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Winter jujube (*Zizyphus jujuba* Mill.) quality forecasting method based on electronic nose

Hui Guohua [a,b,*], Jin Jiaojiao [b], Shanggui Deng [c], Ye Xiao [b], Zhao Mengtian [b], Wang Minmin [b], Ye Dandan [b]

[a] *School of Computer Science and Information Engineering, Zhejiang Gongshang University, Hangzhou 310018, China*
[b] *College of Food Science and Biotechnology, Zhejiang Gongshang University, Hangzhou 310018, China*
[c] *College of Food and Pharmacy, Zhejiang Ocean University, 316000 Zhoushan, China*

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ABSTRACT

Winter jujube (*Zizyphus jujuba* Mill.) quality forecasting method utilising electronic nose (*EN*) and double-layered cascaded series stochastic resonance (DCSSR) was investigated. *EN* responses to jujubes stored at room temperature were continuously measured for 8 days. Jujubes' physical/chemical indexes, such as firmness, colour, total soluble solids (TSS), and ascorbic acid (AA), were synchronously examined. Examination results indicated that jujubes were getting ripe during storage. *EN* measurement data was processed by stochastic resonance (SR) and DCSSR. SR and DCSSR output signal-to-noise ratio (SNR) maximums (SNR-MAX) discriminated jujubes under different storage time successfully. Multiple variable regression (MVR) results between physical/chemical indexes and SR/DCSSR eigen values demonstrated that DCSSR eigen values were more suitable for jujube quality determination. Quality forecasting model was developed using non-linear fitting regression of DCSSR eigen values. Validating experiments demonstrated that forecasting accuracy of this model is 97.35%. This method also presented other advantages including fast response, non-destructive, etc.

1. Introduction

Winter jujube (*Zizyphus jujuba* Mill.) is an important kind of fruit in China. It is deeply favored by people for its good taste and abundant nutrition, such as vitamin C, amino acids, cyclic AMP, carbohydrate, and minerals (eg. potassium, iron), etc. (Gao et al., 2011; Liu et al., 2014; Sun et al., 2008; Wang et al., 2011). Its extracts are used as food additives, such as analeptic, palliative, and antibacterial materials (Li, Ai, Yang, Liu, & Shan, 2013). Winter jujube deteriorates easily during storage, which causes huge economic loss during postharvest storage and transportation (Yan, Cao, Jiang, & Zhao, 2012). Many researchers report that a series of chemical changes happen to jujubes after harvest (Ibrahim, Hussaini, Sani, Aliero, & Yakubu, 2011; Qu, Yu, Jin, Wang, & Luo, 2013; Visai & Vanoli, 1997). Traditional methods for fruit quality evaluation include human sensory analysis, chemical examination and instrumentation analysis (Wang et al., 2012; Wu, Gao, Guo, Yu, & Wang, 2012; Zozio et al., 2014). Although these methods have been widely applied, they still have some limitations. For example, human sensory analysis method presents food quality information fast, but it is limited in stability, measurement standardization, reproducibility, etc. Chemical examination is objective and precise. But it is usually destructive and time-consuming. Instrumentation analysis, such as gas chromatography (GC) and GC coupled with mass spectrometry (GC/MS), is only suitable for food quality examination in laboratory condition. Moreover, instrumentation analysis depends on expensive equipments, and its detecting cost is relatively high. Some well-trained operators are specially demanded to ensure detection accuracy. In recent years, spectroscopy methods present their potentials in jujube quality analysis. Zhang et al. establish a simple identification model for fresh jujube subtle bruises using visible-near infrared reflectance (NIR) spectroscopy (Zhang, Zhang, Zhao, Guo, & Zhao, 2013). Wang et al. study a nondestructive jujube internal insect infestation and jujube quality by visible–NIR spectroscopy (Wang, Nakano, & Ohashi, 2011a, 2011b). Although NIR methods accomplish jujube quality or damage detection, these methods have some difficulty in discrimination of jujubes in different quality.

EN, as a kind of bionic olfactory technology, has been widely applied in food quality and safety analysis during past two decades. It usually consists of an array of several gas sensors with partial specific sensitivities. *EN* gas sensors respond to the specific volatile gases emitted by the detected samples, and generate measurement

* Corresponding author at: School of Computer Science and Information Engineering, Zhejiang Gongshang University, Hangzhou 310018, China. Fax: +86 571 88071024.
E-mail address: ghui@zjgsu.edu.cn (G. Hui).

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signals. Patterns from the known samples are utilised to establish a database and train a pattern recognition system. Then, under certain circumstances, the unknown pattern of new sample measurements can be classified and identified by the established pattern recognition system (Hui, Wang, Mo, & Zhang, 2012). *EN* has exhibited potential in food analysis, such as tomato microbial contamination (Concina et al., 2009), tomato shelf life determination (Berna, Lammertyn, Saevels, Di Natale, & Nicolai, 2004; Gomez, Wang, Hu, & Pereira, 2008), peach sensorial properties analysis and freshness determination (Di Natale et al., 2011; Hui et al., 2012), mandarin storage shelf-life analysis (Gomez, Wang, Hu, & Pereira, 2007), pear odour discrimination (Oshita et al., 2000), apple optimal harvest date evaluation (Saevels et al., 2003), apple storage time prediction (Hui, Wu, Ye, & Ding, 2013), and onion postharvest diseases evaluation (Li, Schmidt, & Gitaitis, 2011), etc.

Some pattern recognition methods, including principal component analysis (PCA), partial least square (PLS), artificial neural networks (ANN), etc, are frequently used in *EN* data analysis. PCA scores by calculating principal component functions, and focuses on a comprehensive evaluation of information contribution to the influence of the raw data. The meaning of its evaluating function is not clear when the factor loadings of the principal component symbol are both positive and negative. PLS regression modeling can be effectively overcome the problem when the sample size is less than the number of variables. But the impact of one or more existing points will lead to regression failure. ANN is an artificial intelligence theory. The training efficiency and forecast accuracy declines remarkably with the input of large numbers of samples. SR is a counterintuitive non-linear dynamic model, and develops fast in the few past decades. This theory was proposed by Italian scientist Benzi in 1982, and used to explain the periodical emergence of Earth's ice age (Benzi, Sutera, & Vulpiana, 1981). SR has been considerably expanded in theoretical research and experimental investigation in recent years, such as chemistry dynamics study, biomedical engineering, and signal processing (Chapeau-Blondeau & Godivier, 1997; Dutta, Das, Stocks, & Morgan, 2006; Gammaitoni, Hanggi, Jung, & Marchesoni, 1998). In SR analysis, the non-linear dynamics system can get into resonance state with the stimulation of external white Gaussian noise with proper dose. In the resonance state, the energy of intrinsic noise has been transferred into the aimed weak input signal. So the aimed weak input signal can be amplified so that it can be characterised qualitatively or quantitatively (Hui, Ji, Mi, & Deng, 2013; Hui, Mi, Chen, & Chen, 2014; Hui, Mi, & Deng, 2012).

In this paper, winter jujube (*Zizyphus jujuba* Mill.) quality forecasting method using *EN* was investigated. *EN* responses to jujubes stored at room temperature were continuously measured for 8 days. At the same time, physical/chemical indexes, such as firmness, surface colour, TSS, and AA were synchronously examined. Jujubes under different storage time could not be qualitative or quantitatively discriminated by PCA. *EN* measurement data was analysed by SR and DCSSR. SR and DCSSR SNR spectrum successfully discriminated jujubes of different quality. MVR analysis results demonstrated that DCSSR eigen values had more significant linearity relation with physical/chemical indexes than SR eigen values did. DCSSR eigen values were more suitable for winter jujube quality determination. Jujube quality forecasting model was developed based on non-linear fitting regression on DCSSR eigen values. Validating experiments demonstrated that the developed model forecasted jujube quality with high accuracy.

2. Materials and methods

2.1. Winter jujube samples

Fresh winter jujubes used in the experiments were purchased from Wen'er fruit market, Hangzhou, China, and transported to our laboratory at room temperature. The winter jujubes were selected for uniformity of size and colour, free from disease and at the same physiologically mature stage, and were not subjected to any mechanical damage or postharvest process. All samples were stored at room temperature and 85% relative humidity (RH). Each day, 20 jujubes were selected for firmness, colour, TSS, AA, and *EN* measurement respectively. The experiments last for 8 days. In validating experiments, 70 jujubes are stored for 8 days. In each day, 4 jujubes were randomly taken out for *EN* measurement.

2.2. Chemicals

Standard ascorbic acid solution, sodium bicarbonate and 2,6-dichlorophenol indophenol sodium are purchased from Zhanyun Limited Company, Shanghai, China.

2.3. Firmness measurement

Firmness measurement is conducted using penetrometer (FMH-5, Takemura Electric Works, Japan).

2.4. Colour measurement

The surface fresh colour of jujubes is measured using a chromatic meter (TES-135, Taiwan Taishi Electronic Technology Co., Ltd.) and reported as L^*, a^*, and b^* as CIELab coordinates. Parameters of L^*, a^*, and b^* indicate the lightness (the scale range of 0–100 points from black to white), red (+) or green (−), and yellow (+) or blue (−), respectively.

2.5. Total soluble solids (TSS)

Winter jujube is ground in a mortar and squeezed with a hand press for juice. The juice is used for TSS measurement. The measurement is conducted utilising refractometer (WZ113/ATC, China) at 25 °C temperature.

2.6. Ascorbic acid (AA) examination

AA measurement method can be referred to China National Standard protocol GB 6195-86: determination of vitamin C in vegetables and fruits (2, 6,-dichloro-indophenol titration method) (GB 6195-86, 1986).

2.7. EN system

Structure of *EN* system which used in our experiment is shown in Fig. 1(a). *EN* sensor array consists of eight metal oxide semiconductor (M.O.S) gas sensors, whose sensing species is showed in Table 1. The gas sensors rely on changes in conductivity induced by the adsorption of molecules in the gas phase and on subsequent surface reactions. They consist of ceramic substrate coated by M.O.S film, and heated by wire resistor. Due to the high temperature (350–500 °C), the volatiles transferred to the sensors' surface are totally combusted to carbon dioxide and water, leading to the changes in electrical resistance. The high temperature avoids water interference and provides sensors fast response and rapid recovery characteristics. Sensor responses are measured as voltage (V). Polytetrafluorethylene (PTFE) is used to fabricate sensor chamber. Each sensor room is separated, which helps to avoid the gas flow's cross-influence. Under the control of unit U2, the sensor response signal is transferred to the computer via USB interface by signal collection board, and to realise the function of data acquisition and storage.