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FAST DETERMINATION OF LYCOPENE CONTENT AND SOLUBLE SOLID CONTENT OF CHERRY TOMATOES USING METAL OXIDE SENSORS BASED ELECTRONIC NOSE

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Lycopene content (LC) and soluble solid content (SSC) are important quality indicators for cherry tomatoes. This study attempted simultaneous analysis of inner quality of cherry tomato by Electronic nose (E-nose) using multivariate analysis. E-nose was used for data acquisition, the response signals were regressed by multiple linear regression (MLR) and partial least square regression (PLS) to build predictive models. The performances of the predictive models were tested according to root mean square and correlation coefficient (R^2) in the training set and prediction set. The results showed that MLR models were superior to PLS model, with higher value of R^2 and lower values of for RMSE firmness, pH, SSC, and LC. Together with MLR, E-nose could be used to obtain firmness, pH, soluble solid and lycopene contents in cherry tomatoes.

Keywords: electronic nose, cherry tomato, multivariate analysis, lycopene content, soluble solid content

Compared with tomatoes, cherry tomatoes are characterized by higher dry matter and soluble solids levels. Ranked first as source of lycopene (71.6%) and second source of vitamin C (12.0%) (GARCÍA-CLOSAS et al., 2004), cherry tomato is one of the most important types for fresh consumption with many benefits. Lycopene has been associated with the prevention of cardiovascular disease (MORDENTE et al., 2011) and different types of cancer, such as breast, colon, and prostate.

There were many studies on the quality of tomato, studies dealt with organoleptic quality and nutritional properties (TEE & LIM, 1991; RAFFO et al., 2002, 2006) were reported. However, few studies were conducnted by nondestructive methods. Methods for determining the carotenoid content (TEE & LIM, 1991) require extraction of the analyte as well as other cleanup steps, and methods for detecting pH and soluble solid content (SSC) are all destructive, slow, and not suited for automation, even though they have been successfully used for studies of fruit quality. Rapid and non-destructive quantification of inner quality of cherry tomato is mostly done by near infrared spectroscopy (NIR) methods, but the overall odour of volatile components is seldom studied.

Sensory techniques provide information for overall aroma perception, olfactory thresholds, and consumer acceptability, whereas instrumental analyses identify and quantify single aroma volatiles. The most common instrumental techniques used to evaluate the aroma of fruit and vegetables are headspace or dynamic headspace gas chromatography coupled

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with mass spectrometry (GC-MS) (KRUMBEIN et al., 2004; BERNA et al., 2005), and more recently, solid phase micro-extraction sampling followed by GC-MS (SERRANO et al., 2009). But they are time consuming, expensive, needing experienced workers. Electronic nose (E-nose) is a new tool used in aroma perception. Comprising an array of sensors with partial specificity, an appropriate pattern recognition system, E-nose is capable of recognising simple or complex odours. With the advantages of simple and fast approach, non-damage analysis, no need for sample preparation makes it one of the most powerful and widely used sampling tools for collecting volatile compounds. Although E-nose does not allow the identification of compounds and has a high detection limit in comparison with GC-MS, it has been successfully used in processing monitoring, shelf-life investigation, freshness evaluation, and authenticity assessment in a wide range of food products, including fruit and their products.

Volatile compounds could be used as cues to reflect the ripeness and nutritional quality of fruit. The possibility of using E-nose to detect the volatiles emitted by tomato was investigated for aims of reflecting its ripeness and nutritional quality. In the previous works, E-nose have shown its ability in the ripeness monitoring (GÓMEZ et al., 2006), quality assessment (BERNA et al., 2005), shelf-life measurements (BERNA et al., 2004a, b), prediction of quality indices (GÓMEZ et al., 2008), freshness prediction (MESSINA et al., 2012), and microbiological quality control (CONCINA et al., 2009) for tomatoes. However, most of the researches mainly focused on the qualitative discrimination and classification of fruit, with few studies performed on the correlation between quality indices and E-nose responses. In this study, the variations of internal structure and chemical-physical characteristics of cherry tomatoes were analysed by destructive methods and correlated with E-nose responses.

The objective of this experiment is to evaluate the potential of E-nose for fast qualitative and quantitative determination of odours in cherry tomato of different maturities. The responses of E-nose will be compared with quality indices. Then, the ability of E-nose to predict the chemical composition and maturity of cherry tomato will be investigated by multivariate statistical techniques.

1. Material and methods

1.1. Materials

The No. 2 of Culture 3122 cherry tomatoes were obtained from “Hangzhou Chunyi vegetable Professional Cooperatives” in Hangzhou, China. One hundred cherry tomatoes per mature stages (USDA, 1997) were hand-picked, subsequently transported to laboratory, and inspected to ensure that they were uniform, non-damaged, and not attacked by worm. All cherry tomatoes were washed with clean water and dried by towel, then evaluated at the day of picking.

1.2. The E-nose and detection procedures

A PEN2 E-nose (Airsense Corporation, Germany) was used to obtain the odour of samples. The basic system, described in previous researches (ZHANG et al., 2007), consisted of a sampling apparatus, a detector unit containing the sensor array, and pattern recognition software (Win Muster v.1.6). The sensor array was composed of 10 different metal oxide sensors. Each sensor has a certain degree of affinity towards specific chemical or volatile compounds. The nomenclature and characteristics of the sensors have been reported (ZHOU & WANG, 2011).

Five intact cherry tomatoes of similar size were randomly picked and placed in a beaker of 500 ml. The beaker was sealed by smell-less plastic film for 40 min at 25±3 °C to reach a stable headspace. The E-nose system is stabilized by flushing dry clean nitrogen for more than 30 min before samples were measured. The sample headspace was pumped over the sensors with flow rate of 200 ml min^{-1} for 70 s at an interval of 1 s, the responses of sensors were acquired by Win muster. After one sample was detected, the sensors were cleaned with dry clean nitrogen for 60 s. Eighteen repetitions were performed for each maturity.

1.3. Measurement of quality indices

1.3.1. Fruit firmness. The fruit firmness was obtained by method described by ZHANG (ZHANG et al., 2012) by using Universal Testing Machine (Model 5543 Single Column, USA). The tests were conducted with an indenter of 6.6 mm in diameter, the loading rate of the crosshead was 5 mm min^{-1}. The firmness was the mean of "the maximum force" for three points.

1.3.2. pH and soluble solid content (SSC). The undiluted cherry tomato juice was used to measure SSC by digital refractometer (WYT-J 0-32%, China) and pH by a pH meter (PHS-4CT, China) with three repetitions for each mature stage.

1.3.3. Lycopene content (LC). A sample of 0.2 g of homogenized cherry tomato juice were placed in 10 ml flask and dehydrated with methanol to wipe the yellow pigment. Then the lycopene was extracted with methylbenzene and determined at 485 nm in a Pharmacia Ultrospec 4000 UV-visible spectrophotometer, using red dye Sudan I as standard solutions. Three repetitions for each mature stage were measured.

1.4. Data analysis

Tukey's test was performed to find differences for LC, SSC, pH, and firmness of cherry tomatoes with different maturity. The ability to discriminate cherry tomato maturities was studied by principle component analysis (PCA) and canonical discriminate analysis (CDA). Multiple linear regression (MLR) and partial least square regression (PLS) were performed to study the predictive capacity of E-nose for LC, SSC, pH, and firmness. SAS v8 (SAS Institute Inc., Gary, USA) was employed.

2. Results and discussion

2.1. Quality indices

The results of Tukey's test (α<0.05) for cherry tomatoes with different maturities are shown in Table 1. With the ripeness of cherry tomatoes, the SSC increased from 4.57 to 7.1 (55.36%), pH increased from 3.93 to 4.16, firmness fell from 17.73 to 7.28, with a whole decrease of 58.94% from green-ripened stage (GRS) to red-ripened stage (RRS). Cherry tomatoes of RRS were optimum for eating, while cherry tomatoes of turning colour stage (TCS) were optimum for transportation and storage according to expert's experience.

Table 1. Mean values (with standard deviation) of maturity indices for cherry tomatoes

Mature stages	Firmness, N	pH	SSC, %	LC, mg/100 g
Green-ripened stages	17.73±1.51A	3.93±0.01C	4.57±0.06C	1.18±0.06C
Turning colour stages	9.82±1.21B	4.08±0.01B	5±0.01B	1.76±0.06B
Red-ripened stages	7.28±0.74C	4.16±0.01A	7.1±0.1A	3.98±0.05A

A, B, C: significantly different at $P \leq 0.05$

2.2. E-nose response to cherry tomato

Figure 1 shows the typical responses of 10 sensors of E-nose to cherry tomatoes of different maturity. The response is expressed by G/G_0, where G and G_0 are the resistance of a sensor in clean air and detecting gas, respectively. The response intensity of cherry tomatoes of GRS was lower than the signals for samples of TCS and RRS, while they were similar to each other. After an initial period of low and stable conductivity, the conductivity increased sharply and then stabilized after 40 s. In this research, the stable signals at 60^{th} s were extracted and used to analyse. The average values of sensor responses at the 60^{th} s of each maturity were compared in Fig. 2. Sensors' responses to cherry tomatoes of GRS were lower than that of TCS and RRS, which were quite similar to each other, but slightly differed in S4, S6, S8, S9, and S10.

2.3. Results of PCA and CDA

The 60^{th} s sensor responses were analysed by PCA and CDA, the results are shown in Fig. 3. The first two PCs explained 90.43% of the total variance. It can be inferred that the first two PCs gave most information of original data. In Figure 3A, cherry tomatoes of GRS are scattered in the left part with PC1<–2. In the right part, samples of TCS are located in the upper of the chart with PC2>0, while cherry tomatoes of RRS are plotted in the lower part of the chart with PC2<–0.5, although there were one sample of TCS and two samples of RRS located near the line of PC2= –0.5. Three maturity stages of cherry tomatoes could be classified by sensor signals of E-nose.

Better results were obtained by CDA. The CAN1 and CAN2 explained 100% of the total variance, giving all the information of sensor responses. As shown in Figure 3B, samples of three maturities fell into their own group with strong convergence.

2.4. Prediction of quality indices

In order to establish relationship between the E-nose responses and firmness, pH, SSC, and LC in cherry tomatoes, MLR and PLS were employed, the prediction results were compared to find better models.

The E-nose responses of 18 samples for each maturity were collected, there were 18×3=54 in total, and 2/3 of the samples were randomly selected to train the predictive models, and the rest were used as test set. The correlation coefficient (R^2) and root mean square error (RMSE) between predicted and experimental values were used to evaluate the performance of the predictive models. Larger R^2 and lower RMSE lead to better predictive models. Results are presented in Table 2.

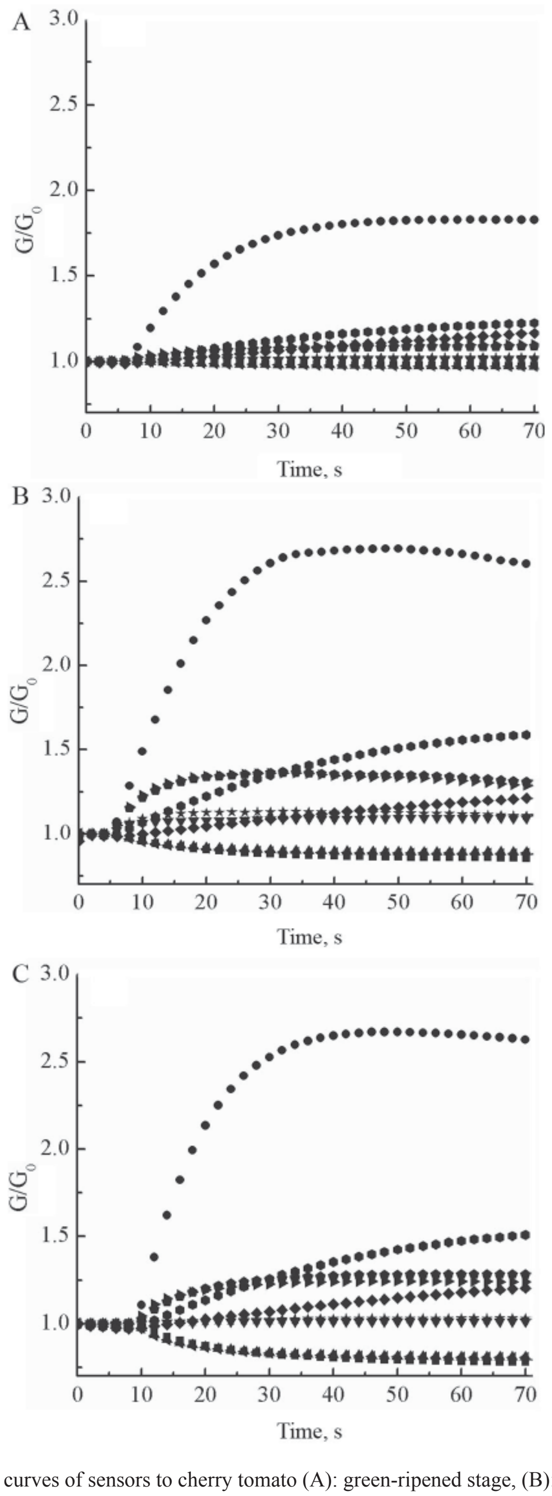

Fig. 1. Type response curves of sensors to cherry tomato (A): green-ripened stage, (B): turning colour stage, (C): red-ripened stage. ■: S1; ●: S2; ▲: S3; ▼: S4; ◄: S5; ►: S6; ◆: S7; ⬟: S8; ⬢: S9; ★: S10

Table 2. Comparison of two predictive models for quality indices

Indices	Regression methods	Training		Test	
		R^2	RMSEC	R^2	RMSEP
Firmness	MLR	0.966	0.84	0.917	1.37
	PLS	0.960	0.91	0.924	1.40
pH	MLR	0.979	0.01	0.941	0.02
	PLS	0.975	0.02	0.928	0.03
SSC	MLR	0.953	0.24	0.808	0.52
	PLS	0.946	0.26	0.802	0.52
LC	MLR	0.954	0.26	0.815	0.54
	PLS	0.947	0.28	0.822	0.54

The leave-one-out technique was applied for PLS. In Table 2, good correlations were found between E-nose responses and firmness, pH, SSC, and LC of cherry tomato with the R^2 of 0.96, 0.975, 0.946, and 0.947, respectively. When the models were used for the test set, the correlations between predicted and true value were higher for firmness (0.924) and pH (0.928), lower for SSC (0.802) and LC (0.822).

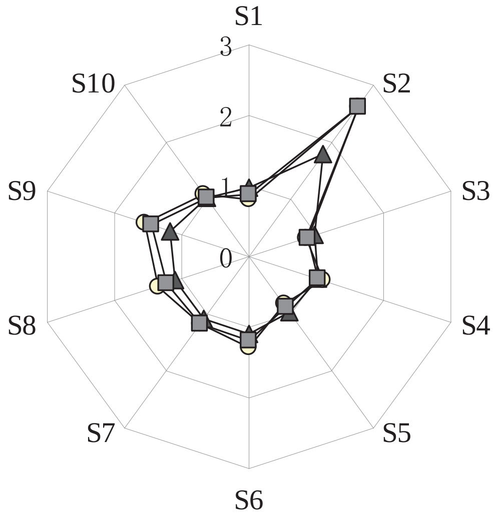

Fig. 2. Radar plot of cherry tomato with different maturity.
▲: Green-ripened stage; ○: turning colour stage; ■: red-ripened stage

The linear correlation between the sensor responses and the physical-chemical indices, such as firmness, pH, SSC, and LC, were better illustrated by MLR, with higher value of R^2 (higher than 0.95) and lower value of RMSE. The MLR method showed high predictive ability for prediction of inner quality of tomato with E-nose. When the predictive models were applied for test set, the R^2 between predicted results and true values were also higher for firmness (0.917) and pH (0.941), lower for SSC (0.808) and LC (0.815).

For training and test data set, R^2 built by MLR were higher than that of PLS, except for the prediction of firmness and LC, and RMSE built by MLR were lower than or equal to that of PLS. In conclusion, both methods exhibited excellent predictive ability for quality indices. It can be concluded that the predictive models were satisfactory to predict quality indices of cherry tomato both by PLS and MLR, and models built by MLR were better than that of PLS.

Considering the correlation coefficients between the predicted value and true content of lycopene, E-nose displayed better ability in the determination of LC using PLS and MLR than the determination of LC in tomato juice by infrared spectroscopy (r=0.97 and 0.96) (De Nardo et al., 2009) with PLS. When it comes to the internal quality, the correlation coefficients were in the range of 0.81 to 0.95 by hand-held and bench top infrared spectrometers (r= 0.81~0.95) with PLS (Wilkerson et al., 2013). Beside the lower value of correlation coefficient, these two fast methods for determinations of inner quality were all destructive detections.

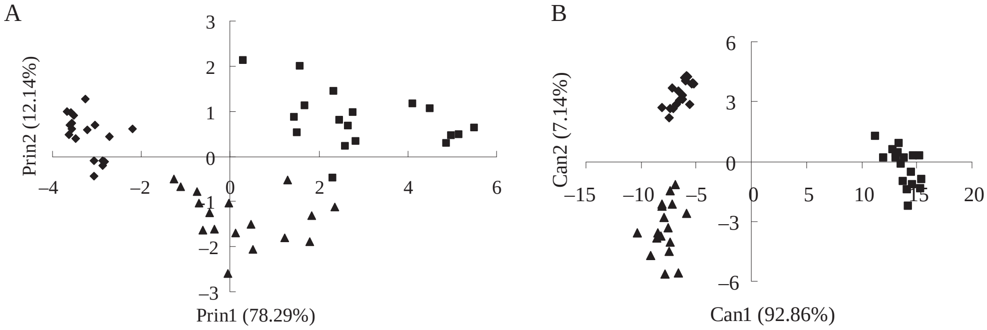

Fig. 3. Scatter plot of PCA and CDA (A: PCA, B: CDA).
◆: Green-ripened stage; ■: turning colour stage; ▲: red-ripened stage

3. Conclusions

The potential of E-nose to classify cherry tomato maturities and quantify their quality indices was evaluated. It has been found that E-nose can be successfully applied for the monitoring of cherry tomato ripeness and prediction of the physicochemical indices directly without any preliminary sample preparation. Predictive models built by MLR and PLS showed high capacity in the prediction of firmness and pH, while R^2 for SSC (R^2=0.808 and 0.802) and LC (R^2=0.802 and 0.822) were lower. What's more, MLR was a more effective method for the prediction of quality indices. E-nose could provide the cherry tomato industry with a simple, rapid technique for the determination of cherry tomato quality.

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