Litchi freshness rapid non-destructive evaluating method using electronic nose and non-linear dynamics stochastic resonance model

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In this paper, litchi freshness rapid non-destructive evaluating method using electronic nose (e-nose) and non-linear stochastic resonance (SR) was proposed. EN responses to litchi samples were continuously detected for 6 d. Principal component analysis (PCA) and non-linear stochastic resonance (SR) methods were utilized to analyze EN detection data. PCA method could not totally discriminate litchi samples, while SR signal-to-noise ratio (SNR) eigen spectrum successfully discriminated all litchi samples. Litchi freshness predictive model developed using SNR eigen values shows high predictive accuracy with regression coefficients $R^2 = 0.99396$.

Introduction

Litchi (Litchi chinensis Sonn) belongs to subtropical fruit. Its main produce areas in China include Guangxi, Guangdong, Fujian, Hainan, Taiwan, etc. This fruit is well known for its abundant nutrition (such as vitamin, sugar, amino acid, protein, etc), delicious taste and the function of beauty as well as anticancer effect. After harvest, litchi still precedes metabolism reactions by consuming its internal nutrition substances. What’s more, microbial growth and multiplication also influence litchi’s inner structure. Fruit quality declines even decay, leading to food safety risks. With the improvement of living standard, people’s requirements for fruit quality highly improved. Neog et al as well as Ruenroengklin et al successfully examined litchi’s physicochemical indexes (such as PPO specific activity, total phenols, pericarp browning, etc) to monitor litchi’s freshness change using a UV-VIS spectrometer. Sun et al analyzed the contents of major PPO substrates for enzymatic browning using HPLC and measured total phenol content using a UV spectrophotometer to obtain litchi fruit’s quality change. However, these methods cover some severe drawbacks, such as long detecting period, strict operating requirements, high detecting cost, etc.

E-nose concept is firstly proposed in 1982. E-nose imitates human’s olfactory function and measures samples with sensor array combined with pattern recognition system. In the past 2 decades, it has been widely applied in food area, such as pork meat TVB-N evaluation, non-destructive red onion flavor evaluation, pork adulteration analysis in minced mutton, cherry tomato juices adulteration detection, discrimination of Chinese green tea, etc. The species and content of volatile substances in fruits and vegetables are extremely different at different ripen period. Hence, the method based on e-nose is hopeful to realize the assessment of sample’s ripeness and freshness by detecting and analyzing its volatile substances using some pattern recognition approaches. Previous studies have reported some successful applications about e-nose in fruit freshness determination.

In this paper, litchi freshness rapid non-destructive evaluating method using e-nose was studied. PCA method could not discriminate all litchi samples with different storage time, while SNR spectrum successfully discriminated all samples. And litchi freshness predictive model was built by linear fitting Max-SNR eigen values. The proposed model presents high predicting accuracy with high regression coefficients $R^2 = 0.99396$.

Results and Discussions

E-nose measurement result

E-nose sensor original responses to litchi samples are displayed in Figure 1a. The volatile gases existing in the headspace of samples are inhaled into EN gas chambers and sensed by the functional materials settled in gas sensors. All sensors’ initiative responses to litchi samples are close to zero. Sensors’ responses gradually increase and finally reach their stable values. S1, S4 and S3 have big response values, and their final steady values are about 0.80, 0.60 and 0.40 V, respectively. S5 and S6 have a similar response value about 0.25 V, while the rest 3 sensors (S2, S7 and S8) present low response values near zero.
PCA analysis result

The PCA analysis result of litchi samples is displayed in Figure 1b. Five sensors including S1, S3, S4, S5 and S6 were chosen and their final stable response values were set as eigen values to represent litchi sample’s freshness. The first principal components (PC1) and the second principal components (PC2) capture 82.22% of data variance. It is apparent that this method can well classify litchi samples in the first 2 d However, it cannot clearly discriminate litchi samples in the following 4 d Hence, the PCA method is not suitable for quantitative discrimination toward litchi samples.

SR analysis result

Litchi sample’s SNR spectrum analysis result is shown in Figure 1c. Samples’ initial SNR values are in the range from -77.5 to -62.5 dB and their Max-SNR values range between -59.5 to -55.0 dB. Eigen peak appears at the stimulating noise intensity of 100 or so. Some derivative vales arise before the formation of eigen peaks. After that, each SNR value gradually decreases with the increase of stimulating noise intensity and finally reaches their stable value about -85.0 dB. So, litchi samples under different storage days can be clearly discriminated using Max-SNR values.

For the further step, a litchi freshness predictive model using Max-SNR values as eigen values is built and Eq. (1) is obtained by linear-fitting. The result with regression coefficients $R^2 = 0.99396$ is displayed in Figure 1d, which indicates the proposed predictive model can successfully discriminate all litchi samples under different storage days. Some samples may bring about minor errors.

$$\text{Freshness} = 85.83122 + 1.43403 \times \text{MaxSNR}, \quad R^2 = 0.99396$$

(1)

In this research, PCA and SR analysis methods were used to analyze the detected e-nose data. The result indicated that PCA could not discriminate all litchi samples with different storage days. SNR spectrum eigen values calculated by SR successfully discriminated all litchi samples. The rapid predictive model about litchi freshness built by linear-fitting Max-SNR eigen values shows a satisfying result with prediction accuracy $R^2 = 0.99396$.

Materials and methods

Litchi samples
Litchi samples were purchased from Gouzhuang fruit whole market (Hangzhou, China). Samples (nearly the same in weight, size, and ripeness) without any freshness pretreatment were selected for the experiments. All litchi samples were stored in an ice bubble chamber and all measurements were performed at room temperature.

Methods
E-nose detection
E-nose structure is displayed in Fig. 2. It consists of 3 main parts: data acquisition, modulating and transmitting unit (U1); sensor array and chamber unit (U2); power and gas supply unit (U3). E-nose consists of 8 M.O.S. gas sensors with different sensitive species. The selectivity toward volatile compound classes of M.O.S sensors is indicated by the supplier: S1 (TGS-825, hydrogen sulfide), S2 (TGS-821, hydrogen), S3 (TGS-826, ammonia), S4 (TGS-822, ethanol, methylbenzene, xylene gas), S5 (TGS-842, hydrocarbon component gas), S6 (TGS-813, methane, propane, and butane), S7 (TGS-2610, propane, butane), S8 (TGS-2201, nitrogen oxides). Each sensor is installed in independent chamber to avoid cross-influence of gas flow.

In e-nose detection, each sample was placed into a 50 mL air-tight vial, and sealed with sealing membrane. The vials were equilibrated for 30 min at room temperature. Turned on e-nose power, and started washing pump and valve 2. The sampling pump and valve 1 remained off. The air was filtered by active carbon to obtain zero gas. Sensor array were recovered by zero gas. When sensors’ responses returned to the baseline, washing pump and valve 2 were shut off. Then sampling pump and valve 1 were turned on. The gases in sample’s headspace were inhaled into gas sensor chambers by sampling
SR is a typical non-linear model and proposed by Benzi for the explanation for Earth climate periodic changes.\textsuperscript{18,19} SR phenomenon has 3 elements: a bistable system, a coherent input, and a noise source, which can be described as:

\[
\frac{dx}{dt} = -\frac{dV(x)}{dx} + MI(t) + D\xi(t) \quad (2)
\]

Where \(x\) is the position of the Brownian particle, \(t\) is the time, \(M\) and \(D\) are adjustable parameters, \(I(t) = S(t) + N(t)\) denotes an input signal 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.

\[
V(x) = -\frac{1}{2}ax^2 + \frac{b}{4}x^4
\]

Eq. (2) can be written as

\[
\frac{dx}{dt} = ax - bx^3 + MI(t) + D\xi(t) \quad (4)
\]

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. 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 \(I(t) = A\sin(2\pi ft + \varphi)\), where \(A\) is signal intensity, \(f\) is signal frequency, \(D\) is external noise intensity. SNR is the common quantifier for SR and it can be approximately described as:

\[
SNR = \sqrt{\Delta U} \left(\frac{A}{D}\right)^2 e^{-\Delta U/D} \quad (5)
\]

**Conclusions**

Litchi (Litchi chinensis Sonn) freshness rapid non-destructive evaluating method based on e-nose and non-linear stochastic resonance was proposed in this research. PCA method cannot discriminate all litchi samples with different qualities, while SR SNR spectrum successfully discriminated all samples. Litchi freshness rapid evaluating model was built by linear fitting regression of Max-SNR values. The developed model exhibited high evaluating accuracy for litchi samples with regression coefficients \(R^2 = 0.99396\). The method proposed in this research exhibits many unique characteristics including rapid response, high accuracy, low cost, etc.

**Disclosure of Potential Conflicts of Interest**

No potential conflicts of interest were disclosed.

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