

# Comparative analyses of apple aroma by a tin-oxide gas sensor array device and GC/MS

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## Abstract

The apple cultivars “fuji”, “jina” and “huanui” aroma volatiles were collected and analyzed using a tin-oxide gas sensor array device and the gas chromatography combined with mass spectrometry (GC-MS). Twenty two of the most abundant volatile compounds were taken into account for further study. Eight compounds were found in every cultivar. The principal components analysis (PCA), partial least squares (PLS) and back-propagation feed-forward artificial neural network (BP-ANN) were used to analyze the sensor array and SPME-GC-MS measurements. From the plots of the first two PCs by PCA, different apple cultivars could be clearly distinguished by SPME-GC-MS measurements, while there was slight overlap by sensor array measurements. BP-ANN was used to distinguish different cultivars based on gas sensor array responses, and the accuracy was 87%. Due to the composition of gas sensors in the array, results of PLS models showed that the correlation between fourteen gas sensor array responses and the two PCs of twenty-two compounds were better than the correlation between those and each volatile compound. Furthermore, an ANN was used to build the relationship between the two predicted PCs by PLS model and the three cultivars. The recognition probability was increased to 97%.

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*Keywords:* Apple; Aromas; Gas sensor array; GC-MS; Principal component analysis; BP-ANN; PLS

## 1. Introduction

China has an annual apple production of over 20 million tons every year. After the apples are picked, they are transported to the packing plant to be tested for various quality attributes that determine their price and destination. The aroma volatiles are becoming more important to the purchasers of apples. Aroma has been the subject of much research. Traditionally, the flavour of horticultural products is measured by means of sensory panels. Such a panel consists of typically 10 or 12 panelists trained to recognize and score well-defined flavour attributes. The procedure is, however, subjective and expensive. Alternatively, instrumental techniques such as gas chromatography (GC) with headspace sampling, and techniques such as GC combined with mass spectrometry (GC-MS) can be used to identify

and quantify individual aroma components (Brezmes, Llobet, & Vilanova, 2001; Frank, Owen, & Patterson, 2004; Riu-Aumate, Castellari, Lopez-Tamames, Galassi, & Buxaderas, 2004). The two basic techniques used to assess aroma, sensory analysis and conventional gas chromatography-mass spectrometry (GC-MS), are generally too time-consuming, complex and labour intensive for routine quality application.

In the last 20 years, there has been increasing research in order to achieve a faster and more objective system for evaluating aromas, which has led to the development of the gas sensor array device (Electronic nose system) technology (Gardner & Bartlett, 1994; Patrick, 1996; Stijn, Jeroen, & Amalia, 2003). Electronic nose instruments are designed to mimic the human olfactory system; they consist of an array of sensors that react differently in the presence of volatiles. Unlike most chemical sensors, which are designed to detect specific gas molecules, the sensors in the array are not specific to a particular volatile (Gardner

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& Bartlett, 1994). Gas sensor array devices have several applications in environmental control, medical diagnostics and the food industry. Volatile production of apples during ripening stage and shelf life has been measured by means of electronic noses (Amalia, Jeroen, & Stijn, 2004; Brezmes et al., 2001; Herrmann, Thorsten, & Joachim, 2002; Stijn et al., 2003).

The results of GC-MS gives detailed information of apples aroma, such as the name and proportion of volatile compounds. Meanwhile, the gas sensor array device gives over-all result of apple aroma. Therefore, analyses of fruit aroma (particularly of apple aroma) with GC-MS and gas sensor array device have been widely reported (Penza & Cassano, 2003; Rye & Donald, 2003). If gas sensor array responses and GC-MS profiles could be statistically correlated, analytical results of gas sensor array device might be interpreted on the basis of GC-MS data or chemical information. However, this correlation was rarely mentioned in literature. Recently, Santos, Arroyo, and Alexandre (2004) investigated the volatiles of wines by gas sensor array device and GC-MS, similar studies has been explored by Garrigues, Taloua, and Nesab (2004).

The research in this area has to be applied to different cultivars of apples, a task which we are doing in our labs. This paper describes an experiment where tin oxide gas sensor array responses and GC-MS measurements were used to characterize the apples at the same time. The relationship between the gas sensor array responses and GC-MS measurements were analyzed.

## 2. Materials and methods

### 2.1. Fruit material

Three different cultivars apples: “Jina”, “fuji”, “Huaniu” which were the most saleable apples in China were investigated. The orchard is located in Shanxi, in the north-west part of China. Sixty apples in each cultivar were collected in a single harvest day, the one that is considered optimal by experts on the field. “Jina” and “Huaniu” apples were harvest at September 10, 2005, while “fuji” apples harvest at October 20, 2005. Care was taken to obtain apples of approximately the same size for each

variety. The masses and volumes of each apple were determined.

### 2.2. Design of the gas sensor array device

Gas sensor array devices were based on a chemical sensor array and suitable pattern recognition techniques (Boilot, Hines, Gongora, & Folland, 2003; Brudzewskia, Osowskib, & Markiewicz, 2004; Penza & Cassano, 2004; Rye & Donald, 2003). The device used in this paper was an evolution of that described by Garrigues et al. (2004). This general approach was implemented in different modules for each application. Fig. 1 shows a schematic diagram of our tin-oxide gas sensor array device which comprises three basic modules.

#### 2.2.1. Headspace module

This module controlled the air flow circuit during the measurement process. Inside this module, two chambers, an air pump, tubes and several electrovalves were included. The gas sensor array device was placed in a temperature controlled environment at 23 °C.

The fruit was placed in the concentration chamber. It had a volume of 1.5 L and its main purpose was to accumulate all the aromatic compounds released by the fruit during the concentration phase. Its size allowed one apple to be measured. The measurement chamber that houses the sensor array was made of three glass column casing. Its volume was about 0.5 L.

A membrane pump created a constant air flow of 70 mL min<sup>-1</sup>. During the measurement, three different phases could be distinguished: concentration, measurement and stand-by. The electro-valves, controlled by a computer program, guided the air through different circuits depending on the measurement phase. Air flow pre-filtered by silica gel and active carbon was kept constant through the measurement chamber.

Fig. 2 shows a schematic view of the different air flow paths. When the system was at the concentration phase, air did not cross the concentration chamber since electrovalves closed that path to seal the fruit vessel. The pump drew pre-filtered air from the lab and the electrovalves guided it through the measurement chamber. Finally, the

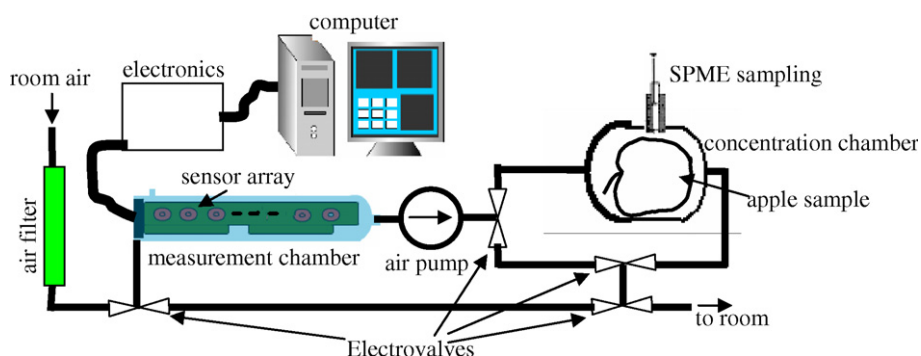


Fig. 1. Schematic diagram of the electronic system.

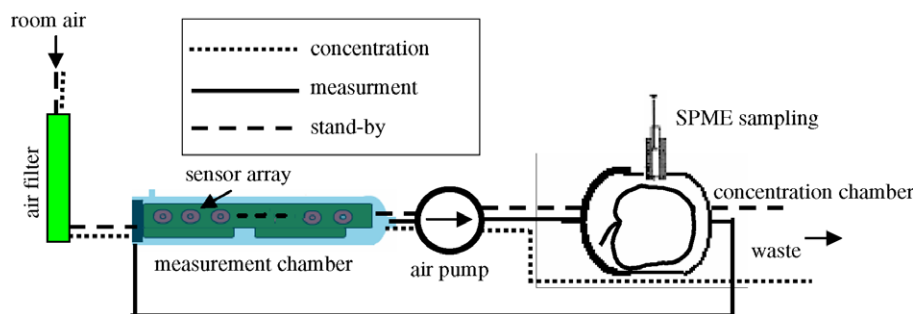


Fig. 2. Air flow paths at different measurement phase.

air exited the system. This phase lasted 40 min and was designed to strengthen the aromatic concentration to obtain higher sensor responses.

During the measurement phase, the pump pushed the volatiles through a closed loop that included the measurement and concentration chambers. No air entered nor exited the loop. The measurement phase lasted 6 min, time enough for sensors to reach a stable value. Finally, when a measurement was completed, a stand-by phase was activated. Its main purpose was to clean the circuit and return sensors to their baseline. Clean air entered the circuit, crossed the measurement chamber first, the empty concentration chamber afterwards, and pushed the remaining volatiles out of the circuit. Between measurements, a rest time of 15 min was considered appropriate.

### 2.2.2. Sensor array module

In this module, we included the gas sensor array and the associated electronics necessary to power sensors. The sensor array included 14 tin oxide gas sensors, and was housed in the measurement chamber. Table 1 lists all the sensors used and their main applications. All of the gas sensors that formed the array were semiconductor metal oxide devices made by Figaro Inc. Electronics were necessary to heat the sensor elements and to translate conductivity changes into voltage signals the computer could acquire, store

and process. Power supply and signal conditioning were necessary for temperature and humidity probes.

### 2.2.3. Computer module

A PC compatible computer controlled the measurement process and afterwards processed raw data into useful information for the user, using pattern recognition algorithms. With the help of a commercial acquisition board PCL-816 (Advantech Inc., Taiwan, China) with analogue and digital input/output channels, a computer program controlled the measuring process. Electrovalves were controlled by binary output signals generated by the program to redirect air flow during the different phases of each measurement. When sensors were exposed to volatiles, during the measurement phase, the computer recorded the resistance changes that the sensors experienced. When a measurement was completed, the acquired data was stored in a hard disk as a text file for later use. In this study, 14 gas sensor array responses were automatically recorded and pre-processed as described literature (Zou & Wu, 2002; Zou & Zhao, 2002, 2003).

## 2.3. GC-MS measurements

### 2.3.1. Headspace solid phase micro-extraction

A SPME fiber (Supelco, Bellefonte, PA) coated with a 100  $\mu\text{m}$  layer of polydimethylsiloxane (PDMS) was used in all of the experiments. In preliminary studies, the utility of polydimethylsiloxane/divinylbenzene (PDMS/DVB), Carboxen/polydimethylsiloxane (CAR/PDMS), and polyacrylate fibers was also investigated. Before the very first measurement, the SPME fibre was preconditioned at 250  $^{\circ}\text{C}$  for 2 h under helium flow in the GC injection port. During the concentration phase (40 min, 23  $^{\circ}\text{C}$ ), the volatiles were sampled by means of solid-phase micro-extraction (SPME).

### 2.3.2. GC-MS measurements

The volatiles adsorbed in SPME were subsequently desorbed for 5 min at 250  $^{\circ}\text{C}$  into the glass-lined, split-less injection port of the GC (6890N, Agilent Technologies) and separated on a capillary column (HP-5, 30 m  $\times$  0.1 mm i.d., 0.33  $\mu\text{m}$  coating thickness). The carrier gas was ultra-purified helium (99.999%) at a constant flow rate of

Table 1  
Sensors used in the electronic nose

Sensors	Application
TGS800-1	Air quality; cigarette smoke, gasoline vapours
TGS800-2	Air quality; cigarette smoke, gasoline vapours
TGS821-1	Hydrogen
TGS824-1	Ammonia
TGS825-1	Hydrogen sulfide
TGS880-1	Kitchen control: food odours, fumes, vapours, humidity
TGS880-2	Kitchen control: food odours, fumes, vapours, humidity
TGS822-1	Organic solvents
TGS813-1	Combustible gas
TGS883T-1	Food odours, fumes, vapours, humidity
TGS823-1	Alcohol, toluene, dimethylbenzene
TGS82620-1	Alcohol
TGS830-1	Organic gas
TGS2610-1	Combustible gas:mathne

40 cm s<sup>-1</sup>. The temperature program started at 40 °C and held for 2.5 min, was then raised at the rate of 10 °C min<sup>-1</sup> to 200 °C and held for 5 min. The GC-MS transfer line temperature was 260 °C. Volatile compound identification was performed using an MS with electron impact ionization (5973 Network Mass Selective detector, Agilent Technologies). Mass spectra were collected at a rate of 8 spectra/s over a *m/z* range of 33–450 amu. The ionization energy was 70 eV. Data were analyzed using Chemstation software (G1701CA, Agilent Technologies). Identification of volatile components was confirmed by comparison of collected mass spectra with those of authenticated standards and spectra of the National Institute for Standards and Technology (NIST) mass spectral library, Search Version 2.0.

### 2.3.3. Chemicals used and standard solution

Hexanal (>97%), 2-hexenal (97%), isopentyl acetate (97%), pentyl acetate (97%), hexyl acetate (>97%), hexyl 2-methyl-butanoate (97%), 2-octanol (97%) were purchased from Sigma–Aldrich, Steinheim, Germany. Methanol was purchased from Shanghai.

A standard mixed-solution for hexanal, 2-hexenal, isopentyl acetate, pentyl acetate, hexyl acetate, hexyl 2-methyl-butanoate and 2-octanol, was prepared in methanol in concentrations of about 10 mg L<sup>-1</sup>. The mixed standard solution was diluted 10, 20, 100, 200-fold with tap water floating for about 1 min before use. Tap water was preferred to distilled or deionized water as it showed the lowest amount of volatile compounds interfering with the analyses (verified by headspace SPME-GC-MS). The standard solutions were stored at 4 °C until use.

### 2.4. Data analysis

The pattern recognition techniques used in this work are:

- (1) Principal component analysis (PCA) (Zou & Zhao, 2003; Santos et al., 2004), a procedure that extracts useful information from the data, and explores the data structure, the relationship between objects, the relationship between objects and variables and the global correlation of the variables.
- (2) Back-propagation feed-forward artificial neural network (BP-ANN) (Zou & Zhao, 2002, 2002), a pattern recognition procedure that can achieve complicated non-linear mapping, was chosen to analysis Gas sensor array (Fig. 3). In Fig. 3,  $w_{ij}$  and  $v_{jk}$  are the weights, and *I*, *H*, and *O* represent the input layer, hidden layer, and output layer of the ANN, respectively. The selected activation function is a sigmoidal function ( $a_i$ ) using

$$a_i = g_i(p_i) = \frac{1}{1 + \exp(-c \times p_i)}, \quad (1)$$

where the weight coefficient (*c*) is the steepness of the activation function, by which the curve slope can be ad-

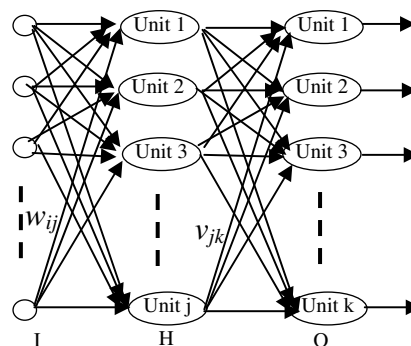


Fig. 3. The structure of the back-propagation feed forward artificial neural network.

justed. The feature of this function is that, when  $p_i$  changes from  $(-\infty)$  to  $(+\infty)$ , the value of  $a_i$  varies only between 0.0 and 1.0. Moreover, when  $p_i$  is around 0.5, the small change in  $p_i$  can lead to a large change in the response of the function. It is worth noticing that  $g_i(p_i)$  is continuously derivable.

- (3) Partial least squares (PLS) regression analysis, which described by Tetsuo (2004), is currently one of the most powerful multivariate calibration techniques, has been recognized as an indispensable regression technique among analysts working in spectroscopy, chromatography and sensory sciences, was used. Leave-one out cross-validation was used to evaluate the quality of the model. In this technique, all but one sample is used to build a calibration model and then the model is used to predict the remaining sample. Thereafter, a second sample is left out from all samples and a newly constructed model is used to predict that sample. This procedure is repeated until each sample is left out and predicted by a model once. The number of latent variables in the PLS models is determined by the average square error (Ssq). The correlation coefficient (*r*) and predictive residual error sum of squares (PRESS) of PLS models are determined as follows:

$$r = \frac{\sum_{i=1}^N (\hat{y}_i - \bar{\hat{y}})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^N (\hat{y}_i - \bar{\hat{y}})^2 \sum_{i=1}^N (y_i - \bar{y})^2}}, \quad (2)$$

$$\text{Ssq} = \sqrt{\frac{1}{N} \sum_{i=1}^N (\hat{y}_i - y_i)^2}, \quad (3)$$

where  $\hat{y}_i$  is the predicted value of the *i*th observation,  $\bar{\hat{y}}$  is the mean value of  $\hat{y}$ ,  $y_i$  is the measure value of *i*th observation,  $\bar{y}$  is the mean value of *y*, *N* is the number of observation set.

The volatiles obtained by GC-MS and the 14 gas sensor array responses were analysed by PCA. The BP-ANN was used to analyse the 14 gas sensor array responses in order to distinguish the three apple cultivars. The correlation between gas sensor array responses and GC-MS profiles were investigated by PLS regression.

### 3. Results and discussion

#### 3.1. Volatile composition of the “Jina”, “fuji”, “Huaniu” headspace identified with GC-MS

##### 3.1.1. Calibration and quantification

Extraction of apple aroma by SPME was first optimized by choice of fiber as it described in the existing literature (Lee, Diono, Kim, & Min, 2003; Lecanu, Ducruet, Jouquand, Gratadoux, & Feigenbaum, 2002; Liu & Yang, 2002). At the outset of a related study, standard mix-solution was the target molecule, and of the four fibers evaluated (PDMS, PDMS/DVB, CAR/PDMS, and polyacrylate), PDMS gave the highest levels of this molecule. It was also the best for ester recovery and was thus chosen for this study.

Calibration curves for the compounds were prepared using the experimental parameters (e.g. 23 °C of adsorption temperature, 40 min of adsorption time) in the concentration range of 0.05–10 mg L<sup>-1</sup> (0.05, 0.1, 0.5, 1, 10) standard mixed-solution. Linear regression was used for all calibrations. Table 2 shows the linear range of standard compounds. The correlation coefficients between concentration of compounds and relative peak area were 0.9962–0.9997. The recovery percent of standard samples are shown in Table 3. The recovery percent of isopentyl acetate and 2-octanol is not good as other standard compounds. However, it is better than the 67% obtained by Matich, Rowan, and Banks (1996).

##### 3.1.2. Volatile composition

Table 4 gives an overview of 22 most abundant compounds of “Jina”, “fuji”, “Huaniu” apple sampled with SPME and identified with GC-MS. Although the SPME sampling method discriminates between different compounds and does not reflect the actual headspace composition of the apple fruit, Stijn et al. (2003) demonstrated that

the change in volatile composition among different apple cultivars can be measured and analysed with this technique. It can be seen that composition and content of aroma differ from various cultivars. There are eighteen, seventeen and ten compounds which have been detected in “fuji”, “Jina” and “Huaniu” respectively. Among the 22 compounds, only eight volatiles are detected in every apple cultivar, they are 1-butanol; 1-butanol,2-methyl; hexanal; 2-hexenal; 1-hexanol; 5-hepten-2-one, 6-methyl; 2-methyl hexyl butyrate; hexyl hexanoate. It was found that the esters in “Huaniu” apples were higher than they in “Jina” or “fuji” apples, such as ethyl propionate, butyl acetate, propyl butyrate etc.

The 22 volatiles were analyzed by principal component analysis (PCA) in order to reduce the dimensions and investigate whether different cultivars apples could be visualized. All the variables were weighted (1/standard deviation). Fig. 4 shows a PCA score plot of the first two principal components. The first two principal components explain together 92.8% of all the variance, which makes it possible to interpret the two-dimensional score plot. The samples from the different cultivars were clearly separated. This experiment yielded good results, but was too time-consuming, complex and expensive. Each test takes at least 45 min and the SPME could be reused for 50–60 times, as recommended by Supelco agent in China. Therefore, a gas sensor array system was developed to analysis the volatile compounds of apples.

#### 3.2. Sensor array data analysis

In order to distinguish different cultivars apples by the sensor array, PCA and BP-ANN were applied to analyze the 180 measurements (Fig. 5). Although, 86.7% of the variance present in the data set was described by two principal components, different cultivars apples were not separated clearly, especially for “jina” and “fuji”. The results were

Table 2  
Linear range of standard compounds

Standard compound	Linear range (mg L <sup>-1</sup> )	Regression equation	Correlation coefficient
Hexanal	77.9–8,671	$\rho = -0.764 + 4.98 \times 10^{-2} A$	0.9987
2-Hexenal	84–9,367	$\rho = -11.124 + 0.237 A$	0.9997
Pentyl acetate	42.8–6,184	$\rho = -1.743 + 2.40 \times 10^{-2} A$	0.9992
2-Octanol	52.1–4,728	$\rho = -3.844 + 2.73 \times 10^{-2} A$	0.9994
Isopentyl acetate	197.6–413.8	$\rho = -11.543 + 9.73 \times 10^{-2} A$	0.9995
Hexyl acetate	201.4–3,638	$\rho = -0.986 + 8.97 \times 10^{-4} A$	0.9996
Hexyl 2-methyl butyrate	193–3,894	$\rho = -1.494 + 3.77 \times 10^{-4} A$	0.9962

A: peak area.

Table 3  
The recovery percent of standard samples

Standard sample	Hexanal	2-Hexenal	Isopentyl acetate	2-Octanol	Hexyl 2-methyl butyrate	Pentyl acetate	Hexyl acetate
Actual content (mg L <sup>-1</sup> )	7.13	7.12	7.12	7.12	7.15	7.15	7.15
Found by SPME (mg L <sup>-1</sup> )	7.101	6.422	5.43	5.53	7.13	6.25	7.092
Recovery percent (%)	99	90.2	76.1	78.2	99	88.3	99.2

Table 4

The mean values of the 22 most abundant volatile compounds in “Jina”, “fuji”, “Huaniu” apples identified by SPME-GC-MS (ug/L) together with their retention times and correlation coefficients (*R*) between the specific volatiles and the first two principal components of the principal component analysis of all the compounds

Volatile compounds	Retentiontime (min)	Content of different volatiles $\bar{x} \pm \sigma$ (ug/L)			<i>R</i>	
		“Jina”	“fuji”	“Huaniu”	PC1	PC2
Ethanol	1.57		416 ± 26		0.0013	−0.0129
1-Butanol	2.67	875.2 ± 83	350 ± 18	1205 ± 24	0.0019	0.0233
Ethyl propionate	3.34			8211 ± 35	0.0897	0.1755
1-Butanol,2-methyl	3.81	54340 ± 306	19800 ± 503	3070 ± 32	−0.6702	−0.0279
Hexenal	5.14	5430 ± 167	9090 ± 95	688 ± 24	−0.0401	−0.2145
Butyl acetate	5.56	533 ± 23	9700 ± 78		0.0234	−0.2948
2-Hexenal	6.85	41931 ± 133	6063 ± 143	3404 ± 54	−0.5353	0.2855
1-Hexanol	7.10	407 ± 14	816 ± 76	7035 ± 485	0.0737	0.129
1-Butanol,2-methayl acetate	7.39	1961 ± 12	648 ± 106		−0.0256	−0.0013
Propyl butyrate	7.95	17913 ± 132			−0.2528	0.171
Propyl acetate	8.28	20673 ± 185			−0.2918	0.1973
Pentyl acetate	8.46	9748 ± 121	21280 ± 212		−0.0696	−0.5649
5-Hepten-2-1,6-methyl	10.92	820 ± 45	695 ± 36	7781 ± 434	0.0756	0.1526
Butyl lbutanoate	11.01		684 ± 25		0.0022	−0.0211
Hexyl acetate	11.56	399.8 ± 45	695 ± 54		−0.0034	−0.0177
2-Metyl-1-hexynol	12.04	697 ± 63			−0.0098	0.0067
2-Methyl butyl butyrate	12.44	838.8 ± 72	3060 ± 87		−0.0021	−0.0866
Ehyl hexyrate	14.04		1769 ± 132		0.0056	−0.0547
Hexyl butyrate	16.94	265.3 ± 67	3312 ± 271		0.0068	−0.0999
2-Methyl hexyl butyrate	18.24	354 ± 34	3955 ± 154	466.3 ± 34	0.0127	−0.1089
Butyl butyrate	19.35		1975 ± 131	1663 ± 44	0.0245	−0.0255
Hexyl hexanoate	22.27	27604 ± 534	26580 ± 567	823.9 ± 45	−0.2957	−0.5407

$\bar{x}$ : mean value,  $\sigma$ : standard deviation.

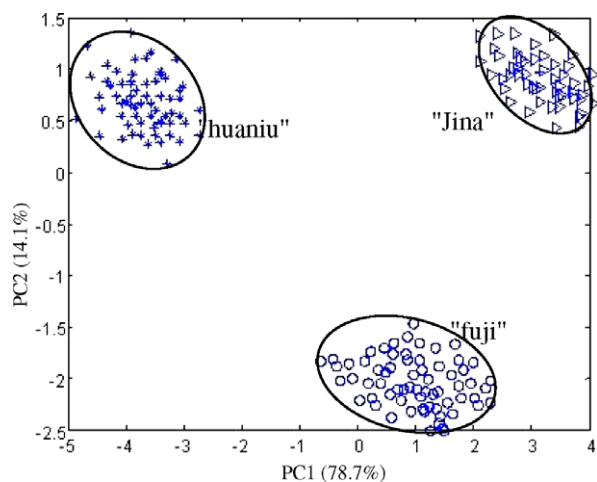


Fig. 4. Score plot of PCA of the 22 selected volatile compounds of three different cultivars apples measured by means of SPME-GC/MS.

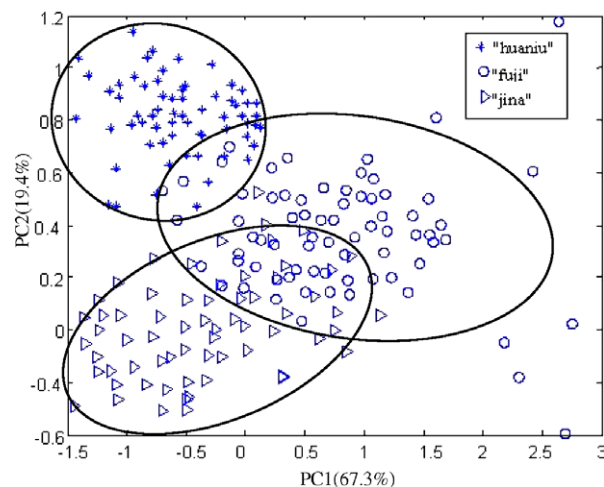


Fig. 5. PCA results for E-nose data.

very similar for sensory analysis by a duo-trial test. The sensory analysis test showed that it was very easy to distinguish “huaniu” from the other two cultivars, while it was more difficult to discriminate between “fuji” and “jina” flavours. This result is reasonable because the flavors of “jina” and “fuji” belong to “sweet aroma”, while the flavors of “huaniu” belong to “red apple aroma”. Fig. 5 shows that the separation between “huaniu” and “fuji” is good but not as clear as “huaniu” and “jina”. About 30% of apples could not be distinguished between “jina”

and “fuji”. This might be explained by loss of information when only two PCs were used. This result suggested that the system could be used to discriminate among different apple cultivars using neural network analysis.

The structure of the neural network was  $14 \times 8 \times 3$ . The 14 gas sensor array responses were transmitted into the input layer. Three apple cultivars were coded to serve as the output layer of the neural network: “fuji” (1, 0, 0); “jina” (0, 1, 0); “huaniu” (0, 0, 1). The artificial neural network was trained with the 120 training samples (40 sam-

ples random selected from each cultivar) until the total error was less than the preset value (0.2). It was then used to classify the testing set, which consisted of 60 samples (20 from each cultivar). The recognition probability of the neural network analysis was defined as the ratio of the number of right answers to that of total trials was 87%. There were only 8 apples (three from “fuji” apples which misclassified to “jina”, four from “jina” which misclassified to “fuji”, one from “huanui” which misclassified to “fuji”) misclassified in the testing set. This result showed that the gas sensor array system could distinguish different apple cultivars.

### 3.3. Correlation between gas sensor array responses and GC-MS measurements

The correlation between GC-MS measurements and gas sensor array responses has seldom been discussed in literature as the algorithms of the two methods are different. From the above analysis, the aroma of different cultivars could be distinguished by SPME-GC-MS using PCA, and it could also be distinguished by gas sensor array using ANN. Therefore, there is some relationship between the two methods.

Measures done with the gas sensor array system were coupled with the values obtained from SPME-GC-MS at the same measurement session as mentioned in Section 2. In this way, a total of 180 pairs of measurements were coupled. Although back-propagation neural networks were initially considered, it seemed inappropriate to use them with such a small number of measurements. Furthermore, there were eight volatiles that were found in every cultivar, the two PCs showed in Fig. 4 could be seen as the global information of the 22 variables compounds. Therefore, the correlation between 14 gas sensor array responses and the 8 volatiles, and the correlation between 14 gas sensor array responses and the two PCs were analysed by PLS regression models. A leave-one-out approach was performed for each volatile compound and the two PCs. 179 measures were used to build the PLS model while the remaining one was predicted. This process, which was repeated 180 times (so that each measure was used once for evaluation and 179 times for training) optimized the use of a small set of measurements (the leave-one-out method sometimes was referred as a cross-validation of order one). For each PLS model built, the data used for training were mean centred and scaled by their variance; the data used for testing was centred and scaled using the mean and variance of the training set.

Table 5 shows the average square error (Ssq), correlation coefficient, optimal number of latent variables (LV), for each volatile compound predicted for apples using 14 gas sensor array responses. The two PCs were better predicted parameters with correlation coefficients ( $r$ ) 0.673 and 0.521, respectively. Table 5 shows that there was some correlation between the volatile alcohols and 14 responses

Table 5

Results of PLS regression models for correlation between 14 gas sensor array signals and GC-MS measurements

Compound	Number of latent variables	$r$	Ssq
1-Butanol	2	0.392	1.0292
1-Butanol,2-methyl	3	0.34	1.1531
Hexenal	2	0.0549	1.5329
2-Hexenal	1	0.0925	1.6340
1-Hexanol	3	0.3259	1.1422
5-Hepten-2-one 6-methyl	1	-0.2727	2.5275
2-Methyl hexyl butyrate	1	-0.3091	2.6100
Hexyl hexanoate	1	-0.3143	2.5900
PC1	3	0.6731	0.7756
PC2	2	0.5521	0.4523

of the sensor array though there were not very high. These alcohols were 1-butanol; 1-butanol, 2-methyl; 1-hexanol. However, the correlations between the sensor array responses and other compounds were very poor. These results were due to the fact that the gas sensors array were tin-oxide sensors, and these sensors were more sensitive to alcohols than other compounds.

Fig. 6 shows the plot of the two predicted PCs parameters by PLS models for the three cultivars. The separation of the three cultivars apples is better than Fig. 5, but not as clear as shown in Fig. 4. The two predicted PCs obtained by PLS were chosen as the input values for the neural network. Three apple cultivars were coded to serve as the output layer of the neural network: “fuji” (1,0,0); “jina” (0,1,0); “huanui” (0,0,1). The artificial neural network was trained with the 120 training samples (40 samples random selected from each cultivar) until the training cycle was larger than the preset value 15,000. It was then used to classify the testing set, which consisted of 60 samples (20 from each cultivar). There were 4 hidden layer nodes which determined by the trial-and-error process. The rec-

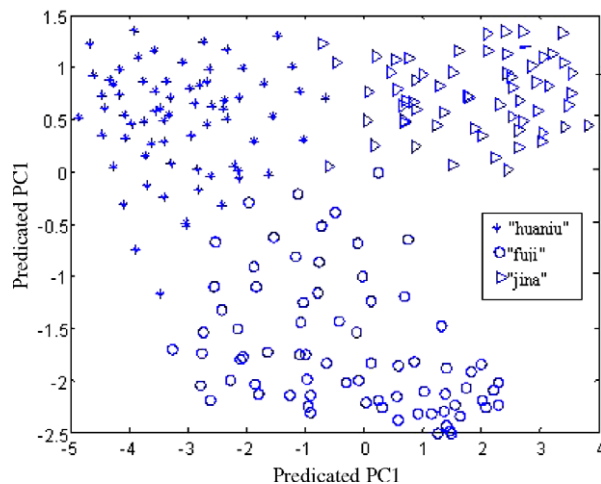


Fig. 6. Score plot of two predicted PCs by PLS model for three cultivars apple.

ognition probability of the neural network analysis defined as the ratio of the number of right answers to that of total trial was 97%. There were only 2 apples (one from “fuji” apples which misclassified to “jina”, one from “fuji” which misclassified to “huaniu”) misclassified in the testing set. The recognition probability was better than that of ANN method mentioned in Section 3.3, because the PLS algorithm could reduce disturbance from noise.

#### 4. Conclusion

The potential of the gas sensor array device and the gas chromatography combined with mass spectrometry (GC-MS) to the characterization of three apple cultivars “Jina”, “fuji”, “Huaniu” volatiles was studied. A gas sensor array device which was an evolution of the device described by Garriguesa et al. (2004), was set up to measure the volatiles of apples. The twenty-two most abundant volatile compounds were taken into account in the SPME-GC-MS measurements. Eight volatiles were found in every cultivar.

The principal components analysis (PCA) was used to analyse the sensor array and SPME-GC-MS measurements. Different apple cultivars were clearly distinguished by SPME-GC-MS measurements, while there was slight overlap by sensor array measurements. Due to the composition of the gas sensors in array, the results of PLS models showed that the correlation between 14 gas sensor array responses and the two PCs of 22 compounds were better than the correlations between those and the 8 individual volatile compounds.

Although the gas sensor array technique did not give exact information about the different volatile compounds, the major advantage of this technique over the standard GC-MS measurements is, without doubt, the shorter analysis time. Future research will involve monitoring the quality of apples during their ripeness stage and storage stage, and optimizing the gas sensor array device for more accurate measurements. Also, the sensor array measurements should be correlated with some sensory analysis in order to predict the consumer acceptance of apples that are stored under a controlled atmosphere. In this way, the Gas sensor array device could be used as a fast and non-destructive screening technique for measuring the volatile quality of apples.

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