Food Analytical Methods
https://doi.org/10.1007/s12161-018-1286-y

Rapid and Non-Destructive Detection of Decay in Peach Fruit at the Cold Environment Using a Self-Developed Handheld Electronic-Nose System

Xun Wei [1,2] · Yuchen Zhang [1] · Di Wu [1] · Zhenbo Wei [3] · Kunsong Chen [1]

Received: 12 February 2018 / Accepted: 1 May 2018

Abstract
Non-destructive detection of decay in fruit in real time during cold chain is important to recycle the decayed fruit in time for reverse supply chain. Fruit is commonly stored inside external packages during cold chain, making neither manual observation nor optical inspection techniques available to detect the decay in fruit. In this work, the potential of a self-developed handheld electronic nose (e-nose) instrument to non-destructively acquire volatile substances and then detect decay in peach fruit during cold chain (0 °C) was explored. A desktop e-nose instrument was considered as a comparison. The storage days of peach fruit during storage were also predicted by two instruments. Partial least squares discriminant analysis and least squares support vector machines (LS-SVM) were used for the classification of decay in peach fruit. Partial least squares regression and LS-SVM were used for the prediction of the storage days. Successive projection algorithm (SPA), uninformation variable elimination (UVE), UVE-SPA, and competitive adaptive reweighted sampling were applied to select the characteristic variables from e-nose data. The best model for the classification of decayed fruit during cold chain by the handheld e-nose instrument had the correct answer rate of prediction of 95.83% (94.64% for healthy samples and 100.00% for decayed samples). The best model for predicting the storage days of peach fruit during cold chain by the handheld e-nose instrument had the residual predictive deviation value of 9.283. The results indicate that the self-developed handheld e-nose system is a simple and non-destructive tool to detect decay in peach fruit during cold storage.

Keywords Peach fruit · Electronic nose · Decay · Reverse logistics · Supply chain · Cold chain

Introduction

Food supply chains move food products from the place of production to the consumer using food logistic methods. Some food products, especially perishable foods like fruits, may become decayed during storage resulting in losses in market value. Statistical data show that more than one third of harvested fruit and vegetables are lost in the field or after harvest (FAO 2011; OECD 2014; USDA 2014). In recent years, food reverse supply chain, or called reverse logistics, as a new concept has recently received growing importance due to potentials of value recovery from the products and consumer awareness and social responsibilities towards environment protection (Pokharel and Mutha 2009). Food reverse supply chain generally includes food recycling chain and food waste chain. The focus on food reverse supply chain includes waste management and recovery of decayed food product to reduce environment pollution. Food reverse supply chain is important to develop agricultural recycling economy, which requires maximal utilization of agricultural renewable resources and protection of environment. The use of reverse supply chain allows the recycling of decayed food to produce fertilizer and biomass or transportation to landfill rather than discarding them carelessly, resulting in reducing environment pollution and increasing economic benefits.

The major challenge for food reverse supply chain relies on detection of decay in food during their forward supply chain. Poor data measurement and lack of appropriate analyzing

✉ Di Wu
di_wu@zju.edu.cn; china.di.wu@gmail.com

1 College of Agriculture and Biotechnology/Zhejiang Provincial Key Laboratory of Horticultural Plant Integrative Biology/The State Agriculture Ministry Laboratory of Horticultural Plant Growth, Development and Quality Improvement, Zhejiang University, Zijingang Campus, Hangzhou 310058, People's Republic of China

2 China Rural Technology Development Center, Beijing 100045, People's Republic of China

3 Department of Biosystems Engineering, Zhejiang University, Hangzhou 310058, People's Republic of China

information will make wrong decisions like recycling good products or missing decayed food. Fruit is perishable during transportation and storage. Nigro et al. (2000) found that the mean rot rate of strawberry was 94.55% after 6 days of storage at 20 °C. Fallik et al. (2001) found that the decay incidence of Golden Delicious apple was 28 ± 1.8% after 4 weeks of storage at 20 °C and 49 ± 2.1% after 4 months of storage at 1 °C plus 10 days of storage at 20 °C. Therefore, the information about fruit decay is one of the key successful drivers for further fruit reverse logistic operations. Direct observation by naked eyes is commonly used to detect fruit decay for all participates during fruit supply chain, including growers, distributors, sellers, and consumers. But, manual measurement is subjective, time-consuming, tedious, and selective process. Visible and near-infrared (VIS-NIR) spectroscopy and hyperspectral imaging techniques are rapid and non-invasive, and permits an online quality measurement and grading of fruit products, such as defect, bruise, decay, and canker (Wu and Sun 2013a, b). However, the products are commonly placed inside external packages, such as corrugated fiberboard box and plastic container, and wrapped by inner packaging like papers and foam net in some cases during fruit supply chain. Therefore, neither manual observation nor spectral and imaging techniques can evaluate whether the packaged fruit is decayed or not during supply chain. Fruit industry requires alternative techniques to detect the decay in fruit during supply chain.

Volatile substances are one of the most important characteristics related to fruit quality and are specifically sensitive to the quality changes of fruit. It has been already reported that there were relationships between fruit quality and volatile substances (Besada et al. 2013; Mayuoni-Kirshinbaum et al. 2013; Yi et al. 2016). Metabolic activities of fruit generate volatile substances (Baietto and Wilson 2015; Sanaeifar et al. 2016), which change during postharvest (Horvat et al. 1990; Chen et al. 2006; Guohua et al. 2012). Healthy and decayed fruit have different physiological quality, including volatile substances (Migliori et al. 2017). Therefore, volatile substance is a potential indicator for detecting decay in fruit.

Electronic nose (e-nose) is a method to detect volatile compounds of fruit and other agricultural products (Loutfi et al. 2015; Sanaeifar et al. 2017). E-nose has the advantages of relatively rapid and non-damaging measurement of headspace, simple operation, and possibility of real-time analysis. Fruit grades were classified and quality were predicted in numerous applications using e-nose, such as blue berries (Kraujalytė et al. 2015), pears (Zhang et al. 2008), jujube (Hui et al. 2015), litchi (Xu et al. 2016), persimmon fruit (Zhang et al. 2016), Goji berries (Li et al. 2017), and mandarins (Hernández et al. 2007). It should be noted that when fruit is wrapped by packages, even then their volatile substances can be detected when the probes of e-nose systems are inserted into the packages of fruit.

Peach is a popular fruit with tender texture, pleasant flavor and rich nutrition, and is highly perishable during postharvest period. Our group already used e-nose to forecast how many days left until the fruit is decayed (Huang et al. 2017a), showing that there is relationship between volatile substances of peach fruit and its e-nose signal. However, to the best of our knowledge, e-nose has not been used to detect decay in peach fruit. The objective of this study is to use e-nose to measure the volatile signals of fruit and non-destructively distinguish whether the fruit was decayed or not during supply chain. The successful outcome of the study is very advantageous to recycle decayed peach fruit and protect environment. The specific works include (1) non-destructively acquiring volatile substances of healthy and decayed peach fruit stored in both a refrigerated storage and a storage at room temperature by handheld and desktop e-nose instruments, (2) establishing multivariate regression models between the values of storage days of peach fruit and their e-nose fingerprints, (3) building classification models between healthy and decayed peach fruit, (4) selecting optimal e-nose variables to determine how many days peach fruit has been stored for and classify the decayed fruit, and (5) comparing the performances of two e-nose instruments.

Materials and Methods

E-Nose Instruments

The self-developed handheld e-nose system (E-nose I) had 12 MOS sensors. Details of these sensors can be found in Wei et al. (2017)'s work. ANSYS Fluent Software (ANSYS Inc., Canonsburg, PA, USA) was used to design the configuration of the sensors to guarantee each sensor's efficient absorption of the target gas. These sensors were placed in a rectangular chamber made of Teflon. The control module of the e-nose system used MCU STM32F407 to set sampling models (automatic or manual), switch solenoid valve, and choose sampling parameters, such as sampling number, sampling time, gas pump rate, and clean time. The signal circuit and heating circuit of 12 gas sensors were fed separately to better activate these sensors. A commercial desktop Fox 4000 e-nose instrument (ALPHA MOS, Toulouse, France) was also used to acquire volatile substances of peach fruit to evaluate the performance of the self-developed handheld e-nose instrument. The desktop instrument (E-nose II) has 18 MOS sensors in three sensor chambers. The MOS sensors belong to two types of P & T sensors and LY2 sensors. Details of Fox 4000 and its MOS sensors are described in Huang et al. (2015)'s work.

Sample Preparation

Peach fruit (*Prunus persica* L. Batsch) was collected from a commercial orchard in Ningbo, Zhejiang Province, China, on August 4, 2017. The harvested fruit was at commercial maturity. Fruit was transported to the laboratory in Hangzhou, Zhejiang Province, China, on the day of harvest. Fruit of uniform commercial maturity with absence of mechanical damage and disease was selected for further analysis. The selected peach fruit was divided into two groups, which were stored at 20 °C (group I) and 0 °C (group II), respectively. Volatile substances of fruit samples in group I were acquired by both handheld and desktop e-nose instruments at 13-day points from the starting day 1 to day 13 with an interval of 1 day, whereas volatile substances of fruit samples in group II were acquired at 11-day points of 1st, 3rd, 5th, 7th, 9th, 11th, 17th, 25th, 33rd, 41st, and 49th days. There were six samples for each sampling day, resulting in 78 samples for group I and 60 samples for group II. The decayed fruit samples were determined when their decayed areas on fruit pericarp were larger than 1 mm wide (Yang et al. 2011; Yu et al. 2012).

Acquisition of Volatile Substances by e-Nose Instruments

Each fruit was placed in a 500-mL glass beaker, which was sealed with parafilm PM-996 (Pechiney Plastic Packaging, Menasha, WI, USA) for the generation of volatile substances. The sealed beakers from group I were placed at 20 °C and those from group II at 0 °C during the generation process. The headspace-generation time was set as 2 h to ensure that the volatile substances were enough for e-nose data measurement. After the generation of volatile substances emitted from peach fruit, the e-nose signal of the collected headspace gas was measured by E-nose I and E-nose II both at room temperature. There were three phases for the data measurement of the handheld e-nose instrument (E-nose I), namely, acquisition phase for taste information (50 s), acquisition phase for aftertaste information (180 s), and cleaning phase (40 s). The volatile substances from the headspace were pumped into the sensor chamber at a constant rate of 5 mL s^{-1} at the beginning of the phase for taste information. The volatile substances were then continuously absorbed by the MOS sensors for approximately 50 s. Air was used to clean all sensors to their baseline at the constant pumping rate of 10 mL s^{-1} after the data acquisition. For the data acquisition of the desktop e-nose instrument (E-nose II), 2-mL headspace gas was extracted by a syringe and pumped into the sensor chamber at a constant rate of 2.5 mL s^{-1}. The time for data acquisition and cleaning was 120 and 240 s, respectively. Acquisition for each sample by both instruments was repeated twice, and the mean e-nose profile was used as the e-nose data of this sample for further data analysis.

Multivariate Data Analysis

Calibration of e-nose models for predicting storage days of peach fruit was carried out using partial least squares regression (PLSR) and least squares support vector machine (LS-SVM) algorithms based on the e-nose fingerprints of peach fruit. PLSR is a multivariate, statistical, and linear regression method (Wu et al. 2014b; Huang et al. 2017b). The main principle of PLSR is to extract orthogonal factors called latent variables (LVs) and to establish the regression relationship between the dataset and the corresponding reference value. As a comparison, a classical non-linear regression methodology called LS-SVM was also used. LS-SVM is an optimized version of support vector machines based on the least squares algorithm, which is a learning machine used for regression (Wu et al. 2008; Zhu et al. 2017a).

Classification models between healthy and decayed peach fruit were established by two supervised multivariate classification algorithms, namely, partial least squares discriminant analysis (PLS-DA) and LS-SVM. PLS-DA encodes dependent variable of PLSR with dummy variables describing the classes, and then is implemented in the usual way of PLSR. The reference values of the dependent variable were set − 1 and 1 for healthy and decayed peach. For classification, LS-SVM also uses reference values of − 1 and 1 to establish the classification models.

Selection of Optimal Variables

E-nose data usually contains several hundreds and thousands variables. Most of them are non-informative and redundant. To solve the problem of unrelated variables, four variable selection methods, namely, successive projection algorithm (SPA), uninformative variable elimination (UVE), uninformative variable elimination–successive projection algorithm (UVE-SPA), and competitive adaptive reweighted sampling (CARS), were applied to select the characteristic variables from e-nose data. SPA projects the e-nose data into candidate subsets containing variables with minimum of collinearity, then selects the optimal variables from candidate variables according to the performances of their multiple linear regression models (Wu et al. 2012; Zhu et al. 2016). UVE eliminates the uninformative variables based on the stability analysis of PLSR regression coefficients (Wu et al. 2010; Wu and He 2014). Moreover, considering the variables selected by UVE might have a problem of multicollinearity and those selected by SPA might contain variables less related to the dependent variables, UVE-SPA is usually employed (Wu et al. 2014a; Zhu et al. 2017b). In the UVE-SPA calculation, UVE is used for preliminary variable selection from full variables, and then, SPA is applied for further selection. In addition, CARS evaluates every variable based on the absolute value of regression coefficient of PLSR models, and then selects the variables with larger coefficients as the optimal variables (Wu and Sun 2013c, d).

Model Evaluation

Independent sample sets should be different from the calibration sample sets, which is important to evaluate the robustness of the established models. In this work, group I was consisted of 52 samples for calibration and rest of 26 samples were used for the prediction purpose. In group II, 40 samples were used for calibration and rest of 20 samples for prediction purpose. It should be noted that different samples for calibration and prediction will make the established models have different performances. The calibration processes were carried out three times for groups I and II, respectively, to avoid an effect on model accuracy caused by using different samples for model calibration. In particular, samples in groups I and II were randomly and equally divided into three parts. Every time, samples in one part were used for prediction and remaining samples for the calibration (one sample set). After three times of selecting one of the three sample parts for prediction, there were three sample sets obtained. Each sample set had different samples for prediction purpose. The performances of the established e-nose models were compared based on the mean performance of three sample sets.

The performances of the models to predict the storage days of peach fruit were carried out in terms of their root-mean-square error of calibration (RMSEC) and correlation coefficient of calibration (R_c) in the calibration process, as well as its root-mean-square error of prediction (RMSEP), correlation coefficient of prediction (R_p), residual predictive deviation (RPD) in the prediction process, and the absolute difference between the RMSEC and RMSEP (AB_RMSE). These parameters were used to evaluate the predictive ability and accuracy of the regression models. Among them, AB_RMSE indicates the robustness of the regression models. The smaller the AB_RMSE value is, the better the robustness of the model is. A good prediction model should have high R_c, R_p, and RPD values and low RMSEC, RMSEP, and AB_RMSE values.

Correct answer rate (CAR) was used to evaluate the results of the models for the classification of the decayed fruit. CAR is obtained by calculating the ratio of the number of samples correctly classified to the number of all samples. The threshold of zero was used. When the classified value of a sample was less than zero, this sample was identified as healthy. On the contrary, a sample would be classified as decayed when its classified value was larger than zero. There are four evaluation parameters in the evaluation of classification model performance, namely, CAR of calibration, CAR of prediction, mean value of the CAR of calibration and prediction (M_CAR), and the absolute difference between the CAR of calibration and prediction (AB_CAR). Similar to AB_RMSE, AB_CAR was also used to evaluate the robustness of the classification models. The smaller the AB_CAR value is, the better the classification model is. All calculation of multivariate regression, variable selection, and model evaluation were performed in MATLAB 2015a software (The MathWorks Inc., Natick, MA, USA).

Results

E-Nose Response of Peach Fruits

Considering that some sensors had negative variation (decrement) after absorbed the volatile substances of samples, to obtain the representative polar plots of e-nose data, the original data of each sensor was subtracted from the original value of first second of the corresponding sensor; then, the absolute values of the differences were calculated. At last, the maximum value of the absolute values of this sensor was obtained and used to generate Fig. 1. Figure 1a, c shows the samples from group I, and Fig. 1b, d shows the samples from group II. Figure 1a, b shows the 12 angles (0° to 340°) with an interval of 30°, representing the 12 e-nose sensors of E-nose I. The radius vectors with the angles of 0° and 330° represent sensor 1 and sensor 12 in Fig. 1a, b. Figure 1c, d shows the 18 angles from 0° to 340°with an interval of 20° representing 18 e-nose sensors of E-nose II. In specific, the radius vectors with the angles of 0° and 340°in Fig. 1c, d represent sensor 1 and sensor 18. The scales of the sensor response are shown at the top-left corner of the polar plots. It should be noted that when more samples are considered, there will be serious overlapping of e-nose response, making the analysis of the e-nose response values directly by naked eyes much more difficult. Therefore, multivariate calculations were carried out to establish regression models to predict the storage days of peach fruit and to establish classification models to identify decay in fruit. For the data measured by E-nose I (Fig. 1a, b), all sensors had response values. For E-nose I, there were 12 sensors. Each one had 50 variables (50 s), resulting in 600 variables for all 12 sensors. On the contrary, sensors 1, 2, 3, 4, 5, and 6 of E-nose II had very weak response values closing to zero. These sensors were not used for further analysis. For E-nose II, there were 12 sensors left for calculation. Each one had 120 variables (120 s), resulting in 1440 variables for all 12 sensors. All variables of each sensor were used for data analysis. There was no preprocessing method used.

Prediction of Storage Days of Peach Fruit

Prediction Based on All Variables of e-Nose Data

Calibration of regression models was first performed using the full e-nose variables of samples. Two calibration

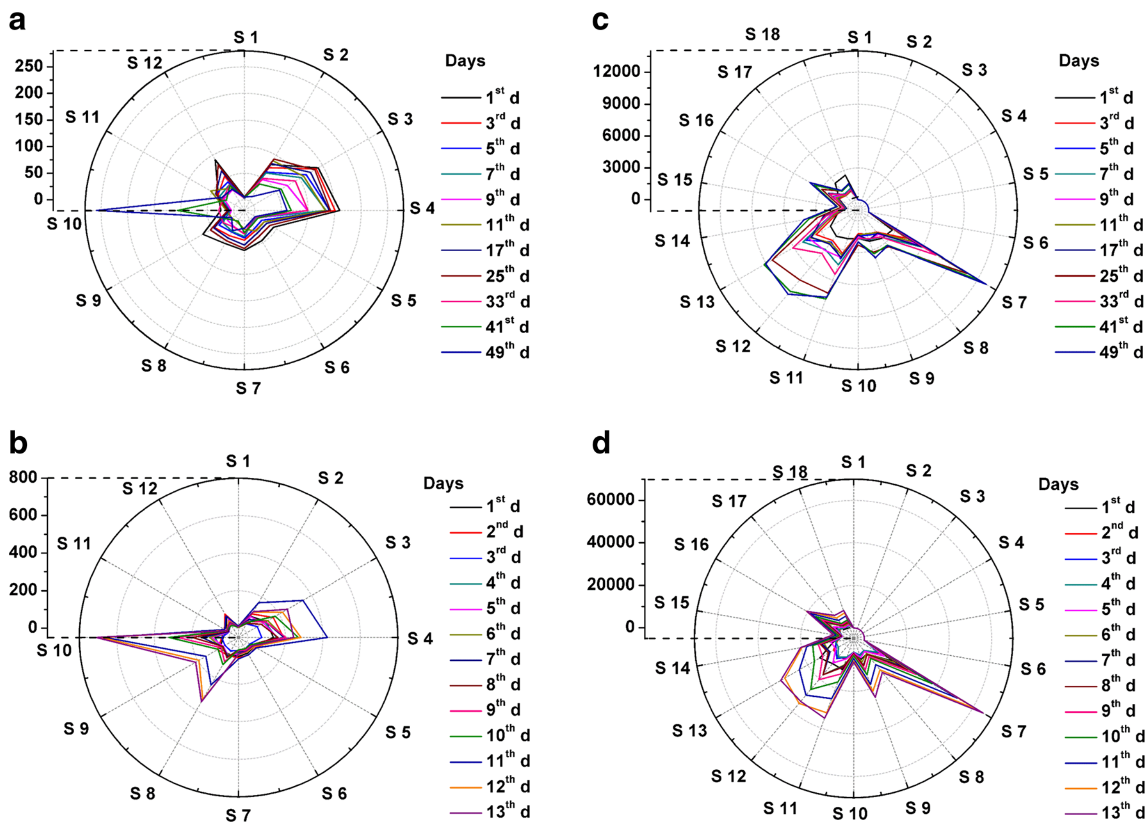

Fig. 1 Polar plots of the mean values of the maximum e-nose response of peach fruit stored at different days at 0 °C (**a**, **c**) and 20 °C (**b**, **d**). Twelve angles (0° to 340°) with an interval of 30° (**a**, **b**) represent the 12 e-nose sensors of the self-developed handheld e-nose system (E-nose I). Eighteen angles from 0° to 340° with an interval of 20° (**c**, **d**) represent the 18 e-nose sensors of the commercial desktop Fox 4000 e-nose instrument (E-nose II)

methods, namely, PLSR and LS-SVM, were used for the purpose of model calibration based on the e-nose data of samples and their corresponding values of storage days. Four kinds of models were obtained, namely, those established based the data of group I measured by E-nose I and E-nose II, respectively, and those based on the data of group II measured by E-nose I and E-nose II, respectively. Tables 1 and 2 show the results of four kinds of models. When fruit store at 20 °C (group I) was considered, E-nose I had good results in terms of calibration with a mean R_c value of 0.991 based on six models (three sample sets × two calibration methods). The independent prediction sets also obtained good results with a mean R_p value of 0.949. Among the six models, the best model was the LS-SVM model based on sample set III, which had R_p of 0.961 and AB_RMSE of only 0.989. On the other hand, the PLSR model based on sample set I was the “worst” model. Even so, it had R_p of 0.914, showing that E-nose I had the capability of predicting the values of storage days of peach fruit based on its volatile substances. Table 1 shows that E-nose II had little worse predictive accuracy than E-nose I, including the mean R_c value of 0.977 and the mean R_p value of 0.911.

Similar to group I, PLSR and LS-SVM were used to analyze the volatile substances of peach fruit stored at 0 °C (group II). Although group II had higher R_c and R_p values than group I, the mean RMSEP values of group II for both E-nose I and E-nose II were twice of those of group I. The handheld system had better performances than the desktop instrument by comparing the results of E-nose I and E-nose II. The mean RMSEP of two models (PLSR and LS-SVM) for the E-nose I and E-nose II were 2.518 and 4.216, respectively. This might be because more sensors had similar response values for group II (Fig. 1d) than group I.

In addition, the correlations were calculated between the values of storage days and all 600 variables of E-nose I and all 1440 variables of E-nose II, respectively. When E-nose II was considered, no variable had the correlation higher than 0.5 for both group I and group II. When E-nose I was considered, 14.5% variables (group II) and 5% variables (group I) had the correlation higher than 0.8. The highest values for group II and group I were 0.834 and 0.868, respectively, which were lower than the R_p values of most models in Tables 1, 2, 3, and 4. Therefore, multivariate modeling showed better predictive capabilities than single variable for the determination of storage days.

Table 1 Results of multivariate regression models between the values of storage days of peach fruit (group I) and their e-nose fingerprints with full variables

E-nose	Sample set	Calibration	Calibration		Prediction			AB_RMSE[d]
			R_c	RMSEC [a]	R_p	RMSEP[b]	RPD[c]	
I	I	PLSR	0.989	0.520	0.914	1.569	2.309	1.049
I	II	PLSR	0.986	0.599	0.965	1.037	3.564	0.438
I	III	PLSR	0.986	0.578	0.944	1.169	3.027	0.592
I	Average	PLSR	0.987	0.566	0.941	1.258	2.967	0.693
I	I	LS-SVM	0.998	0.236	0.938	1.268	2.853	1.032
I	II	LS-SVM	0.999	0.192	0.969	1.031	3.488	0.839
I	III	LS-SVM	0.990	0.495	0.961	0.989	3.580	0.493
I	Average	LS-SVM	0.995	0.308	0.956	1.096	3.307	0.788
II	I	PLSR	0.967	0.909	0.849	2.798	1.893	1.888
II	II	PLSR	0.973	0.820	0.874	2.040	2.044	1.219
II	III	PLSR	0.929	1.308	0.939	1.275	2.912	0.033
II	Average	PLSR	0.956	1.013	0.887	2.037	2.283	1.047
II	I	LS-SVM	0.997	0.254	0.881	2.332	2.114	2.078
II	II	LS-SVM	0.999	0.136	0.955	1.290	3.318	1.155
II	III	LS-SVM	0.994	0.382	0.970	0.932	4.121	0.550
II	Average	LS-SVM	0.997	0.257	0.935	1.518	3.184	1.261

Group I has the fruit stored at 20 °C. E-nose I is the self-developed handheld e-nose system and E-nose II is the commercial e-nose Fox 4000 instrument

[a] Root-mean-square error of calibration

[b] Root-mean-square error of prediction

[c] Residual predictive deviation

[d] Absolute difference between the RMSEC and RMSEP

Prediction Based on Optimal Variables of e-Nose Data

The variable dimension of e-nose data is generally very large, containing some unrelated variables. Possessing hundreds or thousands of e-nose variables might affect the accuracy and robustness of the e-nose models. In this work, suitable mathematical algorithms like SPA, UVE, UVE-SPA, and CARS were used to search for a few optimal e-nose variables, which were the most important and relevant variables to predict the values of storage days of peach fruit. PLSR and LS-SVM models were then calibrated based on the selected variables. Tables 3 and 4 show the corresponding results for groups I and II, respectively. The e-nose data of fruit storing at 20 °C (group I) was analyzed. After SPA calculation, E-nose I had a mean RMSEC value of 0.474 and a mean RMSEP value of 1.040. Compared with the corresponding results of all E-nose I variables, better result was obtained after SPA calculation. The variable number was also greatly reduced from 600 to 8 after SPA calculation. The descending ratio was 98.67%. Moreover, the mean AB_RMSE decreased from 0.741 to 0.566, showing that the robustness of e-nose models was improved. When UVE was applied to the variable selection, the stability value of each variable was used to determine whether this variable is informative or not. The results of UVE were similar to those of SPA, except that the variables selected by UVE were much more than those obtained by SPA. This was because UVE only selects informative variables without considering their multicollinearity. UVE-SPA was further applied to variable selection. However, UVE-SPA did not improve the accuracy as its models had similar results to those of SPA and UVE models. At last, the CARS calculation was carried out by selecting variables with larger absolute values of regression coefficients, resulting in 12 variables. In general, four variable selection methods had similar results in the aspects of bother accuracy and robustness. Mean RMSEP of eight models with selected variables (four variable selection methods × two regression algorithms) was 1.018, better than that of two models with full variables. On the other hand, the variable selection did not improve the accuracy for E-nose II. The mean RMSEP values of eight models with selected variables and two models with full variables were 1.861 and 1.778, respectively.

The variable selection for group II was also carried out. UVE-LS-SVM model had the lowest RMSEP of 1.979 for E-nose I. However, the model had 221 input variables. By comprehensively considering variable number, prediction accuracy, and model robustness, CARS-LS-SVM model was the best for the prediction of storage days when E-nose I was considered. The best model with selected variables had R_p of

Table 2 Results of multivariate regression models between the values of storage days of peach fruit (group II) and their e-nose fingerprints with full variables. Group II has the fruit stored at 0 °C

E-nose	Sample set	Calibration	Calibration		Prediction			AB_RMSE [d]
			R_c	RMSEC [a]	R_p	RMSEP [b]	RPD [c]	
I	I	PLSR	0.997	1.274	0.989	2.586	6.310	1.313
I	II	PLSR	0.998	0.990	0.987	2.613	6.019	1.623
I	III	PLSR	0.997	1.201	0.980	3.268	4.971	2.067
I	Average	PLSR	0.997	1.155	0.985	2.823	5.767	1.668
I	I	LS-SVM	1.000	0.370	0.991	3.005	5.789	2.635
I	II	LS-SVM	1.000	0.489	0.992	2.033	7.799	1.544
I	III	LS-SVM	1.000	0.053	0.995	1.599	9.829	1.546
I	Average	LS-SVM	1.000	0.304	0.993	2.213	7.805	1.908
II	I	PLSR	0.989	2.236	0.986	5.903	3.103	3.668
II	II	PLSR	0.994	1.741	0.971	4.271	3.778	2.531
II	III	PLSR	0.988	2.418	0.974	3.672	4.195	1.255
II	Average	PLSR	0.990	2.131	0.977	4.616	3.692	2.484
II	I	LS-SVM	0.998	0.870	0.991	4.804	3.584	3.934
II	II	LS-SVM	0.994	1.690	0.985	3.335	4.978	1.645
II	III	LS-SVM	0.996	1.383	0.977	3.311	4.660	1.927
II	Average	LS-SVM	0.996	1.315	0.984	3.817	4.407	2.502

E-nose I is the self-developed handheld e-nose system and E-nose II is the commercial e-nose Fox 4000 instrument

[a] Root-mean-square error of calibration

[b] Root-mean-square error of prediction

[c] Residual predictive deviation

[d] Absolute difference between the RMSEC and RMSEP

0.989 and RMSEP of 2.392, which were similar to the best model with full variables (LS-SVM model). However, the best model with selected variables only had 12 input variables, only 2% of the best model with full variables, showing that the variable selection was successful. The lowest RMSEP of E-nose II was also obtained by the UVE-LS-SVM model, which had 325 input variables. The best model with selected variables for E-nose II was chosen as the UVE-SPA-PLSR model, which had the lowest AB_RMSE value of 2.198 among all eight models with selected variables.

Classification of Decayed Peach Fruit

Classification Based on All Variables of e-Nose Data

Calibration of classification models was executed by PLS-DA and LS-SVM algorithms based on the matrix with the e-nose fingerprints with all variables. Tables 5 and 6 show the results of four kinds of models (two groups × two e-nose systems). When group I was considered, 94.97% of mean calibration CAR of six models (three sample sets × two calibration methods) was obtained, whereas the mean CAR of prediction-based independent prediction sets was 88.77%. Among the six models, the best model was the LS-SVM model based on sample set III, which had M_CAR of 91.58% and AB_CAR of only 0.18%. Even the "worst" model (PLS-DA model based on sample set III) had M_CAR of 89.49%, showing that E-nose I could be used to classify the decayed fruit from the healthy fruit based on its volatile substances. By analyzing Table 5, E-nose II had better results than E-nose I. In specific, the mean R_p value of E-nose II was 5.37% higher than that of E-nose I and the mean AB_CAR of E-nose II was only 41.29% of that of E-nose I. Table 6 shows the results of PLS-DA and LS-SVM classification models with full variables based on peach fruit stored at 0 °C (group II). It was found that group II had better results than group I. All 12 models (three sample sets × two calibration methods × two E-nose systems) from group II had M_CAR larger than 95%. By comparing the results of E-nose I and E-nose II, it was found that the desktop system had better results than the handheld instrument. Four of the six models of E-nose II (three sample sets × two calibration methods) had 100% CAR for both calibration and prediction.

Classification Based on Optimal Variables of e-Nose Data

Variable selection was then carried out after the calibration based on full e-nose variables to see if the CAR of e-nose

Table 3 Results of multivariate regression models between the values of storage days of peach fruit (group I) and their e-nose fingerprints with selected variables

E-nose	Calibration	Variable selection	Variable number	Calibration		Prediction			AB_RMSE [d]
				R_c	RMSEC [a]	R_p	RMSEP [b]	RPD [c]	
I	PLSR	SPA	8	0.989	0.521	0.962	0.894	1.138	3.535
I	LS-SVM	SPA	8	0.992	0.427	0.970	0.928	0.941	4.504
I	PLSR	UVE	194	0.985	0.612	0.956	0.904	1.066	3.731
I	LS-SVM	UVE	194	0.991	0.411	0.960	0.917	0.953	4.843
I	PLSR	CARS	12	0.989	0.520	0.960	0.907	1.042	4.123
I	LS-SVM	CARS	12	0.990	0.500	0.965	0.918	0.972	4.387
I	PLSR	UVE-SPA	10	0.993	0.429	0.965	0.911	1.037	4.513
I	LS-SVM	UVE-SPA	10	0.993	0.420	0.967	0.917	0.997	4.441
II	PLSR	SPA	13	0.981	0.679	0.916	1.695	2.551	1.016
II	LS-SVM	SPA	13	0.995	0.359	0.939	1.437	3.343	1.078
II	PLSR	UVE	224	0.969	0.873	0.888	2.014	2.143	1.141
II	LS-SVM	UVE	224	0.993	0.410	0.931	1.720	2.749	1.310
II	PLSR	CARS	16	0.983	0.643	0.872	2.224	2.226	1.581
II	LS-SVM	CARS	16	0.994	0.374	0.920	1.619	3.033	1.244
II	PLSR	UVE-SPA	11	0.969	0.847	0.859	2.201	2.298	1.354
II	LS-SVM	UVE-SPA	11	0.985	0.544	0.869	1.979	2.724	1.436

The statistical data was obtained by calculating the average results of three sample sets. Group I has the fruit stored at 20 °C. E-nose I is the self-developed handheld e-nose system and E-nose II is the commercial e-nose Fox 4000 instrument

[a] Root-mean-square error of calibration

[b] Root-mean-square error of prediction

[c] Residual predictive deviation

[d] Absolute difference between the RMSEC and RMSEP

models could be further improved. Table 7 shows the corresponding results of group I, when fruit was stored at 20 °C. The best model with selected variables for E-nose I was identified as the UVE-LS-SVM model, which had M_CAR of 93.99% and AB_CAR of only 2.12%. The results of SPA-LS-SVM model and CARS-LS-SVM model were also good, which had CAR of prediction higher than 90%. Most models after variable selection had better results than the models with full variables, showing that the process of variable selection was successful for E-nose I. On the other hand, the accuracy was not improved after variable selection for E-nose II. The mean CAR of prediction of eight models with selected variables and two models with full variables were 88.64 and 93.54%, respectively.

Similar to group I, fruit stored at 0 °C was also analyzed in terms of variable selection. Table 8 shows the results. When E-nose I was considered, five eighth models with selected variables had better CAR of prediction than the models with full variables. Two models had the CAR of prediction higher than 98%, namely, the CARS-PLSR model and the SPA-PLSR model. The later was identified as the best model, which had the M_CAR of 98.86% and AB_CAR of only 0.76%. The best model with selected variables for E-nose II was the CARS-PLSR model, which had same results of the models with full variables. Nevertheless, its input variables were much less (18 vs. 1440), showing that the calculation could select a few variables that included the main useful information of the full variables.

Discussion

Tables 6 and 8 show the classification results of decayed fruit in group II by E-nose I. The maximum value of CAR of prediction was associated with the SPA-PLSR model, which had 100% CAR of prediction for healthy samples and 91.67% for decayed samples. However, it is more important to identify the decay in fruit to produce fertilizer and biomass or transportation to landfill. Therefore, the UVE-LS-SVM model was considered as the best one, which had the correct answer rate of prediction of 95.83% (94.64% for healthy samples and 100.00% for decayed samples). Besides, all models had the CAR of prediction higher than 95%, and eight of ten models had the CAR of prediction for decayed samples higher than 90%. On the

Table 4 Results of multivariate regression models between the values of storage days of peach fruit (group II) and their e-nose fingerprints with selected variables

E-nose	Calibration	Variable selection	Variable number	Calibration		Prediction			AB_RMSE [d]
				R_c	RMSEC [a]	R_p	RMSEP [b]	RPD [c]	
I	PLSR	SPA	11	0.995	1.498	0.988	2.600	6.447	1.334
I	LS-SVM	SPA	11	0.999	0.550	0.987	2.725	5.974	2.175
I	PLSR	UVE	221	0.993	1.809	0.983	3.070	5.307	0.946
I	LS-SVM	UVE	221	1.000	0.281	0.994	1.979	9.283	1.697
I	PLSR	CARS	19	0.999	0.686	0.979	3.655	4.595	2.969
I	LS-SVM	CARS	19	0.999	0.512	0.989	2.552	6.533	2.041
I	PLSR	UVE-SPA	12	0.996	1.399	0.979	3.664	4.626	2.265
I	LS-SVM	UVE-SPA	12	0.999	0.622	0.989	2.392	7.951	1.770
II	PLSR	SPA	9	0.987	2.483	0.970	5.229	3.344	2.745
II	LS-SVM	SPA	9	0.993	1.822	0.977	4.756	3.681	2.933
II	PLSR	UVE	325	0.991	2.089	0.973	4.520	3.915	2.430
II	LS-SVM	UVE	325	0.995	1.414	0.983	4.136	4.141	2.721
II	PLSR	CARS	17	0.996	1.319	0.971	4.863	3.542	3.544
II	LS-SVM	CARS	17	0.996	1.332	0.977	4.701	3.943	3.369
II	PLSR	UVE-SPA	10	0.990	2.164	0.975	4.362	3.910	2.198
II	LS-SVM	UVE-SPA	10	0.994	1.695	0.977	4.433	3.757	2.737

The statistical data was obtained by calculating the average results of three sample sets. Group II has the fruit stored at 0 °C. E-nose I is the self-developed handheld e-nose system and E-nose II is the commercial e-nose Fox 4000 instrument

[a] Root-mean-square error of calibration

[b] Root-mean-square error of prediction

[c] Residual predictive deviation

[d] Absolute difference between the RMSEC and RMSEP

other hand, regression models were established to evaluate the feasibility of prediction the storage days of peach fruit. Tables 2 and 4 show the results. The best model was the UVE-LS-SVM model, which had RPD of 9.283. There were only two of ten models having RPD less than five. The above results confirmed the potential of using the self-developed handheld e-nose system to non-destructively classify the decayed peach fruit and predict their storage days.

E-nose is developed to mimic the human sense of smell. Non-selectively, sensors in E-nose interact with odor molecules distinguishing simple or complex odors to assess food quality and safety. Metal oxide semiconductors (MOS) are commonly used sensors of E-nose. MOS sensors have the advantages of sensitive to various chemicals, quick response, short recovery time, low cost, long life of sensors, good reproducibility, and convenient replacement (Sanaeifar et al. 2017). MOS based on e-nose systems have been used for food quality monitoring, such as milk, wines, tea, coffee, meat, and fish (Loutfi et al. 2015). Besides, there are several e-nose applications for fruit identification, ripeness, and quality grading (Baietto and Wilson 2015). Nevertheless, most of previous works about using e-nose to predict quality of peach and other fruits were based on destructive sampling to get fruit pulp (Lebrun et al. 2008; Defilippi et al. 2009; Longobardi et al. 2015). The destructive sampling will obtain more volatile substances, making the detection more easy. However, the sampling of volatile substances by destructive, time-consuming, and laborious ways is not acceptable for fruit supply chain in practice. The data acquisition of volatile substances of fruit should be non-destructive, in real-time, and automatic during supply chain. On the contrary, non-destructive sampling will get less volatile substances, as the fruit pulp is covered by pericarp. Therefore, the non-destructive sampling for e-nose analysis is difficult than destructive sampling. On the other hand, the e-nose data acquisitions in previous works were mostly carried out at the room temperature. Nevertheless, the data acquisition of volatile substances of fruit in cold environment should be evaluated, as fruit supply chain is generally in the cold chain close to 0 °C. Refrigeration, which is a popular way during cold chain and in home kitchens, could greatly inhibit the volatile production of fruit (Wang et al. 2015). As shown in Fig. 1, it is clear that the values of samples stored at 20 °C were higher than those at 0 °C. For E-nose I, the scale for group I

Table 5 Results of classification models between healthy and decayed peach fruit (group I) and their e-nose fingerprints with full variables. Group I has the fruit stored at 20 °C

E-nose	Sample set	Calibration	CAR[a] of calibration (%)			CAR of prediction (%)			M_CAR [b] (%)	AB_CAR [c] (%)
			All	Healthy	Decayed	All	Healthy	Decayed		
I	I	PLS-DA	93.18	93.33	94.44	91.30	92.86	88.89	92.24	1.88
I	II	PLS-DA	97.87	96.55	100.00	87.50	93.33	77.78	92.69	10.37
I	III	PLS-DA	91.49	100.00	77.78	87.50	93.33	77.78	89.49	3.99
I	Average	PLS-DA	94.18	96.63	90.74	88.77	93.17	81.48	91.47	5.41
I	I	LS-SVM	97.92	100.00	94.44	91.30	92.86	88.89	94.61	6.61
I	II	LS-SVM	97.87	96.55	100.00	83.33	77.78	100.00	90.60	14.54
I	III	LS-SVM	91.49	100.00	77.78	91.67	87.50	100.00	91.58	0.18
I	Average	LS-SVM	95.76	98.85	90.74	88.77	86.04	96.30	92.26	6.99
II	I	PLS-DA	100.00	100.00	100.00	82.61	78.57	88.89	91.30	17.39
II	II	PLS-DA	95.74	100.00	89.47	100.00	100.00	100.00	97.87	4.26
II	III	PLS-DA	91.49	93.10	88.89	100.00	100.00	100.00	95.74	8.51
II	Average	PLS-DA	95.74	97.70	92.79	94.20	92.86	96.30	94.97	1.54
II	I	LS-SVM	100.00	100.00	100.00	86.96	85.71	88.89	93.48	13.04
II	II	LS-SVM	93.62	96.43	89.47	95.83	100.00	88.89	94.73	2.22
II	III	LS-SVM	95.74	100.00	88.89	95.83	100.00	90.00	95.79	0.09
II	Average	LS-SVM	96.45	98.81	92.79	92.87	95.24	89.26	94.66	3.58

E-nose I is the self-developed handheld e-nose system and E-nose II is the commercial e-nose Fox 4000 instrument

[a] Correct answer rate

[b] Mean value of the CAR of calibration and prediction

[c] Absolute difference between the CAR of calibration and prediction

(20 °C) was from 0 to 800, whereas the scale for group II (0 °C) was from 0 to 250. For E-nose II, the scale for group I (20 °C) was from 0 to 70,000, whereas the scale for group II (0 °C) was from 0 to 13,500.Therefore, the e-nose sampling at the cold temperature close to 0 °C got less volatile substances, and was more difficult for the decay detection than the e-nose sampling at the room temperature. In addition, the e-nose instruments used in these works are desktop. However, desktop instruments are inconvenient to be installed and operating in refrigerated storage and van/truck. Handheld e-nose instruments are required to detect the decay in fruit during supply chain. Compared with previous works on investigating fruit quality using e-nose, there are some improvements and novelty of this work, including non-destructive e-nose sampling on intact whole fruit, e-nose sampling at the cold temperature close to 0 °C, and using a self-made handheld e-nose instrument. Guohua et al. (2012) predicted peach freshness based on electronic nose and gas chromatography-mass spectrometer techniques. Nevertheless, peach fruit was destructively cut into samples for e-nose measurement in their work. Rizzolo et al. (2013) evaluated quality evolution during a cold storage of 4 weeks by e-nose and static headspace gas chromatography. Samples were destructively sliced, thawing at room temperature for 30 min, and measured in a room kept at 20 ± 1 °C. Pan et al. (2014) classified strawberry with four types of fungal infection and obtained 96.6% accuracy. However, the e-nose measurement in their work was carried out at room temperature (24 °C). The non-destructive e-nose sampling on intact whole fruit at the cold temperature close to 0 °C in this work was more difficult to get enough volatile substances for further data analysis than the destructive e-nose sampling on fruit pulp at the room temperature in previous works.

A desktop e-nose system (E-nose II) was considered to evaluate the performance of the handheld e-nose system (E-nose I). In general, E-nose I had equal capability to E-nose II. Both of the best models of two systems had M_CAR higher than 95% for the classification of decayed samples during cold storage (group II). Moreover, E-nose I had better prediction of storage days than E-nose II during cold storage (group II). The above results indicate that the self-developed handheld e-nose system can be used to replace the commercial e-nose Fox 4000 instrument to detect decay in peach fruit during cold storage. On the other hand, when fruit stored at 20 °C (group I) was considered, E-nose I had also better prediction of storage days than E-nose II. The mean RMSEP values

Table 6 Results of classification models between healthy and decayed peach fruit (group II) and their e-nose fingerprints with full variables

E-nose	Sample set	Calibration	CAR [a] of calibration (%)			CAR of prediction (%)			M_CAR [b] (%)	AB_CAR [c] (%)
			All	Healthy	Decayed	All	Healthy	Decayed		
I	I	PLS-DA	97.73	97.30	100.00	95.24	94.44	100.00	96.48	2.49
I	II	PLS-DA	97.73	97.22	100.00	95.45	94.74	100.00	96.59	2.27
I	III	PLS-DA	100.00	100.00	100.00	95.45	100.00	75.00	97.73	4.55
I	Average	PLS-DA	98.48	98.17	100.00	95.38	96.39	91.67	96.93	3.10
I	I	LS-SVM	97.73	97.30	100.00	95.24	94.44	100.00	96.48	2.49
I	II	LS-SVM	97.73	97.22	100.00	95.45	100.00	75.00	96.59	2.27
I	III	LS-SVM	100.00	100.00	100.00	95.45	94.74	100.00	97.73	4.55
I	Average	LS-SVM	98.48	98.17	100.00	95.38	96.39	91.67	96.93	3.10
II	I	PLS-DA	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
II	II	PLS-DA	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
II	III	PLS-DA	100.00	100.00	100.00	95.83	100.00	66.67	97.92	4.17
II	Average	PLS-DA	100.00	100.00	100.00	98.61	100.00	88.89	99.31	1.39
II	I	LS-SVM	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
II	II	LS-SVM	100.00	100.00	100.00	100.00	100.00	100.00	100.00	0.00
II	III	LS-SVM	100.00	100.00	100.00	95.83	95.24	100.00	97.92	4.17
II	Average	LS-SVM	100.00	100.00	100.00	98.61	98.41	100.00	99.31	1.39

Group II has the fruit stored at 0 °C. E-nose I is the self-developed handheld e-nose system and E-nose II is the commercial e-nose Fox 4000 instrument

[a] Correct answer rate

[b] Mean value of the CAR of calibration and prediction

[c] Absolute difference between the CAR of calibration and prediction

of tem models (two models with full variables and eight models with selected variables) were 1.050 and 1.844 for E-nose I and II, respectively. In addition, by analyzing the polar plots in Fig. 1, it was found that the response values of samples with different storage days measured by E-nose I showed more difference than E-nose II. However, although the samples with different storage days had similar polar patterns for E-nose II, the regression and classification models of E-nose II also obtained good results, showing that chemometric methods had good abilities to mine the useful information hidden inside e-nose data.

In general, cold environment inhibited the volatile production of fruit. Samples stored at 20 °C (group I) were also analyzed as a comparison to evaluate the performances of E-nose I and II. Because the range and standard deviation of storage days in group II was larger than group I, making the models of group II had higher R_c, R_p, and RPD values than group I. However, actually, the mean RMSEP values of ten models (two models with full variables and eight models with selected variables) to predict storage days for group II (2.767 for E-nose I and 4.543 for E-nose II) were much larger than those of group I (1.050 for E-nose I and 1.844 for E-nose II), showing that cold environment made the prediction of storage days of peach fruit based on e-nose data difficult. On the other hand, the classification of decayed fruit had better results for group II than group I. The mean CAR values of prediction of ten models for fruit stored at 0 °C (group II) were 96.45% for E-nose I and 96.94% for E-nose II, whereas those for fruit stored at 20 °C (group I) were 89.28% for E-nose I and 89.62% for E-nose II. The above results show that e-nose technique can be used to detect decay in peach fruit during logistics at both 0 and 20 °C.

Multivariate calibration is an important step to establish relationships between e-nose signal of the target samples and their attributes with explanatory or predictive purposes. Two multivariate methods of PLSR and LS-SVM were used to establish quantitative relationships between the e-nose data of peach fruit and their storage days. In general, the performances of LS-SVM models were better than PLSR models, especially for group II. The mean RMSEP values for group II were 3.162 vs. 2.372 for E-nose I and 4.718 vs. 4.368 for E-nose II. Robustness of two methods was similar by analyzing AB_RMSE. On the other hand, PLS-DA and LS-SVM were used to build classification models to detect decay in fruit. In general, two methods showed similar capabilities of establishing classification models, in the aspects of both accuracy and robustness. PLS-DA had poorer capability to detect decay in fruit than LS-SVM, except

Table 7 Results of classification models between healthy and decayed peach fruit (group I) and their e-nose fingerprints with selected variables

E-nose	Calibration	Variable selection	Variable number	CAR [a] of calibration (%)			CAR of prediction (%)			M_CAR [b] (%)	AB_CAR [c] (%)
				All	Healthy	Decayed	All	Healthy	Decayed		
I	PLS	SPA	7	95.65	97.74	92.59	88.71	93.17	81.48	92.18	6.94
I	LS-SVM	SPA	7	98.61	98.89	98.15	91.55	89.65	96.30	95.08	7.07
I	PLS	UVE	83	94.94	97.74	90.74	85.87	90.79	77.78	90.40	9.07
I	LS-SVM	UVE	83	95.05	98.85	88.89	92.93	93.92	92.96	93.99	2.12
I	PLS	CARS	6	97.07	98.89	94.44	87.20	90.63	81.48	92.13	9.87
I	LS-SVM	CARS	6	95.79	98.89	90.74	91.49	91.83	92.59	93.64	4.30
I	PLS	UVE-SPA	8	96.41	98.85	92.59	88.77	93.17	81.48	92.59	7.64
I	LS-SVM	UVE-SPA	8	97.89	100.00	94.44	88.77	95.40	77.78	93.33	9.12
II	PLS	SPA	8	97.16	97.70	96.39	84.42	83.49	85.93	90.79	12.74
II	LS-SVM	SPA	8	98.58	98.85	98.15	91.49	95.24	85.93	95.03	7.10
II	PLS	UVE	260	95.04	95.32	94.54	85.81	85.71	85.93	90.42	9.23
II	LS-SVM	UVE	260	97.87	98.85	96.39	90.10	92.86	85.93	93.98	7.78
II	PLS	CARS	7	95.74	95.32	96.39	88.59	88.10	89.26	92.17	7.16
II	LS-SVM	CARS	7	95.04	95.32	94.54	88.53	88.10	89.63	91.78	6.51
II	PLS	UVE-SPA	5	96.45	96.51	96.39	90.10	90.63	89.26	93.28	6.36
II	LS-SVM	UVE-SPA	5	97.16	98.85	94.64	90.10	92.86	85.93	93.63	7.07

The statistical data was obtained by calculating the average results of three sample sets. Group I has the fruit stored at 20 °C. E-nose I is the self-developed handheld e-nose system and E-nose II is the commercial e-nose Fox 4000 instrument

[a] Correct answer rate

[b] Mean value of the CAR of calibration and prediction

[c] Absolute difference between the CAR of calibration and prediction

for the case when E-nose I was used to analyze samples in group I.

For variable selection, UVE was better than other methods in most cases, but it also obtained much more variables. On the other hand, variable selection improved the results of E-nose I but had no obvious improvement for E-nose II. However, the input variables for model calibration were much reduced after variable selection, showing that the variable selection was efficient and can reduce most irrelevant variables.

The selection of different samples for calibration and prediction can affect the performances of the established models. In this work, three sample sets were considered. Each set had two thirds of samples for model calibration, and remaining one third of samples for independent prediction. After all three sample sets were used once for model calibration and prediction, all samples had been selected for prediction one time. By comparing the results of different sample sets, in general, they obtained similar results, and there was no much difference among them. Only in a few cases, the difference was large, and most of them were about the prediction of storage days using E-nose II (Tables 1 and 2). The above results show that selecting different samples for model calibration does have some influence on models' performances. Therefore, to reduce the influence of model selection and to make the results more certain, it is important to consider different sample sets for model calibration for e-nose technique.

There were some other issues for this primary study to resolve before practical applications. First, only two storage temperatures of 0 and 20 °C were considered in this work. In future works, more storage environment should be considered, like different temperature, different modified atmosphere, and different pretreatments. Second, the storage environments were constant in this work. The influence of environment variation on e-nose detection should be evaluated. Thirdly, the mechanism of why e-nose technique can detect the decay in fruit should be further explored. It is important to find the main volatile substances related to fruit decay. The identification of specific volatile substances will be helpful to design more targeted e-nose systems. In addition, a larger number of samples from different varieties, years, habitats, orchards, and climates should be acquired in future works to make the e-nose technique much available for the detection of decay in peach fruit in practice. Nevertheless, the results of this study show that the non-destructive detection of decay in peach fruit was feasible by e-nose technology. Considering that fruit is commonly stored inside external

Table 8 Results of classification models between healthy and decayed peach fruit (group II) and their e-nose fingerprints with selected variables

E-nose	Calibration	Variable selection	Variable number	CAR [a] of calibration (%)			CAR of prediction (%)			M_CAR [b] (%)	AB_CAR [c] (%)
				All	Healthy	Decayed	All	Healthy	Decayed		
I	PLS	SPA	3	99.24	100.00	95.24	98.48	100.00	91.67	98.86	0.76
I	LS-SVM	SPA	3	100.00	100.00	100.00	96.83	100.00	77.78	98.41	3.17
I	PLS	UVE	166	99.24	99.10	100.00	95.38	96.39	91.67	97.31	3.86
I	LS-SVM	UVE	166	98.48	98.17	100.00	95.38	94.64	100.00	96.93	3.10
I	PLS	CARS	6	100.00	100.00	100.00	98.48	100.00	91.67	99.24	1.52
I	LS-SVM	CARS	6	100.00	100.00	100.00	96.83	100.00	77.78	98.41	3.17
I	PLS	UVE-SPA	5	97.73	97.27	100.00	96.97	98.25	91.67	97.35	0.76
I	LS-SVM	UVE-SPA	5	97.73	97.27	100.00	95.38	96.39	91.67	96.55	2.34
II	PLS	SPA	7	100.00	100.00	100.00	97.22	100.00	77.78	98.61	2.78
II	LS-SVM	SPA	7	100.00	100.00	100.00	97.22	100.00	77.78	98.61	2.78
II	PLS	UVE	341	98.58	99.19	94.44	95.83	98.41	77.78	97.21	2.75
II	LS-SVM	UVE	341	100.00	100.00	100.00	95.83	96.83	88.89	97.92	4.17
II	PLS	CARS	18	100.00	100.00	100.00	98.61	98.41	100.00	99.31	1.39
II	LS-SVM	CARS	18	100.00	100.00	100.00	97.22	98.41	88.89	98.61	2.78
II	PLS	UVE-SPA	7	100.00	100.00	100.00	94.38	98.41	66.67	97.19	5.62
II	LS-SVM	UVE-SPA	7	99.29	100.00	94.44	95.83	98.41	77.78	97.56	3.46

The statistical data was obtained by calculating the average results of three sample sets. Group II has the fruit stored at 0 °C. E-nose I is the self-developed handheld e-nose system and E-nose II is the commercial e-nose Fox 4000 instrument

[a] Correct answer rate

[b] Mean value of the CAR of calibration and prediction

[c] Absolute difference between the CAR of calibration and prediction

packages during cold chain, the detection of decay in fruit based on its volatile substances would help distributors to recycle decayed fruit in time for reverse supply chain.

Conclusions

This work investigated the potential of a self-developed handheld e-nose instrument to non-destructively detect decay in peach fruit during cold storage. The obtained results show that the best model had the CAR of prediction of 95.83% (94.64% for healthy samples and 100.00% for decayed samples). The results of this study indicate that the self-developed handheld e-nose system hold the advantages of this method to be a simple and non-destructive tool to detect decay in peach fruit at the cold environment. Regression models were also established to predict the storage days of peach fruit during cold chain, and the best model of the handheld e-nose instrument had RPD of 9.283. The performance of the handheld e-nose instrument was similar to the desktop e-nose system, when either samples stored at 20 or 0 °C were considered. As the first study into the non-invasive detection of decay in peach fruit during cold storage, the results of this work are very promising and will promote more effort in detection of decayed or infected fruit and vegetables.

Acknowledgements This study was funded by Project of the Science and Technology Department of Zhejiang Province (2016C04001).

Compliance with Ethical Standards

Conflict of Interest Xun Wei declares that he/she has no conflict of interest. Yuchen Zhang declares that he/she has no conflict of interest. Di Wu declares that he/she has no conflict of interest. Zhenbo Wei declares that he/she has no conflict of interest. Kunsong Chen declares that he/she has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Not applicable.

References

Baietto M, Wilson AD (2015) Electronic-nose applications for fruit identification, ripeness and quality grading. Sensors 15(1):899–931

Besada C, Salvador A, Sdiri S, Gil R, Granell A (2013) A combination of physiological and chemometrics analyses reveals the main associations between quality and ripening traits and volatiles in two loquat cultivars. Metabolomics 9(2):324–336

Chen JL, Wu JH, Wang Q, Deng H, Hu XS (2006) Changes in the volatile compounds and chemical and physical properties of Kuerle fragrant pear (Pyrus serotina Reld) during storage. J Agric Food Chem 54(23):8842–8847

Defilippi B, San Juan W, Valdes H, Moya-León M, Infante R, Campos-Vargas R (2009) The aroma development during storage of Castlebrite apricots as evaluated by gas chromatography, electronic nose, and sensory analysis. Postharvest Biol Technol 51(2):212–219

Fallik E, Tuvia-Alkalai S, Feng X, Lurie S (2001) Ripening characterisation and decay development of stored apples after a short pre-storage hot water rinsing and brushing. Innovative Food Sci Emerg Technol 2(2):127–132

FAO, (2011). Global food losses and food waste: extent, causes and prevention. In: Gustavsson, Cederberg, Sonesson, van Otterdijk, Meybeck (eds). Rome

Guohua H, Yuling W, Dandan Y, Wenwen D, Linshan Z, Lvye W (2012) Study of peach freshness predictive method based on electronic nose. Food Control 28(1):25–32

Hernández GA, Wang J, Hu G, García PA (2007) Discrimination of storage shelf-life for mandarin by electronic nose technique. LWT-Food Sci Technol 40(4):681–689

Horvat R, Chapman Jr G, Robertson J, Meredith F, Scorza R, Callahan A, Morgens P (1990) Comparison of the volatile compounds from several commercial peach cultivars. J Agric Food Chem 38(1):234–237

Huang L, Liu H, Zhang B, Wu D (2015) Application of electronic nose with multivariate analysis and sensor selection for botanical origin identification and quality determination of honey. Food Bioprocess Technol 8(2):359–370

Huang L, Meng L, Zhu N, Wu D (2017a) A primary study on forecasting the days before decay of peach fruit using near-infrared spectroscopy and electronic nose techniques. Postharvest Biol Technol 133: 104–112

Huang L, Zhou Y, Meng L, Wu D, He Y (2017b) Comparison of different CCD detectors and chemometrics for predicting total anthocyanin content and antioxidant activity of mulberry fruit using visible and near infrared hyperspectral imaging technique. Food Chem 224:1–10

Hui G, Jin J, Deng S, Ye X, Zhao M, Wang M, Ye D (2015) Winter jujube (Zizyphus jujuba mill.) quality forecasting method based on electronic nose. Food Chem 170:484–491

Kraujalytė V, Venskutonis PR, Pukalskas A, Česonienė L, Daubaras R (2015) Antioxidant properties, phenolic composition and potentiometric sensor array evaluation of commercial and new blueberry (Vaccinium corymbosum) and bog blueberry (Vaccinium uliginosum) genotypes. Food Chem 188:583–590

Lebrun M, Plotto A, Goodner K, Ducamp M-N, Baldwin E (2008) Discrimination of mango fruit maturity by volatiles using the electronic nose and gas chromatography. Postharvest Biol Technol 48(1):122–131

Li Q, Yu X, Xu L, Gao J-M (2017) Novel method for the producing area identification of Zhongning goji berries by electronic nose. Food Chem 221:1113–1119

Longobardi F, Casiello G, Ventrella A, Mazzilli V, Nardelli A, Sacco D, Catucci L, Agostiano A (2015) Electronic nose and isotope ratio mass spectrometry in combination with chemometrics for the characterization of the geographical origin of Italian sweet cherries. Food Chem 170:90–96

Loutfi A, Coradeschi S, Mani GK, Shankar P, Rayappan JBB (2015) Electronic noses for food quality: a review. J Food Eng 144:103–111

Mayuoni-Kirshinbaum L, Daus A, Porat R (2013) Changes in sensory quality and aroma volatile composition during prolonged storage of 'Wonderful'pomegranate fruit. Int J Food Sci Technol 48(8):1569–1578

Migliori CA, Salvati L, Di Cesare LF, Scalzo RL, Parisi M (2017) Effects of preharvest applications of natural antimicrobial products on tomato fruit decay and quality during long-term storage. Sci Hortic 222:193–202

Nigro F, Ippolito A, Lattanzio V, Di Venere D, Salerno M (2000) Effect of ultraviolet-C light on postharvest decay of strawberry. J Plant Pathol:29–37

OECD (2014) Market and trade impacts of food loss and waste reduction. In: Okawa (ed) . OECD Publishing, Paris

Pan L, Zhang W, Zhu N, Mao S, Tu K (2014) Early detection and classification of pathogenic fungal disease in post-harvest strawberry fruit by electronic nose and gas chromatography–mass spectrometry. Food Res Int 62:162–168

Pokharel S, Mutha A (2009) Perspectives in reverse logistics: a review. Resour Conserv Recycl 53(4):175–182

Rizzolo A, Bianchi G, Vanoli M, Lurie S, Spinelli L, Torricelli A (2013) Electronic nose to detect volatile compound profile and quality changes in "spring Belle" peach (*Prunus persica* L.) during cold storage in relation to fruit optical properties measured by time-resolved reflectance spectroscopy. J Agric Food Chem 61(8): 1671–1685

Sanaeifar A, Mohtasebi SS, Ghasemi-Varnamkhasti M, Ahmadi H (2016) Application of MOS based electronic nose for the prediction of banana quality properties. Measurement 82:105–114

Sanaeifar A, ZakiDizaji H, Jafari A, de la Guardia M (2017) Early detection of contamination and defect in foodstuffs by electronic nose: a review. TrAC-Trends Anal Chem

USDA (2014) The estimated amount, value, and calories of postharvest food losses at the retail and consumer levels in the United States. In: Buzby, Farah-Wells, Hyman (eds) . US Department of Agriculture, Economic Research Service

Wang L, Baldwin EA, Zhao W, Plotto A, Sun X, Wang Z, Brecht JK, Bai J, Yu Z (2015) Suppression of volatile production in tomato fruit exposed to chilling temperature and alleviation of chilling injury by a pre-chilling heat treatment. LWT-Food Sci Technol 62(1):115–121

Wei Z, Xiao X, Wang J, Wang H (2017) Identification of the Rice wines with different marked ages by electronic nose coupled with smartphone and cloud storage platform. Sensors 17(11):2500

Wu D, He Y (2014) Potential of spectroscopic techniques and chemometric analysis for rapid measurement of docosahexaenoic acid and eicosapentaenoic acid in algal oil. Food Chem 158:93–100

Wu D, Sun D-W (2013a) Advanced applications of hyperspectral imaging technology for food quality and safety analysis and assessment: a review - part I: fundamentals. Innovative Food Sci Emerg Technol 19:1–14

Wu D, Sun D-W (2013b) Advanced applications of hyperspectral imaging technology for food quality and safety analysis and assessment: a review - part II: applications. Innovative Food Sci Emerg Technol 19:15–28

Wu D, Sun D-W (2013c) Application of visible and near infrared hyperspectral imaging for non-invasively measuring distribution of water-holding capacity in salmon flesh. Talanta 116:266–276

Wu D, Sun D-W (2013d) Potential of time series-hyperspectral imaging (TS-HSI) for non-invasive determination of microbial spoilage of salmon flesh. Talanta 111:39–46

Wu D, He Y, Feng SJ, Sun D-W (2008) Study on infrared spectroscopy technique for fast measurement of protein content in milk powder based on LS-SVM. J Food Eng 84(1):124–131

Wu D, He Y, Nie P, Cao F, Bao Y (2010) Hybrid variable selection in visible and near-infrared spectral analysis for non-invasive quality determination of grape juice. Anal Chim Acta 659(1–2):229–237

Wu D, Sun D-W, He Y (2012) Application of long-wave near infrared hyperspectral imaging for measurement of color distribution in salmon fillet. Innovative Food Sci Emerg Technol 16:361–372

Wu D, Chen X, Cao F, Sun D-W, He Y, Jiang Y (2014a) Comparison of infrared spectroscopy and nuclear magnetic resonance techniques in tandem with multivariable selection for rapid determination of ω-3 polyunsaturated fatty acids in fish oil. Food Bioproc Technol 7(6): 1555–1569

Wu D, Sun D-W, He Y (2014b) Novel non-invasive distribution measurement of texture profile analysis (TPA) in salmon fillet by using visible and near infrared hyperspectral imaging. Food Chem 145: 417–426

Xu S, Lü E, Lu H, Zhou Z, Wang Y, Yang J, Wang Y (2016) Quality detection of litchi stored in different environments using an electronic nose. Sensors 16(6):852

Yang Z, Cao S, Cai Y, Zheng Y (2011) Combination of salicylic acid and ultrasound to control postharvest blue mold caused by Penicillium expansum in peach fruit. Innovative Food Sci Emerg Technol 12(3): 310–314

Yi J, Kebede BT, Grauwet T, Van Loey A, Hu X, Hendrickx M (2016) A multivariate approach into physicochemical, biochemical and aromatic quality changes of purée based on Hayward kiwifruit during the final phase of ripening. Postharvest Biol Technol 117:206–216

Yu Q, Chen Q, Chen Z, Xu H, Fu M, Li S, Wang H, Xu M (2012) Activating defense responses and reducing postharvest blue mold decay caused by Penicillium expansum in peach fruit by yeast saccharide. Postharvest Biol Technol 74(74):100–107

Zhang H, Wang J, Ye S (2008) Prediction of soluble solids content, firmness and pH of pear by signals of electronic nose sensors. Anal Chim Acta 606(1):112–118

Zhang W, Pan L, Zhao X, Tu K (2016) A study on soluble solids content assessment using electronic nose: persimmon fruit picked on different dates. Int J Food Prop 19(1):53–62

Zhu N, Lin M, Nie Y, Wu D, Chen K (2016) Study on the quantitative measurement of firmness distribution maps at the pixel level inside peach pulp. Comput Electron Agric 130:48–56

Zhu N, Huang W, Wu D, Chen K, He Y (2017a) Quantitative visualization of pectin distribution maps of peach fruits. Sci Rep 7(1):9275

Zhu N, Nie Y, Wu D, He Y, Chen K (2017b) Feasibility study on quantitative pixel-level visualization of internal quality at different cross-sections inside postharvest loquat fruit. Food Anal Method 10:287–297