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Detection of Different Technology on Yunnan Pu'er Tea Aroma Using an Electronic Nose

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Abstract: In this study, we measured 8 kinds of typical Yunnan Pu'er tea utilizing Electronic Nose technology. The analyses are achieved by the software Winmuster and the analyzing methods include Principal Component Analysis (PCA), Linear Diseriminant Analysis (LDA) and loading. The PCA shows that the different aroma of Pu'er tea caused by different processing technic (fermented and unfermented) can be totally (100%) differentiated. The LDA shows that by choosing appropriate discriminant, we can discriminate two kinds of Pu'er tea that are manufactured by the same manufacturer in the same year but proceed by different technic. This illustrates that distinct discrepancy of components of volatiles exist in Pu'er tea proceed by different technic, which can be identified by Electronic Nose. The result of Loading indicates that out of 10 sensors, 3 key sensors labeled as 2, 7, 9 have responded acutely to tea aroma, which have contributed most to the identification. The overall result presents that this new quick and nondestructive technique-Electronic Nose is a effective way to evaluate the quality of tea through aroma, which can be used to the detection of aroma content of Yunnan Pu'er tea because of its excellent discrimination of fermented and unfermented tea.

Keywords: Aroma, electronic nose, Yunnan Pu'er tea

INTRODUCTION

As a world-class beverage, tea has been always considered to be a multi-functional health drink and become more and more popular recently. No matter in developing or developed countries, the consumption of tea is increasing because of its special components and health efficacy. Among various kinds of herbal tea, Yunnan Pu'er is globally renowned due to its long history, unique quality and outstanding efficacy (Shao, 2014). Pu'er tea is made up of fermented Yunnan large-leaf variety crude tea produced within a certain range of Yunnan province. It is a kind of tea with unique characteristic, categorized as "Unfermented" and "Fermented" according to the processing technic (GB/T 22111, 2008). Because of its unique flavor and health efficacy (Zhou *et al*., 2003; Zhao *et al*., 2005; Zhang *et al*., 2005) that is gradually known people, Pu'er tea becomes popular merchandise in both domestic and foreign markets (Ren *et al*., 2011). There is study show that Pu'er tea's unique aroma is formed by microorganism under wet and hot condition during the pile fermentation process. The component of aroma is closely related the quality of Pu'er tea and it is the most important of its price determinant (Zhang *et al*., 2007). Therefore, the component of its aroma is the hot spot of Pu'er related study. Currently, the main method to analyze its component is gas phase chromatography-mass spectrography, searching mass-spectrogram corresponding to peak spectrum of each color. The higher the matching degree is, the higher dependability of characterization is (Lu *et al*., 2006). However, during the real process of analyzing, we observe that the components of aroma contain various kinds of Isomer. Because of their similarity in structure, there is no distinct difference between their mass-spectrogram, which makes it hard to establish the chemical makeup of a compound accurately. Therefore, we need to integrate other method to evaluate.

The Electronic Nose technology is an innovative BioMimetic detection technique, which is designed for the analysis and identification of complex volatile organism. It is based on MOX Sensor Array technology and Mode Identification Technology. Instead of analyzing partial odor information or quantitatively/qualitatively evaluating several elements of sample (Di Natale *et al*., 1998), it gives comprehensive information about volatile components of odor, called "scent-fingerprint" data (Bolin *et al*., 2011), which is the hotspot and tendency of recent detection and research of tea aroma's quality (Yu *et al*., 2003). The rise of Electronic Nose technology has attracting people's attention about the potential of comprehensive analysis of scent information. Recently, the Electronic Nose technology has been applied in various fields including food and beverage industry (Xiaobo *et al*., 2005; Shi *et al*., 2005; Labreche *et al*., 2005; Rajamabki *et al*., 2006; Panigrahi *et al*., 2006; Brezmes *et al*., 2005). One of the most important

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applications is distinguish samples by their volatile. This study is based on three representative Pu'er tea: Dayi 7542(Unfermented), Dayi 7572(Fermented), FuYuanChang Sanxing Sheng(Unfermented) and FuYuanChang Sanxing Shu (Fermented). We have applied Sensor Electronic Nose to analyze the "scent fingerprint". To analyze samples, we have extracted characteristic values of 10 sensors and then adopted PCA, LDA and Loadings as main distinguishing methods to identify the scent quality of Pu'er tea been processed by processing technic.

MATERIALS AND METHODS

Main materials and reagent: This study adopted tealeaves from two of Yunnan's main tea production field: Menghai and Lincang. The samples are Dayi 7542 (Unfermented), Dayi 7572 (Fermented), Fuyuanchang Sanxing Sheng(Unfermented) and Fuyuanchang Sanxing Shu (Fermented), specified in the Table 1:

Main devices and equipments: The Electronic Nose system is PEN3 from AIRSENSE, Germany. This Electronic nose contains 10 different MOX sensor, forming the sensor array.

Methods: Direct Headspace Suction method: putting 10 g tealeaves to transparent plastic cup, injecting 100 mL boiling water, covering plastic wrap, testing by Electronic Nose after 10 min until the 21 samples are all finished.

Electronic nose measuring conditions: Sampling frequency: 1 sec/set; self-cleaning frequency of sensor: 60 sec; sensor resetting frequency: 10 sec; sample preparing frequency: 5 sec; sampling flow: 300 mL/min; analytical sampling frequency: 60 sec.

Processing of data: During the data collecting of each sample in this experiment, the response of each sensor could be examined by checking the changing curve of responding signal, the signal value at each time point from each sensor and the star-shaped radar chart or fingerprint histogram. Through changing sensor setting, we can check the different responses under conditions with different numbers of sensors. Because each sensor is sensitive to a specific kind of characteristic gas, we can determine which kind of characteristic gas the sample volatilized during the analyzing process.

To distinguish samples, the characteristic values from 10 sensors are selected and analyzed by PCA, LDA and Loadings. By applying PCA, the discrepancy

Table 1: Tea Samples

Number	Name	Type	Class	Production date	Place of Production
1	DaYi7572(Fermented)	Ferment	7	2007	MengHai
2	DaYi7572(Fermented)	Ferment	7	2012	MengHai
3	DaYi7542 (Unfermented)	Unferment	4	2007	MengHai
4	DaYi7542(Unfermented)	Unferment	4	2012	MengHai
5	Fuyuanchang Sanxing Shu (Fermented)	Ferment	5	2006	LinCang
6	Fuyuanchang Sanxing Shu (Fermented)	Ferment	5	2007	LinCang
7	Fuyuanchang Sanxing Sheng (Unfermented)	Unferment	5	2006	LinCang
8	Fuyuanchang Sanxing Sheng (Unfermented)	Unferment	5	2007	LinCang

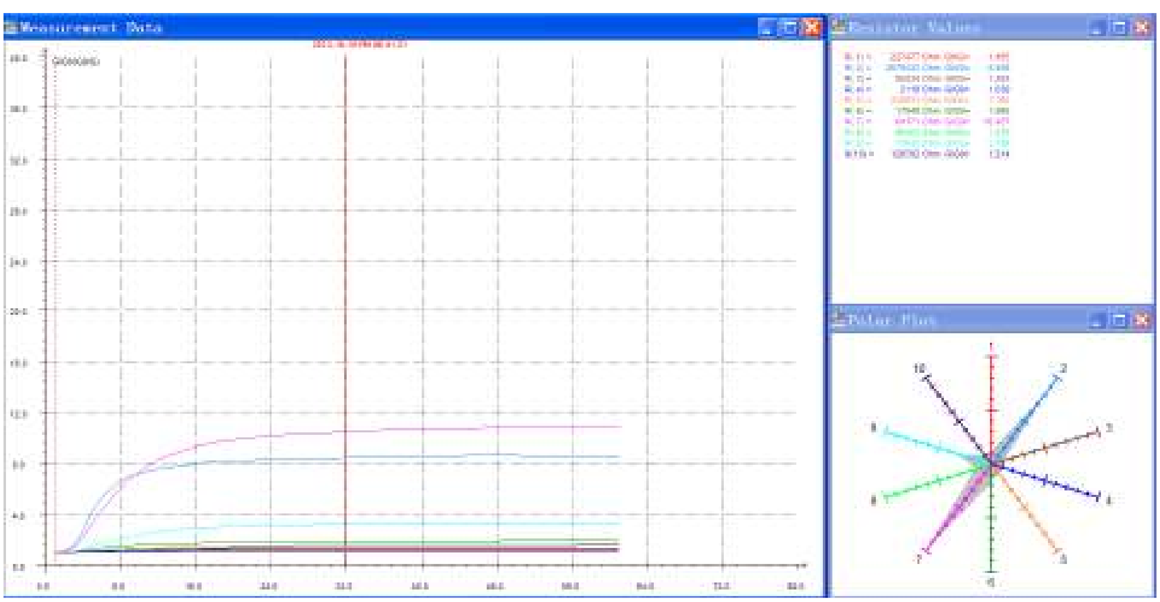

Fig. 1: Sample 1

among samples under each principal constituent can be observed and which component contributes most to the discrepancy among samples. LDA focuses on the classification of different categories and distance analysis among groups. Loadings is related to PCA. They're based on the same algorithm. However, in this experiment, Loadings is focused on the study of sensors. The contributions to sample differentiation from each sensor under certain sample can be determined by this method, which can be utilized to determine which kind of gas contributed most to the distinguishment.

Through Differential Fault Analysis (DFA), Euclidean distance, Mahalanobis distance and Correlation analysis, the category of unknown sample can be identified effectively, achieving an experiment result of verifying sample by applying Electronic Nose.

RESULT ANALYSIS AND DISCUSSION

The response from Electronic Nose to 8 tea samples' volatile: Figure 1 to 8, respectively, are characteristic radar chart of 8 kinds of samples, responding curve from 10 sensors to tea volatile and the corresponding G/GO (GO/G) of each sensor.

PCA analysis of 4 sets of tea samples executed by electronic nose:

Dayi 7572 and Dayi 7542 produced in 2007: The PCA results of 7542 and 7472 produced in 2007 are

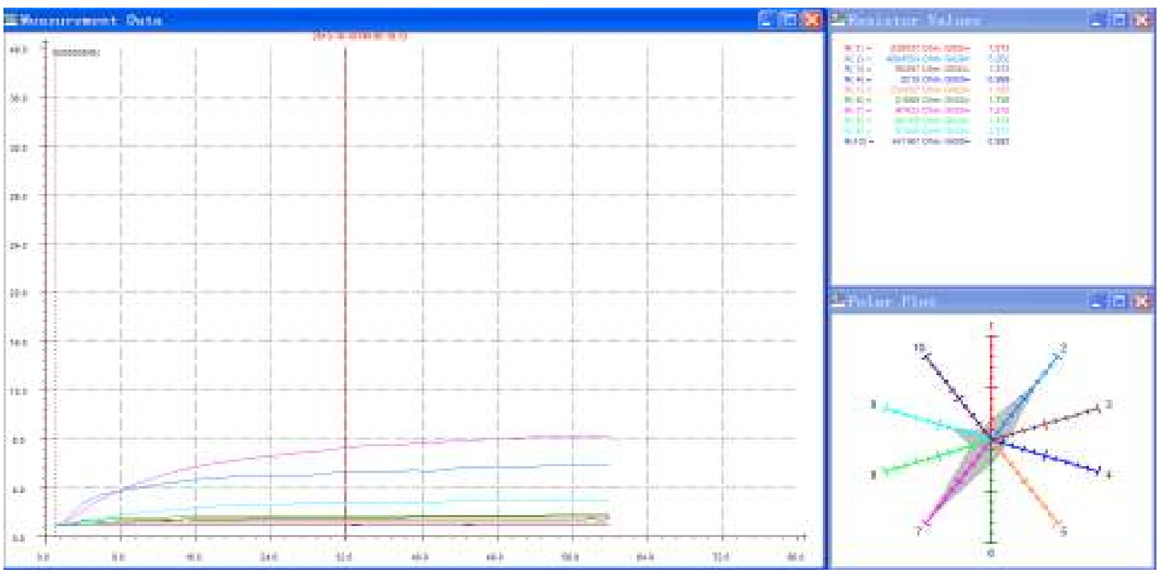

Fig. 2: Sample 2

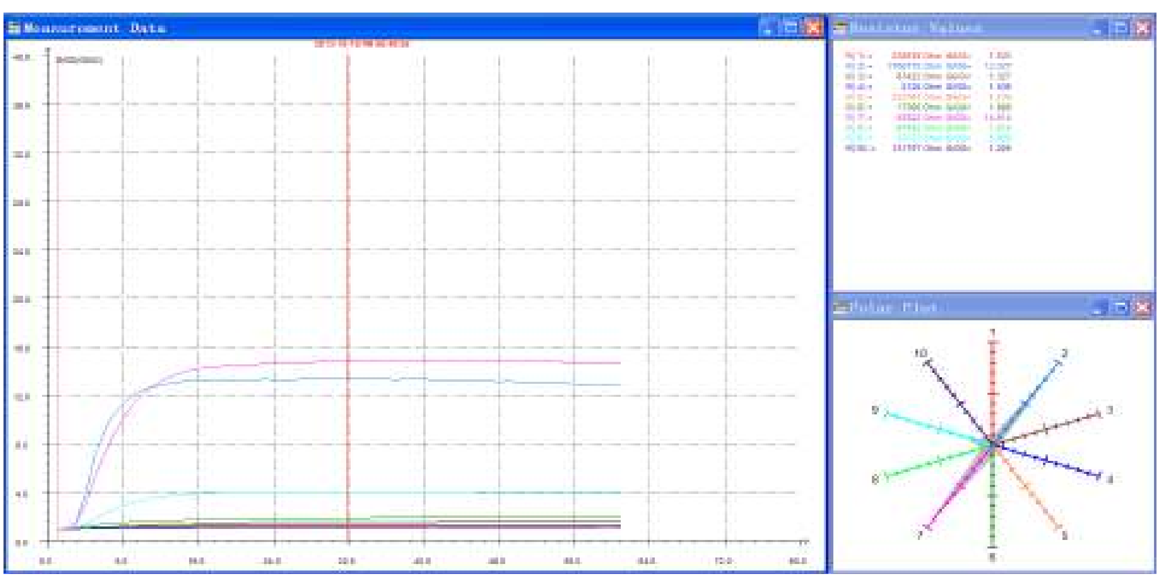

Fig. 3: Sample 3

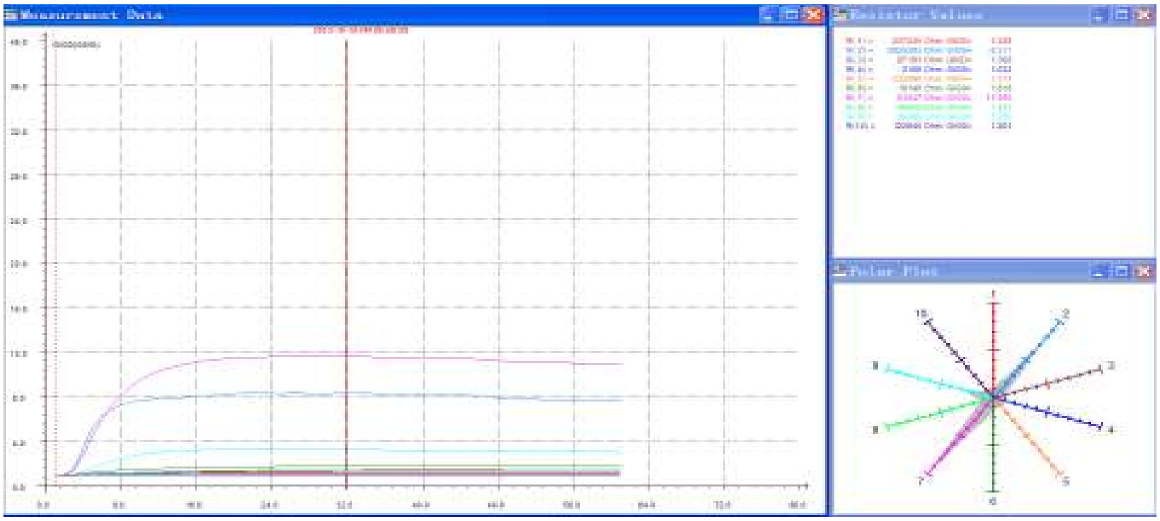

Fig. 4: Sample 4

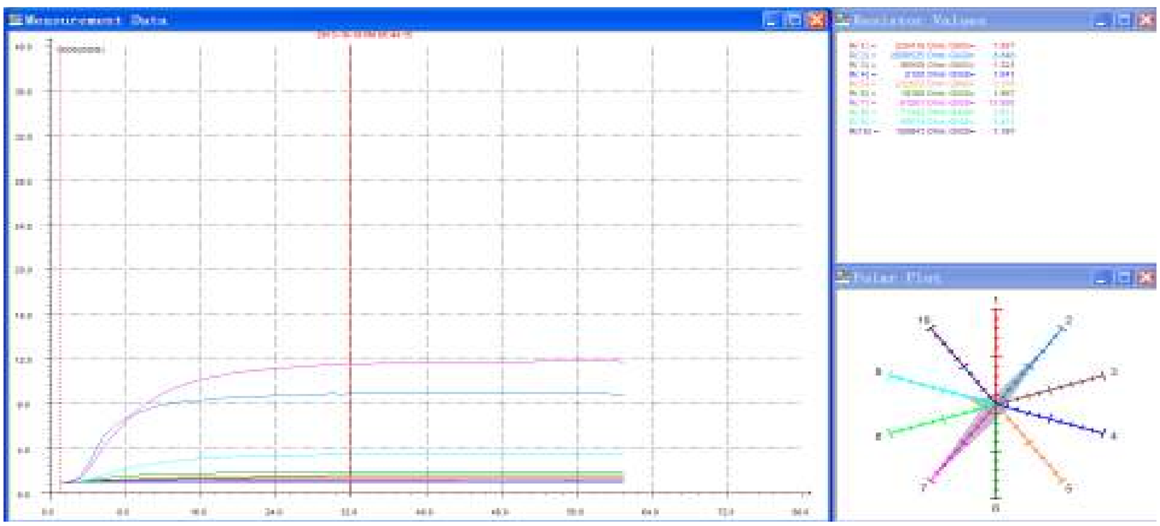

Fig. 5: Sample 5

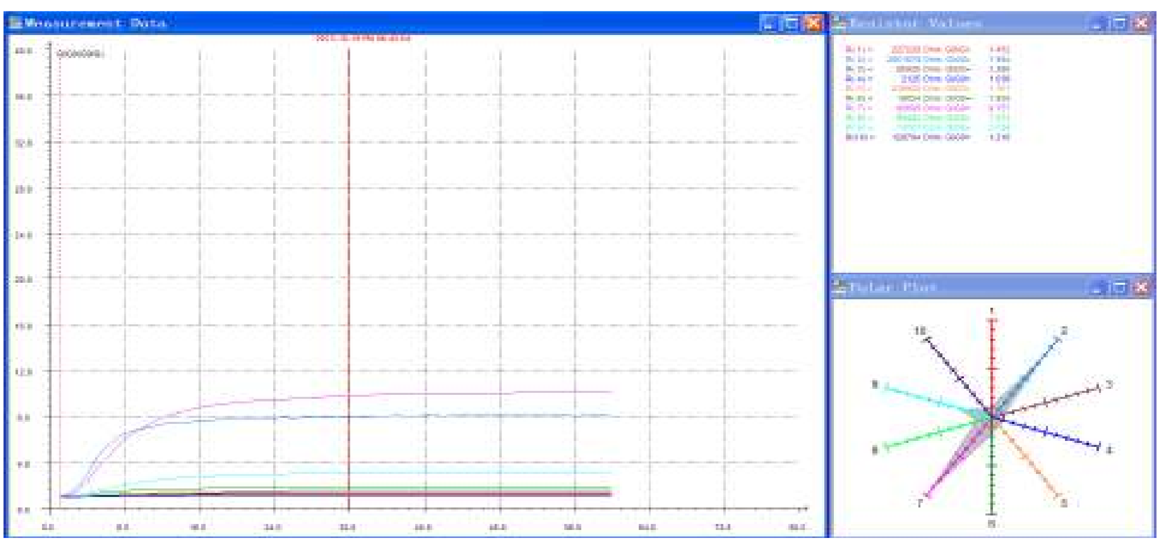

Fig. 6: Sample 6

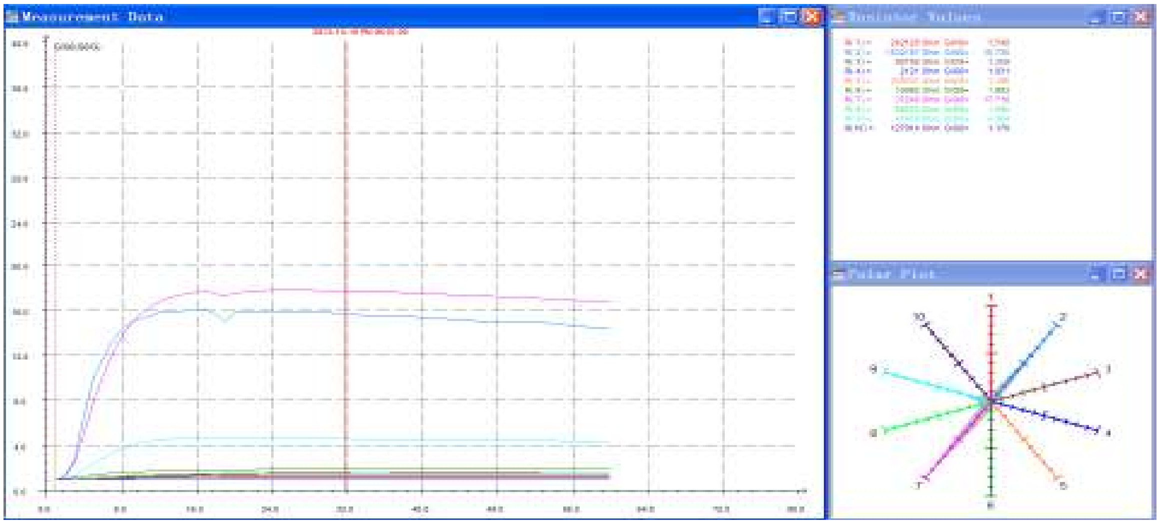

Fig. 7: Sample 7

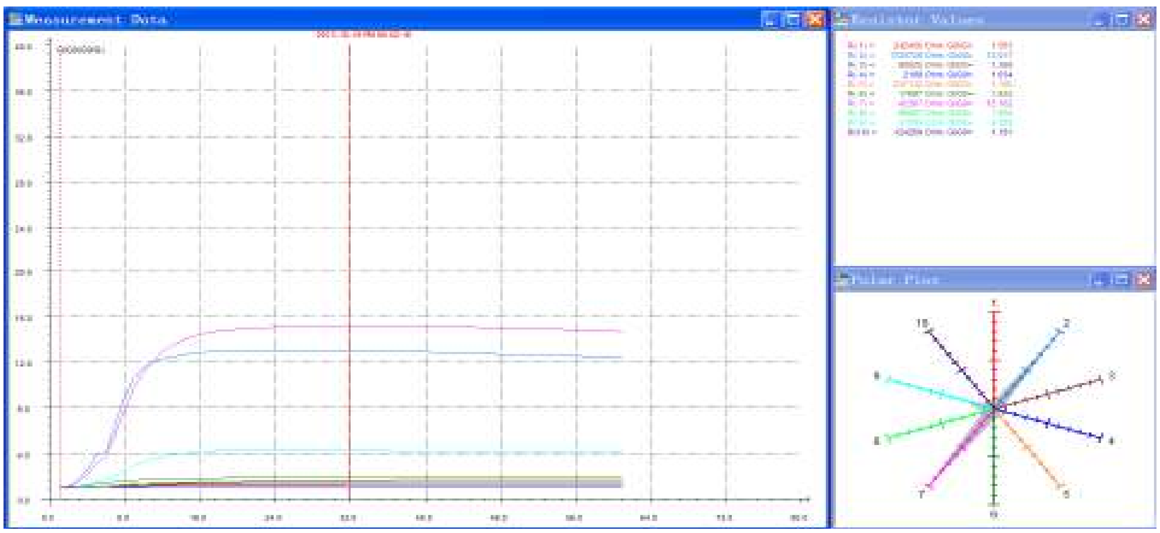

Fig. 8: Sample 8

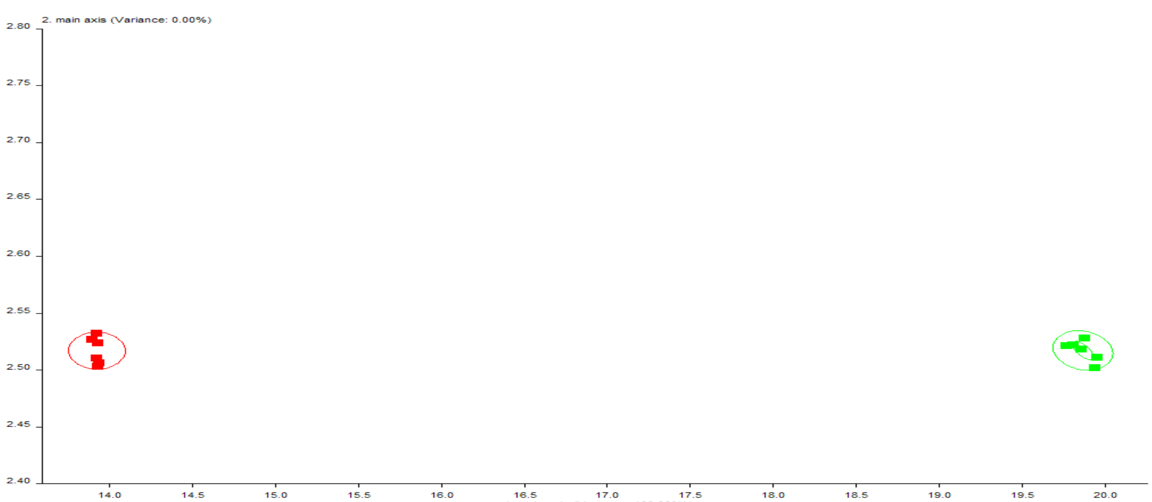

Fig. 9: The PCA-Analysis of tea sample 1and sample 3

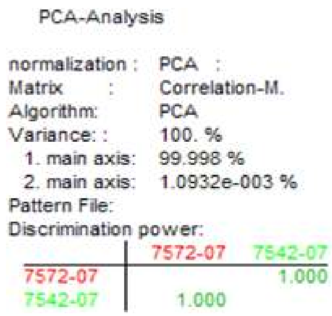

Fig. 10: The PCA-Correlation Matrix mode of sampls 1and sample 3

showed in Fig. 9 and 10. Under Correlation Matrix mode: the first component's contribution rate to distinction is 99.998%; the second component's contribution rate to distinction is 1.0932e-003%. The sum of contribution rates of these two major components is 100%. If the sum is larger than 90%, then it's sufficient to say that the two major components represent the sample's prime information characteristic. In the same time, the discrimination of PCA has reached 100%. The two graphs above present that the discrimination of two samples is distinct and there is an obvious difference between fermented and unfermented tea.

Dayi 7572 and Dayi 7542 produced in 2012: The PCA results of 7542 and 7472 produced in 2012 are showed in Fig. 11 and 12. Under Correlation Matrix mode: the first component's contribution rate to distinction is 99.956%; the second component's contribution rate to distinction is 3.3914e-002%. The sum of contribution rates of these two major components is 99.99%. If the sum is larger than 90%, then it's sufficient to say that the two major components represent the sample's prime information characteristic. In the same time, the discrimination of PCA has reached 100%. The two graphs above present that the discrimination of two samples is distinct and there is an obvious difference between fermented and unfermented tea.

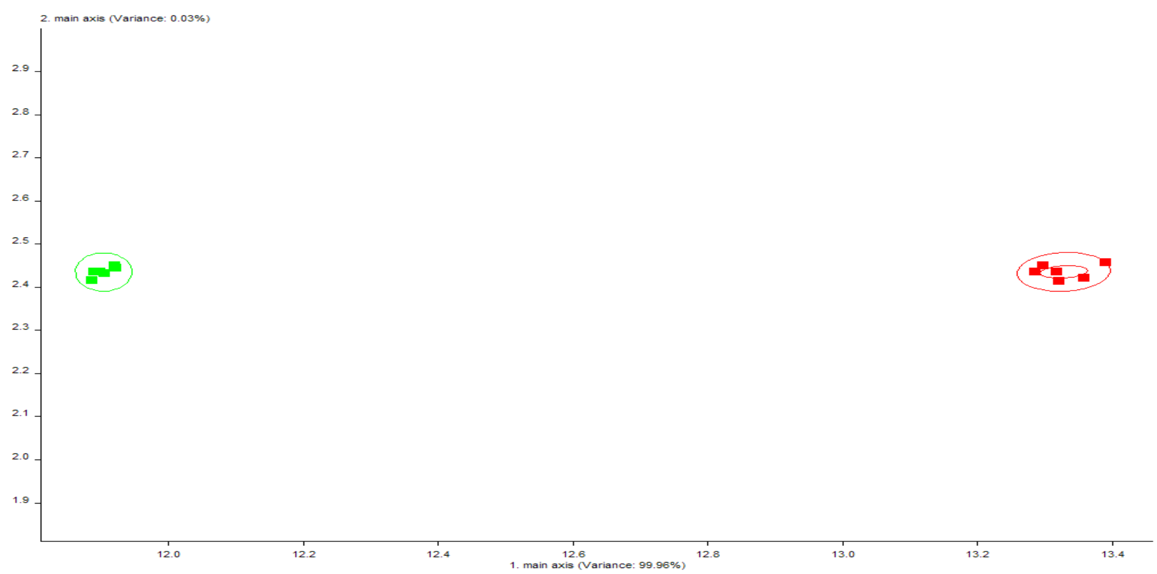

Fig. 11: The PCA-Analysis of sample 2 and sample 4

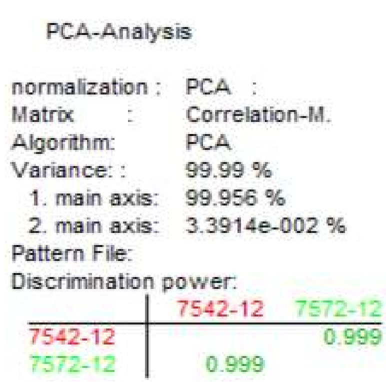

Fig. 12: The PCA-Correlation Matrix mode of tea sample 2 and sample 4

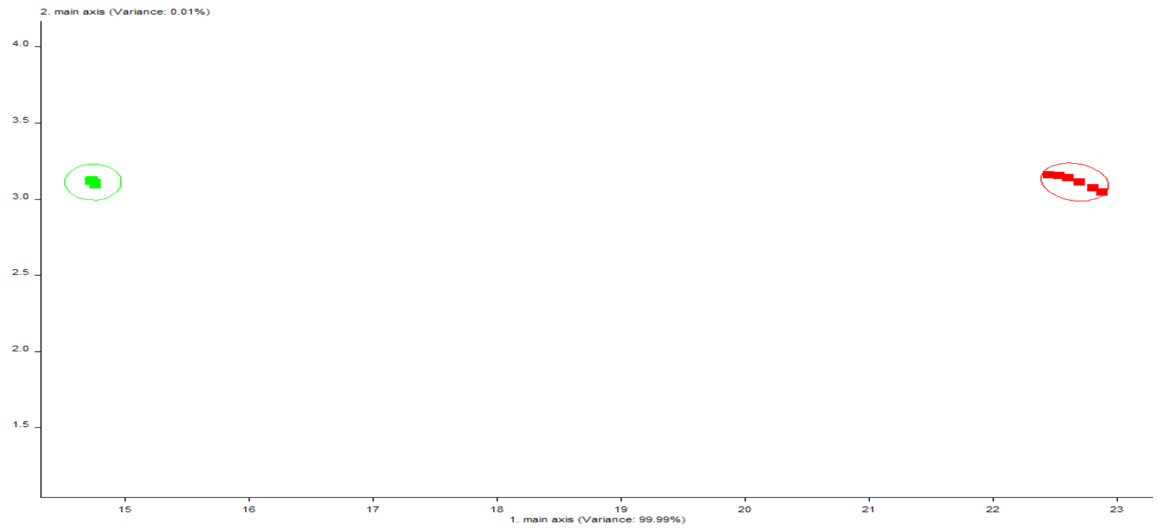

Fig. 13: The PCA-Analysis of sample 5 and sample 7

Fig. 14: The PCA-Correlation Matrix mode of sample 5 and sample 7

Fuyuanchang sanxing sheng (unfermented) and fuyuanchang sanxing shu (fermented) produced in 2006: The PCA results of 7542 and 7472 produced in 2006 are showed in Fig. 13 and 14. Under Correlation Matrix mode: the first component's contribution rate to distinction is 99.994%; the second component's contribution rate to distinction is 6.1394e-003%. The sum of contribution rates of these two major components is 100%. If the sum is larger than 90%, then it's sufficient to say that the two major components represent the sample's prime information characteristic. In the same time, the discrimination of PCA has reached 100%. The two graphs above present that the discrimination of two samples is distinct and there is an obvious difference between fermented and unfermented tea.

Fuyuanchang Sanxing unfermented and Fuyuanchang Sanxing fermented produced in 2007: The PCA results of 7542 and 7472 produced in 2007 are showed in Fig. 15 and 16. Under Correlation Matrix mode: the first component's contribution rate to distinction is 99.95%; the second component's contribution rate to distinction is 3.3914e-002%. The sum of contribution rates of these two major components is 99.99%. If the sum is larger than 90%, then it's sufficient to say that the two major components represent the sample's prime information characteristic. In the same time, the discrimination of PCA has reached 100%. The two graphs above present that the discrimination of two samples is distinct and there is an obvious difference between fermented and unfermented tea.

LDA analysis of 4 sets of tea samples executed by electronic nose:

- LDA analysis graphs of aroma of Dayi 7572 and Dayi 7542 produced in 2007
- LDA analysis graphs of aroma of Dayi 7572 and Dayi 7542 produced in 2012
- LDA analysis graphs of aroma of FuYuanChang Sanxing Sheng (Unfermented) and FuYuanChang Sanxing Shu (Fermented) produced in 2006
- LDA analysis graphs of aroma of FuYuanChang SanXing Sheng (Unfermented) and FuYuanChang SanXing Shu (Fermented) produced in 2007

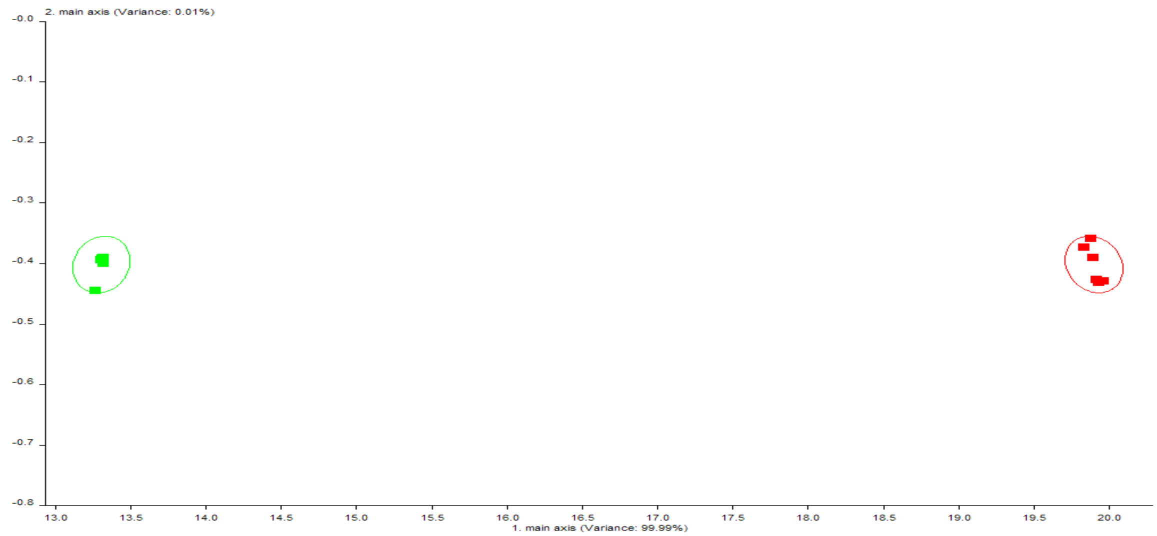

Fig. 15: The PCA-Analysis of sample 6 and sample 8

PCA-Analysis

normalization : PCA :
Matrix : Correlation-M.
Algorithm: PCA
Variance: : 99.999 %
1. main axis: 99.994 %
2. main axis: 5.6069e-003 %
Pattern File:
Discrimination power:

	三星-生茶-07	三星-熟茶-07
三星-生茶-07		1.000
三星-熟茶-07	1.000	

Fig. 16: The PCA-Correlation Matrix mode of sample 6 and sample 8

Fig. 17: LDA analysis graphs of aroma of sample 1 and sample 3

The results of LDA analysis shown in Fig. 17 to 20 indicate that through LDA, by choosing appropriate discriminant, could differentiate two kinds of tea produced by same manufacturer in the same year but processed by different process, which shows that there is significant difference of volatile between tea

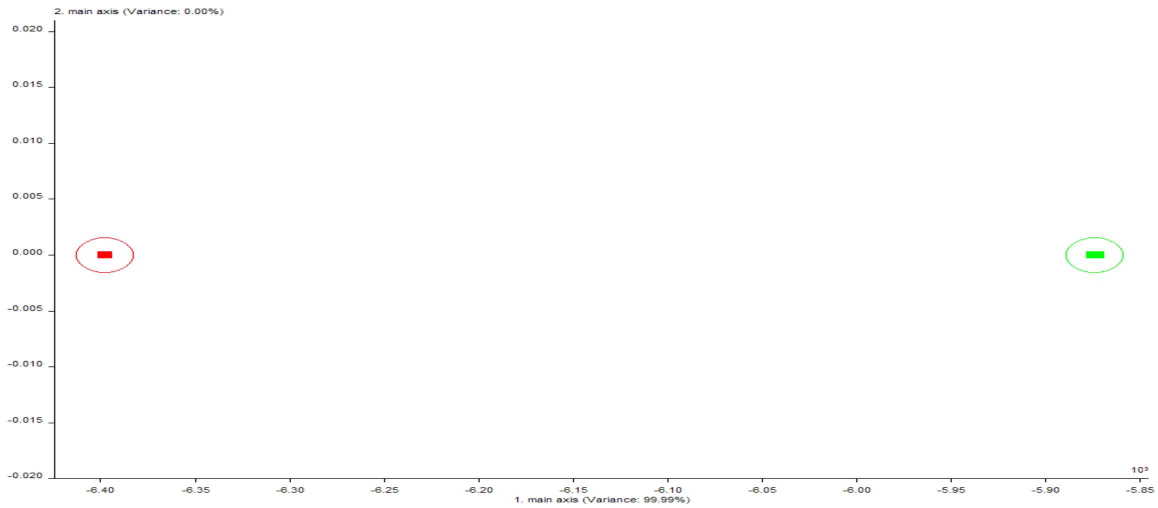

Fig. 18: LDA analysis graphs of aroma of sample 2 and sample 4

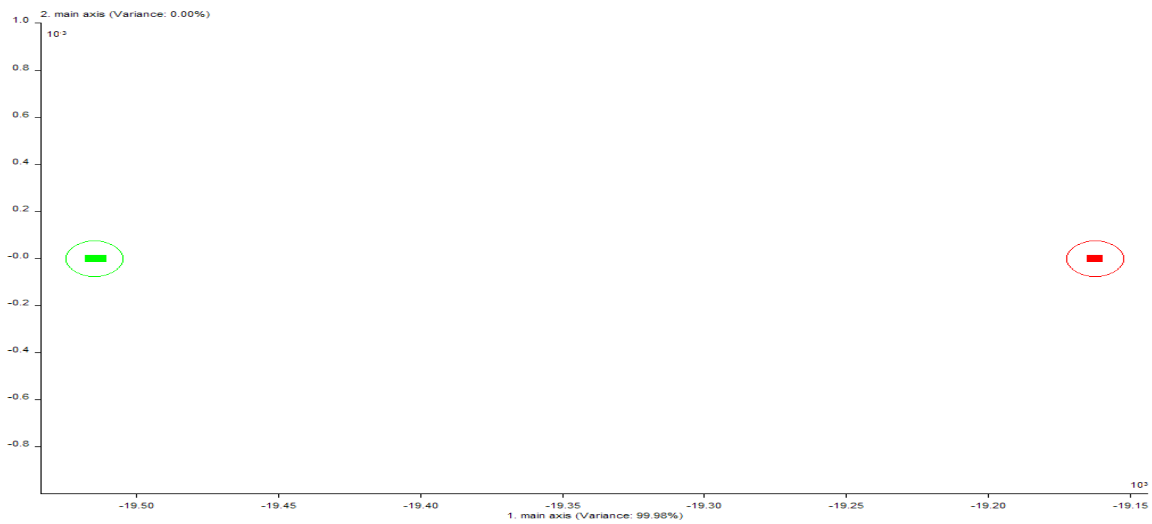

Fig. 19: LDA analysis graphs of aroma of sample 5 and sample 7

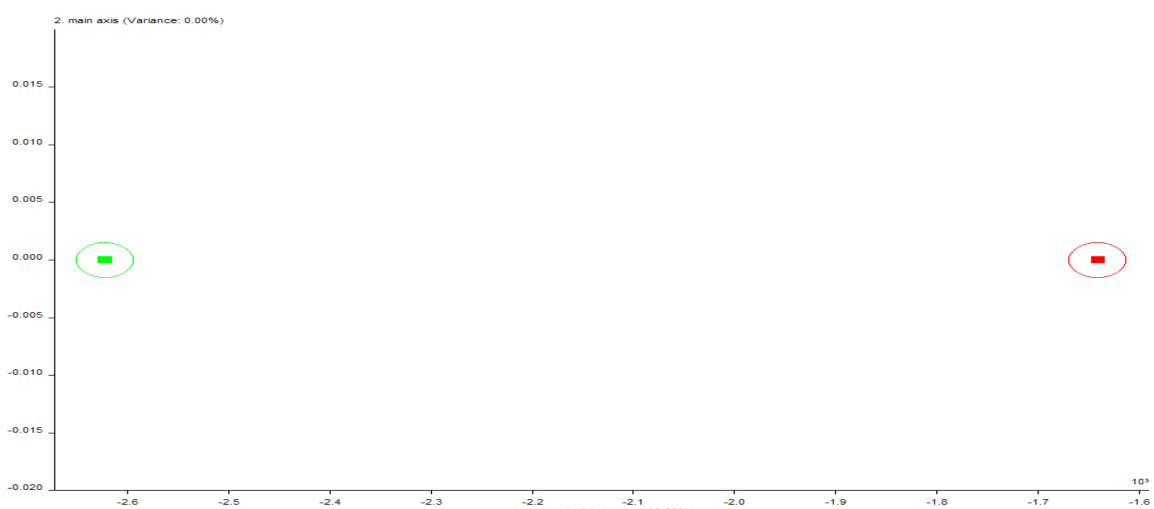

Fig. 20: LDA analysis graphs of aroma of sample 6 and sample 8

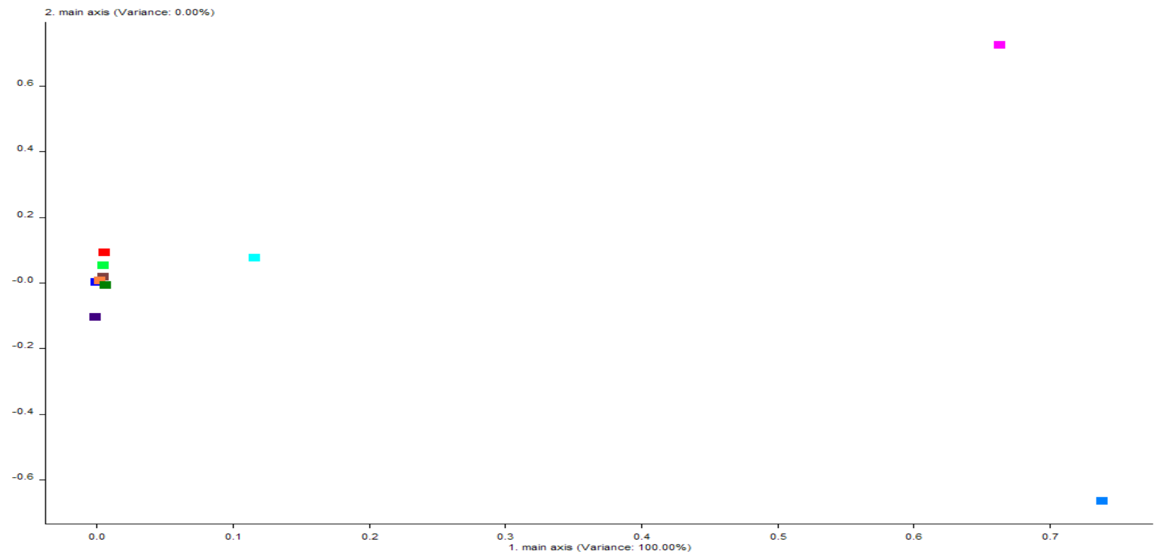

Fig. 21: Loadings-Analysis of sample 1 and sample 3

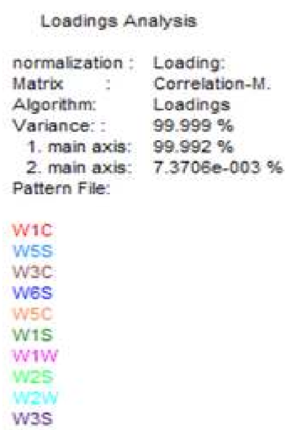

Fig. 22: Contribution of sensor

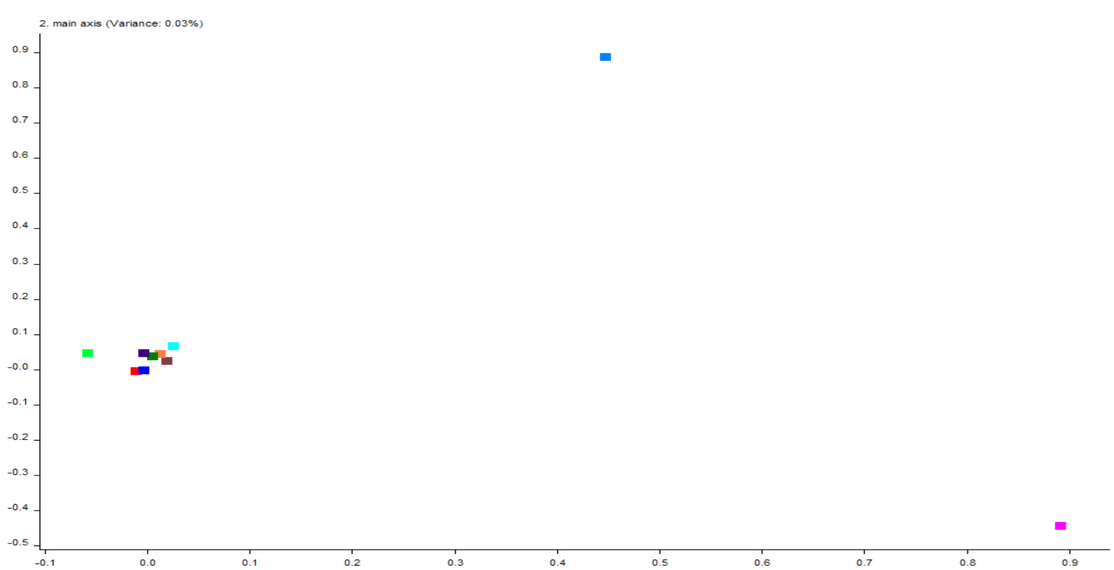

Fig. 23: Loadings-Analysis of sample 2 and sample 4

processed by different processing technique (fermented and unfermented), which can be detected by Electronic Nose.

Loading analysis of 4 sets of tea samples executed by electronic nose: The device PN3 contains 10 metal sensors. The Loading algorithm is mainly focused on the analysis of sensors. By utilizing this algorithm, the researchers could identify the significance contributed to the sample discrimination by each sensor. Consequently, which kind of gas plays the most important role in sample discrimination can be determined.

DaYi 7572 and DaYi 7542 produced in 2007: The correlation matrix from Loading analysis: the No.2 sensor contributes most to the first component differentiation, the following are No.7 and No.9 sensors and No.7sensor contributes most to the second component differentiation (Fig. 21 to 28).

DaYi 7572 and DaYi 7542 produced in 2012: The correlation matrix from Loading analysis: the No.7 sensor contributes most to the first component differentiation, the following are No.2 and No.9 sensors and No.2 sensor contributes most to the second component differentiation.

FuYuanCang Sanxing unfermented and Sanxing fermented tea produced in 2006: The correlation matrix from Loading analysis: The No.2 sensor contributes most to the first component differentiation, the following are No.7 and No.9 sensors and No.7 sensor contributes most to the second component differentiation.

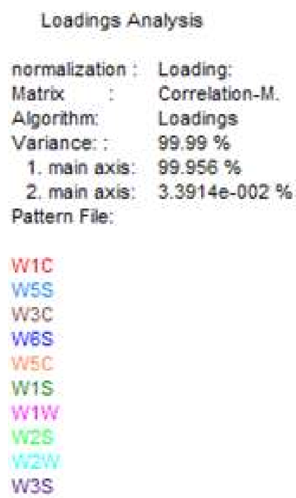

Fig. 24: Contribution of sensor

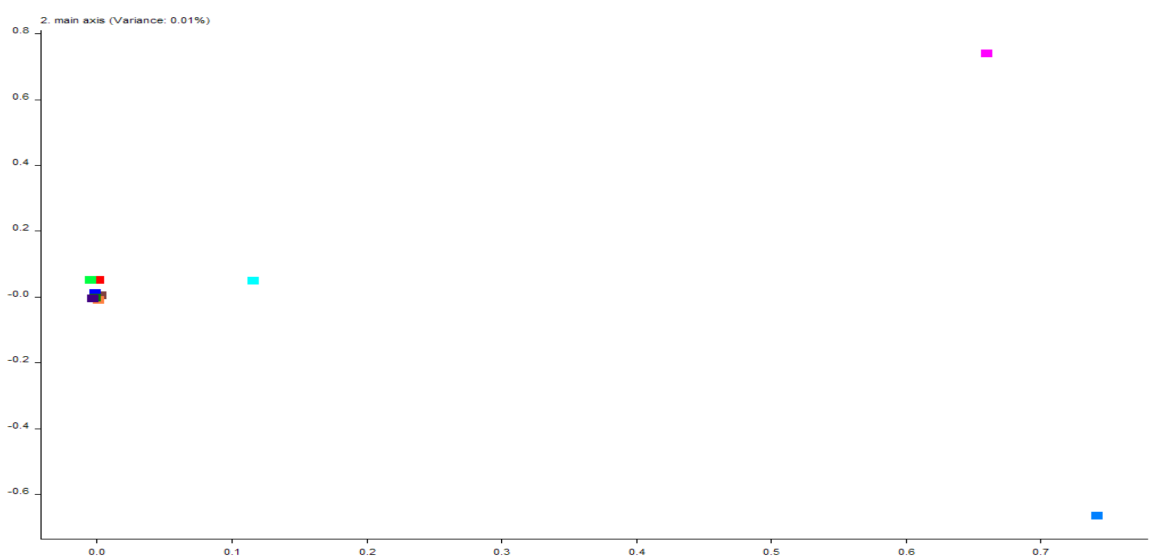

Fig. 25: LDA analysis graphs of aroma of sample 5 and sample 7

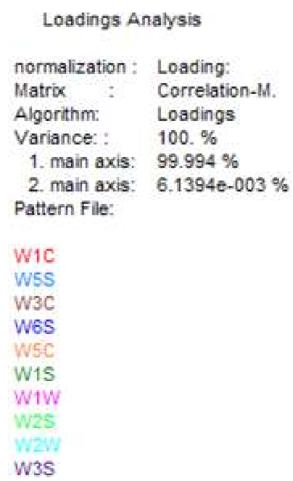

Fig. 26: Contribution of sensor

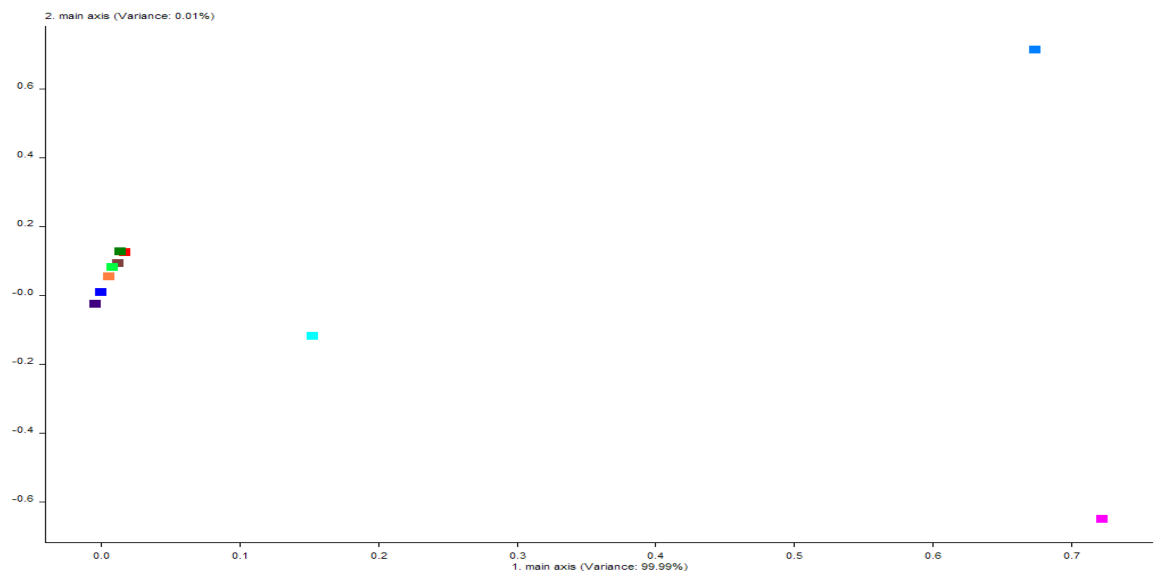

Fig. 27: LDA analysis graphs of aroma of sample 6 and sample 8

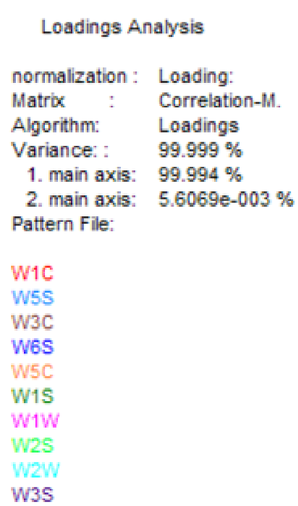

Fig. 28: Contribution of sensor

FuYuanCang Sanxing unfermented and FuYuanCang Sanxing fermented tea produced in 2007: The correlation matrix from Loading analysis: the No.7 sensor contributes most to the first component differentiation, the following are No.2 and No.9 sensors and No.2 sensor contributes most to the second component differentiation.

DISCUSSION

In this research, 8 representative kinds of Yunnan Pu'er tea are analyzed by utilizing Electronic Nose technique and the relationship between the change of tea's component of aroma and the change of Electronic Nose signal. Through Winmuster, the Principal Component Analysis (PCA), Linear Diseriminant Analysis (LDA) and Loading analysis are adopted. The result shows that by adopting Electronic Nose as detecting method, with AIRSENSE's PEN3 Electronic Nose, the two kinds of Pu'er tea that is produced in the same year by the same manufacturer can be differentiated and fermented/unfermented tea can be differentiated easily. Among all the sensors, the No.2, No.7 and No.9 sensor are key sensors in this analysis. They respond acutely to tea aroma and contribute most to the discrimination. According to the description of PN3 sensor performance, nitrogen oxides and sulfide plays the most important role in sample discrimination can be determined. Electronic Nose possesses the advantages including requiring easier process of sample, quicker analyzing speed and clearer result. Its complementary software supplies multifunctional and easy-operating multivariable statistical analyzing algorithm, which can provide reference to fast-identification of aroma quality. Therefore, the method constructed to detect the tea aroma generated by different kinds of Yunnan Pu'er tea processed with different processing technique could make Electronic Nose be utilized in researches focusing on the components of Yunnan Pu'er tea aroma extensively. It is able to differentiate Pu'er tea processed by different processing technique, grown in different place, produced in different year and classified differently.

REFERENCES

Brezmes, J., P. Cabré, S. Rojo and E. Llobet, 2005. Discrimination between different samples of olive oil using variable select ion techniques and modified fuzzy artmap neural networks [J]. IEEE Sensors J., 5(3): 463-470.

Bolin, S., Z. Lei, Z. Ruicong, X. Xingjun and Z. Dazhou, 2011. Aroma quality discrimination of Xihu-Longjing tea by electronic nose [J].Trans. CSAE, 27(Supp.2): 302-306.

Di Natale, C., A. Macagnano, R. Paolesso and *et al*., 1998. Electronic nose and sensorial an alysis: Comparison of performances in selected case [J]. Sensor Actuators B, 50(2): 246-252.

GB/T 22111, 2008. National Standard of People's Republic of China. Geographical Indication Products Pu-erh Tea.

Labreche, S., S. Bazzo, S. Cade and e. chanie, 2005. Shelf life determination by electronic nose: Application to m ilk [J]. Sensors Actuators B: Chem- ical, 106(1): 199-206.

Lu, H., Q.L. Li and M.F.Wang, 2006. Analysis of the pathways of the formation of the important aroma materials in Pu'er tea during post-fermentation and aging [J]. J. Southwest Agri. Univ., Natural Sci., 28(5): 820-824.

Panigrahi, S., S. Balasubramanian, H. Gu, C. Logue and M. Marchello, 2006. Neural-network- integrated electronic nose system for identification of spoiled beef [J]. LW T-Food Sci. Technol., 39 (2): 135-145.

Ren, H.T., B. Zhou, K.G. Xia and *et al*., 2011. Compare analysis of fermentation degree on the aromatic components of pu-erh tea [J]. Food Res. Develop., 32(11).

Rajamabki, T., H.L. Alakomi, T. Ritvanen, E. Skyttäa, M. Smolandera and R. Ahvenainena, 2006. Application of an electronic nose for quality assessment of modified atmosphere packaged poultry meat [J]. Food Control, 17(1): 5-13.

Shi, Z., Z. Chuncheng and Y. Changming, 2005. Experimental study on a bionic nose system [J].Trans. Chinese Soc. Agri. Mach., 36(2): 70-72.

Shao, W., 2014. Science Reading on Pu 'er tea Health Benefits [M]. Yunnan Science and Technology Press, China, 2014:1.

Xiaobo, Z., Z. Jiewen, P. Yinfei and H. Xingyi, 2005. Quality Evaluation of apples using electronic nose based on GA-RBF network [J]. Trans. Chinese Soc. Agri. Mach., 36(1): 61-64.

Yu, Y., J. Wang and M. Zhong, 2003. Research developments of electronic nose and its application in processing of agriculture products [J]. J. Zhejiang Univ., Agri. Life Sci., 29(5): 579-584.

Zhou, H., M. Ming, H. Jun and *et al*., 2003. Research progress in quality formation mechanism of Pu'er tea and its functions [J]. J. Tea, 29(2): 75-77.

Zhao, L., H. Zhou and W. An, 2005. Study on the health functions of Pu 'er tea [J]. Food res. Develop., 26(2): 114-118.

Zhang, D., Z. Shi and Y. Liu, 2005.The progress on pharmacological effects of Pu 'er tea [J] Tea Fujian, 1: 43-44.

Zhang, L., W. Chen, D. Wang and *et al*., 2007. Effect of drying methods on the aromatic character of Pu'er tea [J]. J. Tea Sci., 27(1): 71-75.