7.050	$\checkmark$
A-sam16	4.237	4	5.925	$\checkmark$
A-sam17	5.308	6	11.533	х
A-sam18	10.437	10	4.370	$\checkmark$
A-sam19	8.218	8	2.725	$\checkmark$
A-sam20	2.169	2	8.450	$\checkmark$
A-sam21	0.086	0	/	$\checkmark$
A-sam22	0.069	0	/	$\checkmark$
A-sam23	3.584	4	10.400	х
A-sam24	4.153	4	3.825	$\checkmark$
A-sam25	0.077	0	/	$\checkmark$
A-sam26	9.734	10	2.660	

 $\sqrt{\text{right}}, X \text{wrong}, / \text{not calculated}$ 

The apple quality assessment method based on linear fitting regression presents good predicting accuracy. This method also avoids the drawbacks of microbial measurements, such as time-consuming, fussy procedure, etc. Thus, it is promising in fruit quality evaluating applications.

# Conclusions

In this paper, E-nose-based apple storage time prediction method has been investigated. PCA method discriminates acceptable groups (fresh and medium class) from bad group (aged class), but it is difficult to discriminate fresh apples from medium apples. The SNR spectrum is calculated using stochastic resonance. The individual SNR maximum values are used to develop the apple storage time prediction model. Validating experiments indicates that the predicting accuracy of this model is 84.62 %. This method presents some advantages including fast detecting, easy operation, high accuracy, and repeatability. It is promising in fruit quality evaluating applications. Acknowledgments This work was supported by Zhejiang Province Science and Technology Research Project (Grant No. 2011C21051), National Natural Science Foundation (Grant No. 81000645), and Zhejiang Province Natural Science Foundation (Grant No. Y1100150, Y1110995). Student Scientific Research Project of Zhejiang Gongshang University (Grant No. 11-143, 11-145, 11-159).

#### References

- Ameer Q, Adeloju SB (2005) Polypyrrole-based electronic noses for environmental and industrial analysis. Sensors and Actuators B: Chemical 106:541–552
- Apetrei C, Apetrei IM, Villanueva S, de Saja JA, Gutierrez-Rosales F, Rodriguez-Mendez ML (2010) Combination of an e-nose, an etongue and an e-eye for the characterisation of olive oils with different degree of bitterness. Anal Chim Acta 663:91–97
- Balasubramanian S, Panigrahi S, Logue CM, Doetkott C, Marchello M, Sherwood JS (2008) Independent component analysisprocessed electronic nose data for predicting *Salmonella typhimurium* populations in contaminated beef. Food Control 19:236– 246
- Benady M, Simon JE, Charles DJ, Miles GE (1995) Fruit ripeness determination by electronic sensing of aromatic volatiles. Trans ASAE 38:251–257
- Benzi R, Sutera A, Vulpiana A (1981) The mechanism of stochastic resonance. Journal of Physics A 14:L453–L456

- Berna AZ, Lammertyn J, Saevels S, Di Natale C, Nicolai BM (2004) Electronic nose systems to study shelf life and cultivar effect on tomato aroma profile. Sensors and Actuators B: Chemical 97:324–333
- Bernabei M, Pennazza G, Santortico M, Corsi C, Roscioni C, Paolesse R, Di Natale C, D'Amico A (2008) A preliminary study on the possibility to diagnose urinary tract cancers by an electronic nose. Sensors and Actuators B: Chem 131:1–4
- Canhoto OF, Magan N (2003) Potential for detection of microorganisms and heavy metals in potable water using electronic nose technology. Biosens Bioelectron 18:751–754
- Concina I, Falasconi M, Gobbi E, Bianchi F, Musci M, Mattarozzi M, Pardo M, Mangia A, Careri M, Sberveglieri G (2009) Early detection of microbial contamination in processed tomatoes by electronic nose. Food Control 20:873–880
- Di Natale C, Macagnano A, Martinelli E, Paolesse R, D'Arcangelo G, Roscioni Finazzi-Agro C, D'Amico A (2003) Lung cancer identification by the analysis of breath by means of an array of nonselective gas sensors. Biosens Bioelectron 18:1209–1218
- Dutta R, Das A, Stocks NG, Morgan D (2006) Stochastic resonancebased electronic nose: a novel way to classify bacteria. Sensors and Actuators B: Chemical 115:17–27
- El Barbri N, Mirhisse J, Ionescu R, El Bari N, Correig X, Bouchikhi B, Llobet E (2009) An electronic nose system based on a micromachined gas sensor array to assess the freshness of sardines. Sensors and Actuators B: Chemical 141:538–543
- Gammaitoni L, Hanggi P, Jung P, Marchesoni F (1998) Stochastic resonance. Review of Modern Physics 70:223–287
- Gardner JW, Bartlett P (1999) Electronic noses: principles and applications. Oxford University Press, Oxford
- Gomez AH, Wang J, Hu GX, Pereira AG (2007) Discrimination of storage shelf-life for mandarin by electronic nose technique. Lwt-Food Science and Technology 40:681–689
- Gomez AH, Wang J, Hu GX, Pereira AG (2008) Monitoring storage shelf life of tomato using electronic nose technique. J Food Eng 85:625–631
- Hammond J, Marquis B, Michaels R, Oickle B, Segee B, Vetelino J, Bushway A, Camire ME, Dentici KD (2002) A semiconducting metal-oxide array for monitoring fish freshness. Sens Actuators B: Chem 84:113–122
- Lamagna A, Reich S, Rodriguez D, Bosell A, Cicerone D (2008) The use of an electronic nose to characterize emissions from a highly polluted river. Sensors and Actuators B: Chemical 131:121–124
- Lerma-Garcia MJ, Simo-Alfonso EF, Bendini A, Cerretani L (2009) Metal oxide semiconductor sensors for monitoring of oxidative status evolution and sensory analysis of virgin olive oils with different phenolic content. Food Chem 117:608–614

- Maul F, Sargent SA, Huber DJ, Balaban MO, Charles AS, Baldwin EA (1999) Harvest maturity and storage temperature affect volatile profiles of ripe tomato fruits: electronic nose and gas chromatographic analyses. In: Proceedings of the fifth international symposium on olfaction and the electronic nose, 1999
- Oshita S, Shima K, Haruta T, Seo Y, Kagawoe Y, Nakayama S, Kawana S (2000) Discrimination of odors emanating from 'La France' pear by semi-conducting polymer sensors. Comput Electro Agric 26:209–216
- Peris M, Escuder-Gilabert L (2009) A 21st century technique for food control: electronic noses. Anal Chim Acta 638:1–15
- Ragazzo-Sanchez JA, Chalier R, Chevalier D, Calderon-Santoyo M, Ghommidh C (2008) Identification of different alcoholic beverages by electronic nose coupled to GC. Sensors and Actuators B: Chem 134:43–48
- Reinhard H, Sager F, Zoller O (2008) Citrus juice classification by SPME-GC-MS and electronic nose measurements. Lwt-Food Science and Technology 41:1906–1912
- Saevels S, Lammertyn J, Berna AZ, Veraverbeke E, Di Natale C, Nicolaï BM (2003) Electronic nose as a non-destructive tool to evaluate the optimal harvest date of apples. Postharvest Biol Technol 30:3–14
- Sarig Y (1998) Utilisation of the olfactory characteristics of fruit and vegetables as the potential method for determining their ripeness and readiness for harvest. In: Proceedings of the international workshop on sensing quality of agricultural products. University of California, Davis, 1998
- Vestergaard J, Martens SM, Turkki P (2007) Application of an electronic nose system for prediction of sensory quality changes of a meat product (pizza topping) during storage. Lwt-Food Science and Technology 40:1095–1101
- Wang B, Xu SY, Sun DW (2010a) Application of the electronic nose to the identification of different milk flavorings. Food Res Int 43:255–262
- Wang TH, Hui GH, Deng SP (2010b) A novel sweet taste cell-based sensor. Biosens Bioelectron 26:929–934
- Zhang HM, Wang J (2007) Detection of age and insect damage incurred by wheat, with an electronic nose. Journal of Stored Products Research 43:489–495
- Zhang HM, Chang M, Wang X, Ye JS (2008) Evaluation of peach quality indices using an electronic nose by MLR, QPST and BP network. Sensors and Actuators B: Chemical 134:332–338
- Zhu LM, Seburg RA, Tsai E, Puech S, Mifsud JC (2004) Flavor analysis in a pharmaceutical oral solution formulation using an electronic-nose. J Pharm Biomed Anal 34:453–461