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# Discrimination of LongJing green-tea grade by electronic nose

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#### Abstract

An investigation was made to evaluate the capacity of an electronic nose (E-nose, PEN2) to classify the tea quality grade. Four tea groups (A120, A280, A380 and A600) with a different quality grade were employed. In the experiment, the volume of vial and the headspace generated time were considered corresponding to the 5 g tea samples, and the optimum experimental procedure was determined by using the variance analysis (ANOVA), multivariance analysis and principle components analysis (PCA). The results showed that the volume of vial affected the result of discrimination, and the headspace generated time had no significant effect on the E-nose response. The four tea groups were measured and response values at four different collection times were conducted by PCA, linear discrimination analysis (LDA) and artificial neural network (ANN). Only A120, A380 and A600 could be discriminated by PCA. However, the four tea groups were discriminated completely by LDA. The response value of the E-nose at 60 s was optimum to be used for discrimination. The method of ANN (network topology 20-12-4) was performed and 90% of the total tea samples were classified correctly by using the back-propagation neural network. © 2006 Elsevier B.V. All rights reserved.

Keywords: Electronic nose; Principal component analysis; Linear discrimination analysis; Artificial neural network; Green-tea

# 1. Introduction

Nowadays, the electronic nose (E-nose) technology has been successfully applied to different fields, including the food field, such as beverage quality control, fruits ripeness monitoring, fruits classification, etc. Positive applications of the E-nose technology have been reported, and many experiments were performed among these fields.

E-noses have been used to evaluate the quality of modified atmosphere packaged poultry meat [1], the spoiled beef [2], fish [3], milk [4] and olive oil [5]. As far as the beverage field is concerned, an E-nose was used to discriminate four types of red wines which were made from the same variety of grapes and came from the same cellar [6]. Successful discrimination of different Spanish wines made from different grapes by an Enose was reported too [7]. The E-noses have been widely used for the quality monitor of all kinds of fruits, such as mandarins [8], oranges [9], melons [10,11], blueberries [12], pears [13], and peaches [14,15]. In this research the datasets obtained by the experiments were analyzed almost by the methods of PCA,

0925-4005/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.snb.2006.05.019 LDA and ANN. However, little detailed information is available on the influence of experiment factors (the volume of vial and the headspace generated time) on the discrimination.

In particular, there were some reports about the E-nose application in the discrimination of different types of teas [16,17]. The E-noses were used to classify the samples with different processing methods. In such cases, a very good sensitivity to the tea aroma and satisfying time stability was observed by metal oxide semiconductor (MOS) sensors. However, no information has been available on the applicability of E-noses for assessment of the same category tea with different quality grades. Because there were a lot of aromatic organic compounds present in low concentrations, the LongJing tea was difficult to be classified by its quality. The volatile compounds present in the tea were correlated with its quality grade [18]. Usually, the quality grade of the tea was classified by a human taste panel, which may vary due to different factors, while an E-nose was an increasingly fast, reliable and robust technology, which can be made easy-to-use and cost-efficient, so that a good correlation between human and E-nose judgment was an important finding [19].

In this paper the utilization of an E-nose for discrimination of LongJing green-teas with different quality grades was described. As is well known, teas of the same category share some features together. Nevertheless, some subtle differences among the odors

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of teas exist according to different qualities. From a chemical point of view the differences are very small and their effects on the odors could be appreciated only by well trained people. According to its chemical complexity, the employment of an appropriate E-nose to detect volatile compounds could be useful to distinguish the different quality grades of the teas.

#### 2. Materials and methods

### 2.1. Samples and experiment procedure

The study was carried out by using LongJing green-tea that was obtained from the Tea Academy of Zhejiang University. Green-teas of four different quality grades were used in the experiment, which were labeled A600, A380, A280 and A120, as shown in Table 1.

In order to decide the optimum experiment conditions, a set of experiments was performed. The quantity of each tea sample was 5 g. Tea samples were measured under different conditions. Four tea group samples were separately sealed in vials of 50 ml, and the headspace generated time was 0.75, 1 and 2 h. Then, same process was carried out for the vials of 150, 250 and 500 ml. Fifteen repeated samples were prepared for each experiment (totally of 720 measurements were performed). Then, a suitable vial and headspace generated time were decided.

Four tea groups were measured based on the optimum experiment conditions. The response value of the E-nose was recorded and analyzed by PCA, LDA and ANN. In this step, 45 repeated samples were prepared for each tea group (totally 180 measurements were performed). All the samples were taken from dynamic headspace sampling.

## 2.2. Electronic nose

Experiments were performed with a portable electronic nose (PEN2) operating with the enrichment and desorption unit (EDU). The system was from WMA (Win Muster Airsense) Analytics Inc. (Germany). PEN2 consisted of a sampling apparatus, a chamber containing an array of sensors, and pattern recognition software (Win Muster v.1.6) for data recording. The sensor array was composed of 10 MOSs, shown in Table 2. The sensor response was expressed as the ratio of conductance  $(G/G_0)$ .

The headspace gas was pumped into the sensor chamber with a constant rate of 400 ml/min via a Teflon-tubing connected to a needle during the measurements process. When the gas accumulated in the headspace of vials was pumped into the sensor chamber, the ratio of conductance of each sensor changed. The

Table 1 Different grades of green-tea

Tea	Grade	Price (¥/500 g)	
A600	А	600	
A380	В	380	
A280	С	280	
A120	D	120	

Table 2 Response feature of the sensor array

Number in array	Sensor-name	Object substances for sensing
MOS 1	W1C	Aromatics
MOS 2	W5S	Nitrogen oxides
MOS 3	W3C	Ammonia and aromatic molecules
MOS 4	W6S	Hydrogen
MOS 5	W5C	Methane, propane and aliphatic
MOS 6	W1S	Broad-methane
MOS 7	W1W	Sulfur-containing organics
MOS 8	W2S	Broad-alcohols
MOS 9	W2W	Aromatics, sulfur- and
		chlorine-containing organics
MOS 10	W3S	Methane and aliphatics

measurement procedure was controlled by a computer program. The measurement phase lasted for 60 s, which was enough for the sensors to reach stable values. The interval for data collection was 1 s. A computer recorded the response of the E-nose every second. When the measurement was completed, the acquired data was properly stored for later use. The temperature of the laboratory was kept  $25 \pm 1$  °C.

# 2.3. Principal component analysis, linear discrimination analysis and artificial neural networks

The data obtained by the process mentioned above was subjected to different pattern recognition techniques such as PCA, LDA and ANN.

PCA is a projection method that allows an easy visualization of all the information contained in a dataset [20,21]. In addition, PCA helps to find out in what respect a sample is different from others and which variables contribute most to this difference.

LDA is one of the most used classification procedures. It has been widely used and proven successfully in many applications. The method maximizes the variance between categories and minimizes the variance within categories.

ANNs are one of the promises for the future in computing. They offer an ability to perform tasks outside the scope of traditional processors. They can recognize patterns within vast datasets and then generalize those patterns into recommended courses of action. A major area where neural networks are being built into pattern recognition systems is the processor for sensors. Sensors can provide so much data that a few meaningful pieces of information can be lost. These neural network systems have been shown successfully in recognizing targets.

While determining the suitable network topology, the network processes the inputs and compares its resulting outputs against the desired outputs. Errors are then propagated back through the system, causing the system to adjust the weights that control the network. This process occurs over and over as the weights are continually tweaked. During the training of a network the same set of data is processed many times as the connection weights are ever refined.

## 3. Results and discussion

#### 3.1. E-nose response to tea aroma

Fig. 1 shows a typical response of 10 sensors during measuring a tea sample. Each curve represents a different sensor transient. The curves represent conductivity of each sensor against time due to the electro-valve action when the volatiles reached the measurement chamber [8]. In the initial period, the conductivity of each sensor was low, then increased continuously, and finally stabilized after about 35 s. In this research, response values of each sensor at 15, 30, 45 and 60 s were extracted and analyzed individually. In this way, response values that represented the different phases of the curve were explored and other response values with little significance were discarded.

#### 3.2. Variance analysis

## 3.2.1. Effect of the mul-factor

The volume of the vial and the headspace generated time were the important parameters; they influenced the response values of the sensors according to a certain mass of tea [20]. To evaluate the effects of the volume (V: 50, 150, 250 and 500 ml), the headspace generated time (HGT: 0.75, 1 and 2 h) and collection time (CT: 1, 2, 3, ..., 60 s) on the response signals of the Enose to tea A280 (the data are the average value of 10 sensors signals), statistical analysis was performed by using statistical



Fig. 1. Response curves of the 10 sensors to the tea sample (equilibrated for 0.75 h; a vial of 250 ml; tea sample A280).

Table 3Result of the VAOAN for the three variances

Source	Sum of squares	Degree of freedom	Mean squares	<i>F</i> -value	Pr
HGT	0.189	2	0.189	0.478	0.489
V	37.426	3	12.475	31.505*	0.001
СТ	48.843	59	0.828	$2.091^{*}$	0.001
$HGT \times V$	5.019	6	1.673	4.225*	0.005
$HGT \times CT$	0.131	118	0.002	0.006	1.000
$V \times CT$	7.692	177	0.043	0.110	1.000
$HGT \times V \times CT$	1.324	354	0.007	0.019	1.000
Error	1710.621	4320	0.396		
Sum	1811.245	5039			

Average response signal of 10 sensors for A280. Headspace generated time: 0.75, 1 and 2 h; vial volume: 50, 150, 250 and 500 ml; collection time: 60 s.

\* Significant at the probability  $P \le 0.05$  level.

Table 4			
Result of multivariance	analysis for the	influence of vial	volume

Volume	Tea samples	Wilks' lambda	F	Pr
A1 (50 ml)	A120, A280, A380, A600	0.237	68.429 <sup>*</sup>	0.001
A2 (150 ml)	A120, A280, A380, A600	0.290	83.883*	0.001
A3 (250 ml)	A120, A280,	0.354	102.225*	0.001
A4 (500 ml)	A380, A600 A120, A280, A380, A600	0.299	86.383*	0.001

Headspace generated time 0.75 h; average at 60 s; 10 sensors.

\* Significant at the probability  $P \le 0.05$  level.

analysis system (SAS). The results are summarized in Table 3. The responses for other three groups of tea samples were quite similar, so that the analysis was omitted.

The magnitudes of the *F*-values in Table 3 indicated the relative importance of the factors. The volume of the vial and the collection time had a significant effect on the response value of the E-nose, and the interaction of the volume and the headspace generated time also had an obvious effect on the response value, but the headspace generated time had no significant effect on the response value. The results showed that after 0.75 h of equilibrium the headspace of the vial reached a steady state and a longer headspace generated time did not change the response value of the E-nose significantly. In order to save time the following experiment was performed after tea samples were equilibrated for 0.75 h.

### 3.2.2. Effect of vial volume

The influence of different vial volumes on the response of the E-nose for four tea groups was analyzed by the multivariance analysis. In this section, only the datasets obtained when tea samples were equilibrated for 0.75 h based on Table 3 were analyzed (totally:  $15 \times 4 \times 4 = 240$  samples). The 10 sensors were considered as 10 variables (indices). The average of response signals in 60 s were computed for each sensor and used for analysis. The results are listed in Table 4. Different vial volumes have significant effect on the E-nose response signal for the four tea groups, as obvious from the *F*-values. The *F*-value was the greatest (*F* = 102.23) when the vial was A3 (250 ml).

### 3.2.3. Effect of collection time

Response values of the E-nose at four different collection times (15, 30, 45 and 60 s) were analyzed by the multivariance analysis for the four groups of tea samples. The headspace generated time of 0.75 h and the vial volume of 250 ml were used according to Tables 3 and 4. The 10 sensors were still considered as 10 variables (indices). Response values at different collection times were analyzed for the four groups of tea samples. The results are shown in Table 5. Different collection times had a significant effect on the E-nose response value for the four tea groups, as obvious from the *F*-values. The difference in E-nose response value among the four tea groups was obvious at the four collection times, especially at 60 s.

Table 5 Result of multivariance analysis for the influence of collection time

Collection time	Samples	Wilks' lambda	F	Pr
15	A120, A280, A380, A600	0.001	133.010*	0.001
30	A120, A280, A380, A600	0.000	49.620 <sup>*</sup>	0.001
45	A120, A280,	0.000	21.370*	0.007
60	A120, A280, A380, A600	0.001	146.570*	0.001

\* Significant at the probability  $P \le 0.05$  level. Headspace generated time 0.75 h; 250 ml vial.

#### 3.3. Pattern recognition

#### 3.3.1. Principal components analysis (PCA)

The dataset obtained from a tea sample of A280 by using four different volume vials was analyzed by PCA. The headspace generated time was 0.75 h. The PCA plot is shown in Fig. 2.

As shown in Fig. 2, the clusters of the data were divided into two groups labeled A and B. The two groups could be attributed to the difference of the volume. Each group was composed of two subclusters. Within each group, the two subclusters were overlapped. This could be explained that the response of the E-nose was similar for the two subclusters in each group and was far different between group A and group B. A different volume of the vial had a significant effect on the E-nose response. Smaller the volume of the vials was, more unstable the response of the E-nose was. Further, the data points in the subcluster labeled '50 ml' were more dispersive than those in others. The subcluster labeled '250 ml' gave better results in the PCA plots (more convergent), which showed that the response signal of the E-nose was more stable by using a vial of 250 ml.

The headspace generated time was one of factors; in general a longer time may increase the sensor response [7]. Therefore,



Fig. 2. PCA plots for tea samples by using vials with different volumes (headspace generated time 0.75 h; tea sample A280).



Fig. 3. PCA plots of different headspace generated times (a vial of 250 ml; tea sample A280).

different headspace generated times (0.75, 1 and 2 h) were investigated based on the tea of A280 and a vial of 250 ml. The results are shown in Fig. 3. When the headspace generated time was 0.75 h, the plot cluster was a little convergent compared with those of the other times. However, the difference was not very significant. The headspace generated time did not have a significant effect on the four tea groups. This could be explained that after the headspace generated time of 0.75 h the volatile component in the headspace already reached a balanced state. A longer headspace generated time would not have a significant effect on the response signal of the E-nose. The results of PCA were the same as those of variance analysis. So, in the following experiments a vial of 250 ml and a headspace generated time 0.75 h were employed.

A series of measurements on the four tea groups with different quality grades were carried out. Fig. 1 shows the typical evolution of the signals generated by the E-nose. For all the tea samples, the response signals of the E-nose at four different collection times (15, 30, 45 and 60 s) were extracted and analyzed. The results are shown in Fig. 4. A120, A380 and A600 were separated in Fig. 4(a)-(d); especially in (a) and (d) a better discrimination result was obtained for A120, A380 and A600. Samples of A280 were overlapped completely with A380 in the plots of (a)–(d). The best classification rate by using PCA in three principal components was 75%. Four grade teas were not identified completely by the PCA. However, the results were in accordance with the fact that the difference of the quality grade among A120, A380 and A600 was obvious and the quality grade of A280 was close to that of A380, and therefore these samples share more similar characteristics.

#### 3.3.2. LDA analysis

The response values of the E-nose at four different collection times were analyzed by LDA for the four tea groups (Fig. 5). The responses of the E-nose to the A280 and A380 were not distinguished completely at 15 s. However, there was just little confusion. In Fig. 5(b)–(d) the four tea groups were distinguished completely by LDA, and the analytical results for the response value at 60 s were better than those at other collection



Fig. 4. Results of four tea groups by PCA at the four different times: (a) 15 s, (b) 30 s, (c) 45 s, and (d) 60 s.

times. The best classification rate by using LDA could reach 100%. The result was satisfied.

#### 3.3.3. ANN analysis

In this study, the ANN with a standard back-propagation algorithm was applied. The 180 samples (45 duplicates for each of the four groups) were divided into two groups; 120 samples (30 samples of each group) for the training set and the rest 60 samples (15 samples of each group) for the test set. In order to get better training results, more datasets were taken as training set. With this partition for the training and testing set, the correction rate of the simulated results for the training set was 100%. The



Fig. 5. Results of four tea groups by LDA at the four different times: (a) 15 s, (b) 30 s, (c) 45 s, and (d) 60 s.

Table 6 Result of ANN analysis

Sample	Desired outputs	Predict resulting outputs		Correct rate (%)
		Correct	Error	
A600	[1000]	15	0	100
A380	[0100]	12	3	80
A280	[0010]	13	2	86.67
A120	[0001]	15	0	100

input vector was 20 dimensions that were composed of the data at 60 s and averages for 1–60 s. The output vector was designed to be four-dimensional corresponding to the four quality grades of the teas. According to the dimension of the input and output vectors, the network topology was designed 20-12-4. The training epoch was 2000 and the training goal was 0.01. The result is shown in Table 6. Three samples of tea A380 were considered as the samples of tea A280, and two samples of tea A280 were estimated as the samples of tea A380.

# 4. Conclusions

The results of the ANOVA and multivariance analysis showed that the vial volume mainly influenced the sensor response in the experiments of 5 g tea samples. A large headspace volume was easier to achieve more reproducible and smoother responses than a small headspace volume at the same amount of tea samples and the same headspace generated time, whereas the influence of the headspace generated time was not obvious for the response of the E-nose.

The response value to sample A280 was overlapped with that to sample A380 completely and thus the two tea samples could not be classified by PCA. A120, A380 and A600 were separated because the quality grade of the teas was more obvious. The results showed that PCA was very useful to identify the tea grade clusters but it only fit to a handful of samples at a time. If the number of tea samples to be investigated increases, the identification of the tea grade clusters in a crowded PCA plot would become difficult.

The results of LDA were superior to those of PCA. The responses of the E-nose at four different collection times were analyzed, and it achieved a clear separation in all the cases using LDA analysis except for the response signal at 15 s. The best classification result was obtained by using the response signal at a collection time of 60 s. This result could be used in further studies to extract the feature vector.

The result of ANN analysis gave a correct discrimination percentage of 100% for tea samples of A120 and A600. The correct discrimination percentage for samples of A280 and A380 was 80% and 86.67%, respectively. The final correct rate of ANN analysis was 90%.

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## References

- T. Rajamäki, H.L. Alakomi, T. Ritvanen, E. Skyttä, M. Smolander, R. Ahvenainen, Application of an electronic nose for quality assessment of modified atmosphere packaged poultry meat, Food Contr. 17 (2006) 5–13.
- [2] S. Panigrahi, S. Balasubramanian, H. Gu, C. Logue, M. Marchello, Neuralnetwork-integrated electronic nose system for identification of spoiled beef, LWT 39 (2006) 135–145.
- [3] G. Olafsdottir, P. Nesvadba, C.D. Natale, M. Careche, Multisensor for fish quality determination, Trends Food Sci. Technol. 15 (2004) 86–93.
- [4] S. Laberche, S. Bazzo, S. Cade, E. Chanie, Shelf life determination by electronic nose: application to milk, Sens. Actuators B 106 (2005) 199–206.
- [5] J. Brezmes, P. Cabré, S. Rojo, E. Llobet, X. Vilanova, X. Correig, Discrimination between different samples of olive oil using variable selection techniques and modified fuzzy artmap neural networks, IEEE Sens. J. 5 (2005) 463–470.
- [6] M. Garcia, M. Aleixandre, J. Gutierrez, M.C. Horrillo, Electronic nose for wine discrimination, Sens. Actuators B 113 (2006) 911–916.
- [7] J.P. Santos, M.J. Fernandez, J.L. Fontecha, J. Lozano, M. Aleixandre, M. Garcia, J. Gutierrez, M.C. Horrillo, SAW sensor array for wine discrimination, Sens. Actuators B 107 (2005) 291–295.
- [8] A.H. Gomez, J. Wang, G.X. Hu, A.G. Pereira, Electronic nose technique potential monitoring mandarin maturity, Sens. Actuators B 113 (2006) 347–353.
- [9] C. Di Natale, A. Macagnano, E. Martinelli, E. Proietti, R. Paolesse, L. Castellari, S. Campani, A. D'Amico, Electronic nose based investigation of the sensorial properties of peach and nectarines, Sens. Actuators B 77 (2001) 561–566.
- [10] J.E. Simon, A. Hetzroni, B. Bordelon, G.E. Miles, D.J. Charles, Electronic sensing of aromatic volatiles for quality sorting of blueberries, J. Food Sci. 61 (1996) 967–969.
- [11] S. Oshita, K. Shima, T. Haruta, Y. Seo, Y. Kagawoe, S. Nakayama, S. Kawana, Discrimination of odors emanating from 'La France' pear by semiconducting polymer sensors, Comput. Electron. Agric. 26 (2000) 209–216.
- [12] E. Moltoi, E. Selfa, J. Ferriz, E. Conesa, A. Gutierrez, An aroma sensor for assessing peach quality, J. Agric. Eng. Res. 72 (1999) 311–316.
- [13] J. Brezmes, E. Llobet, X. Vilanova, G. Saiz, X. Correig, Fruit ripeness monitoring using an electronic nose, Sens. Actuators B 69 (2000) 223–229.
- [14] C. Di Natale, A. Macagnano, E. Martinelli, R. Paolesse, E. Proietti, A. D'Amico, The evaluation of quality of post-harvest orange and apples by means of an electronic nose, Sens. Actuators B 78 (2001) 26–31.
- [15] J. Brezmes, M.L.L. Fructuoso, E. Llobet, X. Vilanova, I. Recasens, J. Orts, G. Saiz, X. Correig, Evaluation of an electronic nose to assess fruit ripeness, IEEE Sens. J. 5 (2005) 97–108.
- [16] R. Dutta, E.L. Hines, J.W. Gardner, K.R. Ksahwan, M. Bhuyan, Tea quality prediction using a tin oxide-based electronic nose: an artificial intelligence approach, Sens. Actuators B 94 (2003) 228–237.
- [17] R. Dutta, K.R. Kashwan, M. Bhuyan, E.L. Hines, J.W. Gardner, Electronic nose based tea quality standardization, Neural Networks 16 (2003) 846–853.
- [18] J. Goschnick, I. Koronczi, M. Frietsch, I. Kiselev, Water pollution recognition with the electronic nose KAMINA, Sens. Actuators B 106 (2005) 182–186.
- [19] T. Rajamaki, H. Leena, T. Ritvanen, E. Skytta, M. Smolander, R. Ahvenainen, Application of an electronic nose for quality assessment of modified atmosphere packaged poultry meat, Food Contr. 17 (2006) 5–13.
- [20] M. Falasconi, M. Pardo, G. Sberveglieri, I. Ricco, A. Bresciani, The novel EOS<sup>835</sup> electronic nose and data analysis for evaluating coffee ripening, Sens. Actuators B 110 (2005) 73–80.
- [21] S. Burattia, S. Benedetti, M. Scampicchio, E.C. Pangerod, Characterization and classification of Italian Barbera wines by using an electronic nose and an amperometric electronic tongue, Anal. Chim. Acta 525 (2004) 133– 139.

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