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Identification and Classification of Flavors in 12 Tobacco Blends Using Electronic Nose

YI HAN[1], YUANXING DUAN[1], TAO ZHANG[1], XIA ZHANG[1], GUANGYU YANG[1], XIA MENG[2], ZHIHUA LIU[1] and CHENGMING ZHANG[1,*]

[1]Key Laboratory of Tobacco Chemistry of Yunnan Province, Yunnan Academy of Tobacco Science, Kunming 650106, P.R. China
[2]Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, Kunming 650223, P.R. China

*Corresponding author: Fax: +86 871 68323296; Tel: +86 871 68315280; E-mail: 13987643543@139.com; 15288389322@163.com

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Cigarette quality is commonly evaluated on the basis of flavor characteristics of the tobacco blend. Flavor analysis of a cigarette is typically performed by human organoleptic analysis, which is often expensive, less objective and harmful to health. An approach using a metal oxide sensor-based instrument (electronic nose) for headspace analysis was explored as an alternative to human sensory perception for consistent qualitative analysis of flavors in tobacco blends. Chemometric methodologies including principal component analysis, soft independent modeling of class analogy and statistical quality control were used for data processing, identification and classification. The use of the electronic nose technique to qualitatively distinguish among six flavors in 12 tobacco blends was demonstrated. Therefore, the instrument can potentially be used for identifying the raw materials and flavored formulations used for flavoring in cigarette production.

Keywords: Flavor analysis, Electronic nose, Tobacco blend, Cigarette, Identification, Classification.

INTRODUCTION

It is well known that a classic approach to the evaluation of the organoleptic quality of cigarettes is based on the exploitation of sensoric analysis, *i.e.* analysis employing the use of taste, flavor, vision and touch senses, carried out by a group of properly trained estimators. Sensoric analysis can be a perfect tool in carrying out market tests of consumer preferences, but because of its reliance on human participation, it contains many limitations. The basic shortcomings of sensoric analysis are low repeatability and reproducibility of results connected to many subjective factors, such as sensoric susceptibility of the estimating person, state of health, comfort, adaptation or fatigue, or objective factors-conditions of carrying out the analysis[1]. The greatest limitation, however, is the potential health risk to estimators because of various toxic components in cigarette smoke inhaled during the sensoric analysis.

Electronic nose is a device developed to reproduce the human olfactory system. It consists of three main parts: sampling system of flavors to be analyzed, sensor system based on an array of multiple sensing elements, or chemical sensors and a data analysis and signal processing unit for obtaining information such as aromatic profiles, flavors and their features, from the original data. Nowadays, commercial instruments take into account two main types of gas sensors, metal oxide sensors and conducting polymer resistive sensors[2]. Metal oxide sensors have high sensitivity (sub-ppm levels for some gases) and respond to oxidizing compounds (zinc oxide, tin dioxide, titanium dioxide, iron oxide) and some reducing compounds, mainly nickel oxide or cobalt oxide. From a chemical point of view, the sensing reaction is based on an oxygen exchange between the volatile gas molecules and the metal coating material. Electrons are attracted to the loaded oxygen and result in decreases in sensor conductivity[3].

As an electronic simulation system of the biological nose, the electronic nose has been developed rapidly in recent years and is widely used to analyze volatile profile characteristics of various products, including food, cosmetics and essential oils[4]. In the tobacco industry, the electronic nose has been utilized to identify cigarette brands[5], distinguish between tobacco types[6,7], analyze cigarette smoke[8], evaluate the quality of cigarettes and flavored cut tobacco[9,10], and control tobacco flavor[11].

In this paper, we describe the use of an electronic nose in the identification and classification of 12 tobacco blends used by different tobacco companies by analysing volatile flavor compositions.

EXPERIMENTAL

Sample preparation: Twelve tobacco blend samples were randomly collected from different commercial cigarette factories across China. 0.5 g of each tobacco blend sample was weighed and sealed in a 10 mL headspace vial for scent detection.

Electronic nose system: Alpha-MOS Fox 4000 (Toulouse, France) electronic nose (Fig. 1 and Table-1 for instrumental parameters) was used to measure volatile flavor compositions generated from tobacco blends in 12 different cigarette brands. Details on the construction and mechanism of the equipment can be found in work of Zhu *et al.*[12] Briefly, the electronic nose is comprised of three main parts: (i) headspace auto-sampler (ii) electronic nose unit (detector chamber) and (iii) data processing unit.

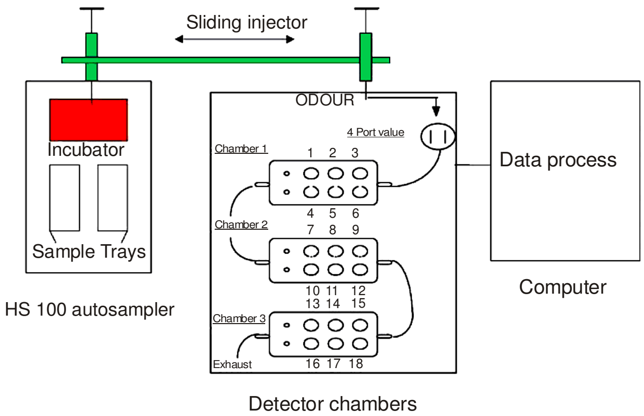

Fig. 1. Instrumental configuration of the electronic-nose 12

TABLE-1
ANALYTICAL CONDITIONS OF THE ELECTRONIC NOSE

Carrier gas	Synthetic dry air 150 (mL/min)
Sample preparation	-
Quantity of sample in the vial (g)	0.50
Total volume of the vial (mL)	10
Headspace generation	-
Headspace generation time (s)	1200
Headspace generation temperature (°C)	65
Agitation speed (rpm)	500
Headspace injection	-
Injected volume (mL)	2.5
Injection speed (mL/s)	2.5
Total volume of the syringe (mL)	5.0
Syringe temperature (°C)	75
Acquisition parameters	-
Acquisition time (s)	120
Time between injections (min)	10

The Alpha software provides various qualitative analysis methods on the basis of chemometric techniques, including Principal component analysis (PCA), discriminant factor analysis (DFA), soft independent modeling of class analogy (SIMCA) and statistical quality control (SQC). A comprehensive qualitative analysis integrated with PCA, SIMCA and SQC was established in this study to identify and classify the tobacco blends.

Partition of olfactive areas and discrimination of flavor clusters and classification and quality control analysis of flavor samples: We used PCA to give a representative map of the different olfactive groups and calculated the discrimination index, which indicates the extent of discrimination between samples in the two-dimensional PCA surface. Soft independent modeling of class analogy shows the composite spectrum of a flavor sample as a point on a three-dimensional plot. The projections from similar flavors cluster together on the plot and those that differ in their volatile composition cluster in different locations. Statistical quality control models were developed to discriminate outlier samples from desirable samples in the control defined acceptable area. Statistical quality control provides the ability to optimize the operating conditions for application and to rapidly access the quality of a product by comparing to a reference to predict new batch quality.

Based on the principal component analysis, the classification of unknown samples was further tested by fitting mathematical models of samples one by one. The most appropriate reference obtained by the fitting process was selected as the reference by employing SIMCA. If the automatically calculated recognition percentage is greater than 90 % the SIMCA model is valid.

RESULTS AND DISCUSSION

Partition of olfactive areas and discrimination of flavor clusters: Twelve tobacco blend samples (Y-1-Y-12) were analyzed and similar response patterns were found among the 12 samples (Fig. 2a and 2b). In order to analyze data more efficiently and accurately, only the maximum responses from each sensor were used. Results from the PCA suggest that Y-8 is clearly distinct from the other scents, whereas Y-1, Y-2, Y-3, Y-5 and Y-6 have similar flavor categories (Fig. 3). Y-4 is similar to Y-5 and Y-6, but sufficiently distinct to be given a unique flavor classification (Fig. 3). Y-7, Y-9 and Y-10 have the most similar flavor characteristics, as do Y-11 and Y-12.

The cumulative variance contribution rate was in excess of 85 % and reached 99.673 % in the PCA. This high value indicates that the raw image data can be adequately stored in the two-dimensional subspace related to the two principal components. As a result, six flavor clusters corresponding to the 12 tobacco blend samples were preliminarily discriminated.

Classification of flavor samples: A model was built on the basis of the DFA in order to compare unknown flavor samples (new flavor lots) to the reference (blend Y-8) and to identify whether unknown samples (Y-1-Y-7 and Y-9-Y-12) belonged to a sample or a group of samples defined by the PCA, employing SIMCA. The unknown samples fall outside the zone of acceptability (Fig. 4) and differ significantly from the model (Y-8). A successful discrimination model is accepted at an index between 80 and 100 and the identification of an unknown sample is accepted at a recognition percentage greater than 90 %[12]. The validation score is 92, indicating that a high degree of identification was achieved. Y-8 is obviously very different from the other samples and belongs to a separate flavor category.

Quality control analysis of flavor samples: In order to expand the capabilities of the electronic nose, SQC models were developed to define the qualified samples in the control defined acceptable area. Statistic quality control allows one to assess the quality of a product with an acceptable variability of this quality. Data on the Y-axis can consist of distances to the target product, concentrations, or sensory panel scores. Various bands can be defined based on the number of grades,

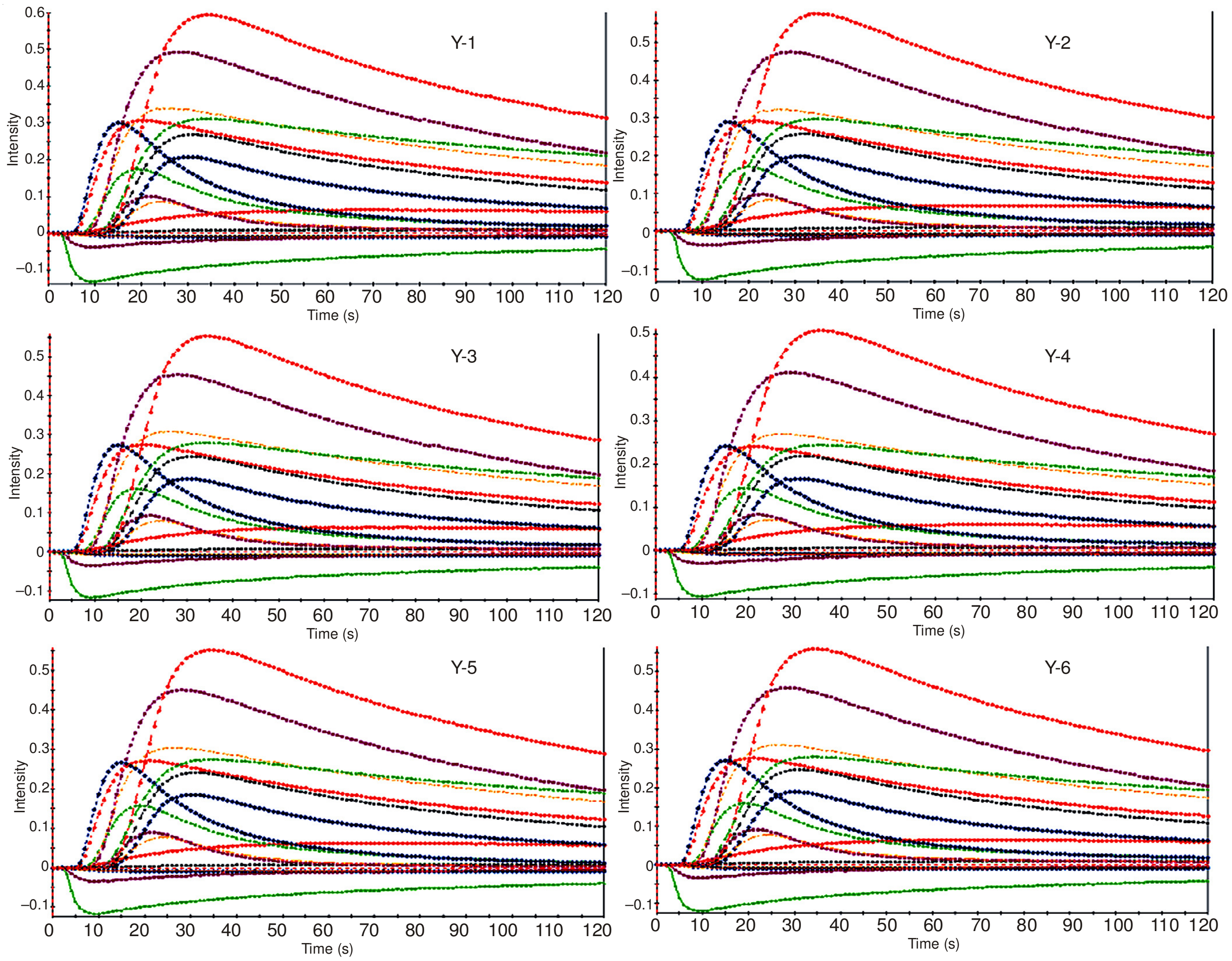

Fig. 2a. Raw sensor signals of tobacco blend samples Y-1-Y-6. Raw signals are presented in response to intensity changes of 18 sensors (indicated by coloured curves) as a function of time for each tobacco blend sample. Each curve in the plot represents the change for each sensor response during the acquisition time of 120s

scores, *etc*. Samples are characterized based on the area where they are plotted[13].

In this study, Y-10 was selected as the reference, an SQC analysis model was built and the comparison of Y-10 with other flavor samples was visually accessed. The flavor categories of Y-7 and Y-9 are close to Y-10 but there is a large discrepancy between Y-10 and the other nine tobacco blend samples (Fig. 5).

Overall, the ability of the electronic nose to differentiate between flavor lots reflects its sensitivity and selectivity and could be useful for accepting or rejecting the flavor of raw material from tobacco suppliers and manufacturers.

Conclusion

In this paper, we have evaluated the application of the Fox 4000 electronic nose for flavor analysis in 12 tobacco blend samples. In summary we found that the flavors of the 12 tobacco blend samples are classified into six groups. The ability of the electronic nose to qualitatively distinguish among 12 flavors was demonstrated. This indicates that the instrument has adequate selectivity and sensitivity to perform flavor identification in tobacco blend products. The flavors from the unknown samples were properly identified and classified using the electronic nose. In addition, the results from the electronic nose correlate with sensoric analysis, indicating that the discrimination ability of the instrument is comparable with human sense. At the same time, health risks arising from sensoric analysis by smoking will be substantially reduced. Therefore, the instrument can be used for identity testing of flavor raw materials and flavored formulations in the tobacco industry by flavors analysis.

Due to variation between individual cigarettes of the same brand, large-scale collection of different batch samples from each brand should be used to acquire complete information in future experiments. In this way, more accurate judgments or decisions for unknown samples and the detection of characteristic information in the same cigarette brand can be made.

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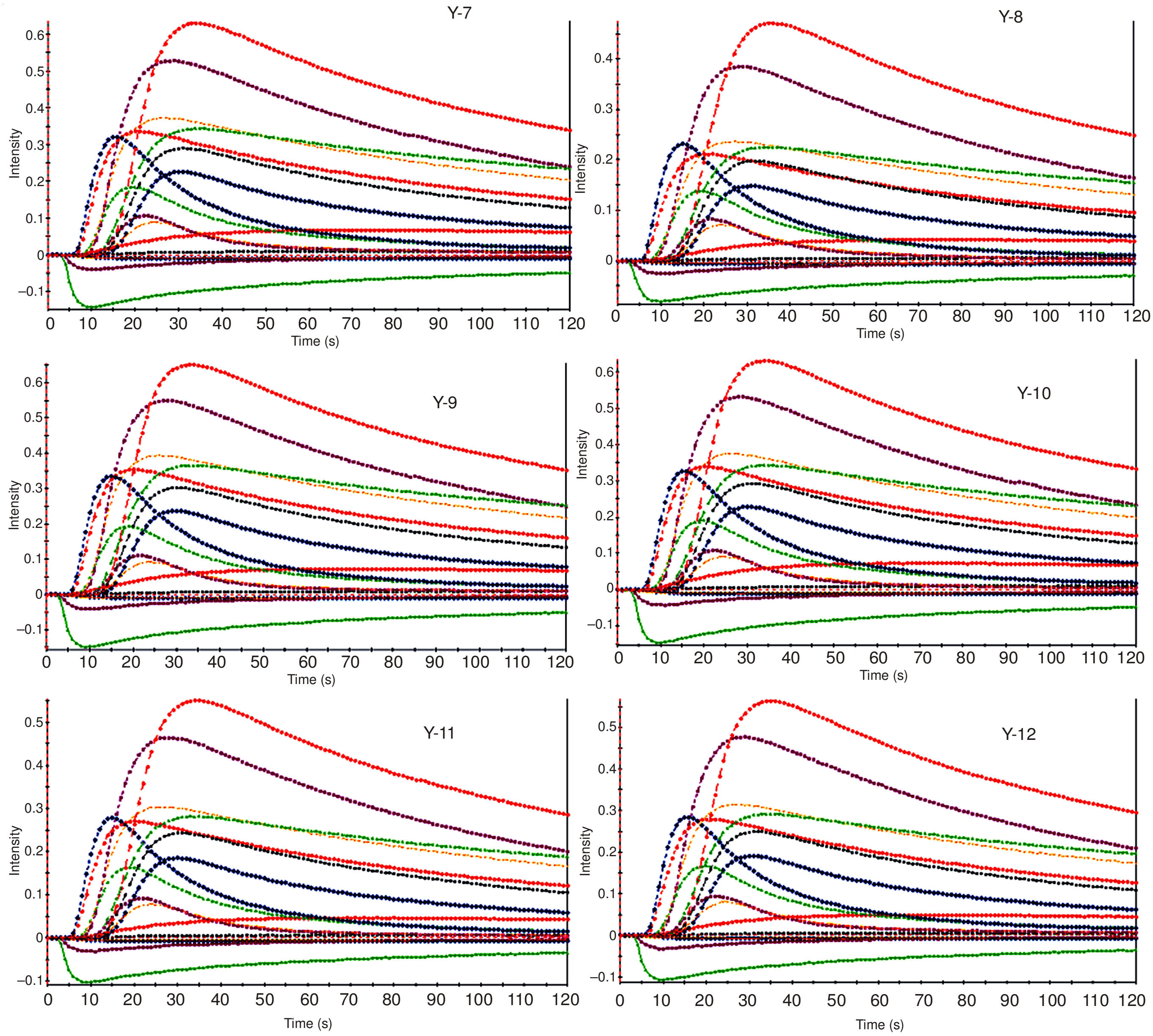

Fig. 2b. Raw sensor signals of tobacco blend samples (Y-7-Y-12). Raw signals are presented in response to intensity changes of 18 sensors (indicated by coloured curves) as a function of time for each tobacco blend sample. Each curve in the plot represents the change for each sensor response during the acquisition time of 120s

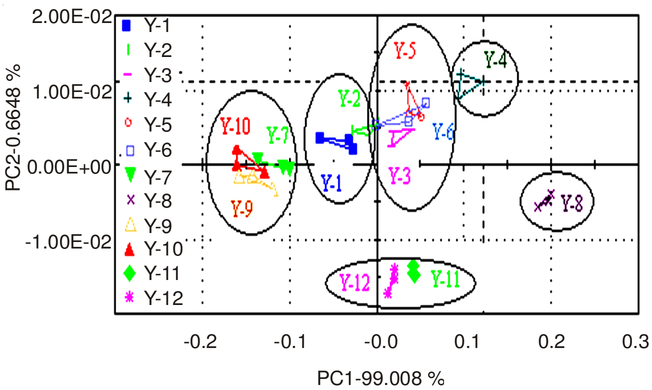

Fig. 3. Principal component analysis (PCA) of tobacco blend samples Y1-Y12. The 12 samples fall into six flavor clusters (indicated by circles)

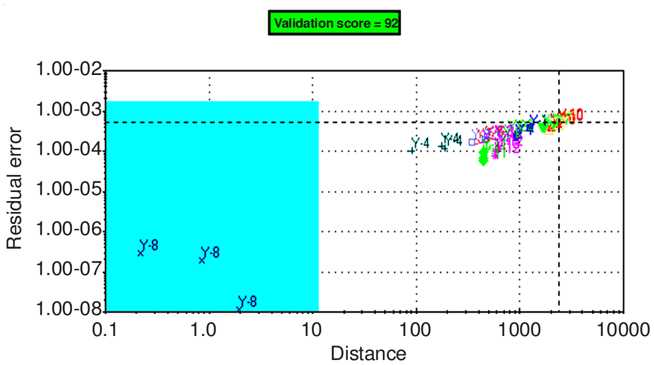

Fig. 4. Flavor classification using soft independent modeling of class analogy (SIMCA). The blue bar is the automatically created "zone of acceptability" and any flavors within this zone would be considered similar to Y-8

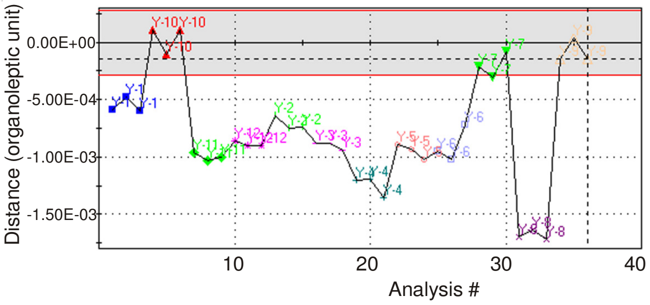

Fig. 5. Statistical quality control (SQC) model of tobacco blend samples. The center line (black full line) is the mean of the quality characteristic being measured. Y-10 falls on the center line and so is used as the quality control sample. Samples are characterized based on the area where they are plotted. The grey bar is a 95 % confidence interval (acceptable area) - samples that fall into this grey area are similar to the control (Y-10). The dotted line in the grey bar represents a range of standard deviation from the mean. The upper control limit (upper red line) is the maximum acceptable variation from the mean for a process that is in a state of control. The lower control limit (lower red line) is the minimum acceptable variation from the mean for a process that is in a state of control

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