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Short communication

Rapid discrimination of Apiaceae plants by electronic nose coupled with multivariate statistical analyses

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ABSTRACT

Since many Apiaceae plants, with antimicrobial activities, have similar characteristics, it is difficult to separate them from one another. The aim of this study is to distinguish different kinds of Apiaceae plants by an electronic nose (EN) and multivariate statistical analyses. The dynamic response of a metal oxide sensor array to Apiaceae plants showed that the response values and different kinds of Apiaceae plants were positively related. Atractylodis Macrocephalae Rhizoma (as the reference sample) and other nine different kinds of Apiaceae plants were measured. Multivariate statistical analyses, including linear discrimination analysis (LDA), principal component analysis (PCA), hierarchical clustering analysis (HCA) and artificial neural network (ANN), were employed. The result showed that these samples could be classified correctly by this method, which suggested that the EN system could be used as a simple and rapid technique for the discrimination of Apiaceae plants.

1. Introduction

To identify volatile compounds from medicinal plants, various authors use gas chromatography (GC), gas chromatography-mass spectrometry (GC–MS) or high performance liquid chromatography-mass spectrometry (HPLC–MS) [1,2]. But those methods will destroy samples used for analysis. Therefore, it is essential to develop a nondestructive and liable technique, which can assess the quality of medicinal plants rapidly.

The electronic nose, one of the analytical devices used for detecting volatile compounds, comprises a sampling system, an array of metal oxide gas sensors with diverse selectivity, and a computer with an appropriate pattern-classification algorithm, capable of qualitative or quantitative analysis of complex gases or odors. Sensors, the key element of an electronic nose, include conductive polymer, polymer composite, quartz crystal microbalance, surface acoustic wave, and calorimetric sensor [3,4]. Currently, the electronic nose technology is being applied in the discrimination of fruits [5,6], the identification of bacteria in human blood culture samples [7], the correct classification of beverages [8] and other fields [9,10].

2. Materials and methods

2.1. Experimental materials

The samples were purchased from Beijing Tongrentang Limited by Share Ltd. (Wangjing, Beijing, China), including nine types of Apiaceae plants and Atractylodis Macrocephalae Rhizoma, which belonged to Asteraceae family, were identified by Professor Yonghong Yan. Details of the samples are listed in Table 1.

2.2. Electronic nose

α-FOX3000 (Alpha MOS, Toulouse, France), which consists of an array of sensors, HS-100 autosampler and pattern recognition software (Alpha Soft V11), was used. 12 commercial metal oxide sensors were divided into chambers as three types: T, P and LY. Table 2 shows a list of sensors used and their main applications.

2.3. Experiment procedure

In total, 60 samples (6 samples for each sampling point) were involved in the experiment. Samples were accurately weighed to 0.20 g and placed in 10 ml glass jar, sealed and loaded into the autosampler tray. The experiment started when the resistance of the gas sensors remained stable. Each sample was incubated in the glass jar at the temperature of 45 °C for 300 s, then 1500 μl of headspace gas was injected into the testing chamber. The time of acquisition was 200 s, a sufficient time for sensors to obtain stable

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Table 1
Details of samples.

No.	Mark	Sample name
1	LC	Chuanxiong Rhizoma
2	LS	Ligustici Rhizoma et Radix
3	AD	Angelicae Dahuricae Radix
4	NI	Notopterygii Rhizoma et Radix
5	AP	Angelicae Pubescentis Radix
6	GL	Glehniae Radix
7	AS	Angelicae Sinensis Radix
8	PP	Peucedani Radix
9	BC	Bupleuri Radix
10	AM	Atractylodis Macrocephalae Rhizoma

Table 2
The components and main application of sensors of α-FOX3000 EN.

No.	Name	Main application
S1	LY2/LG	Oxidizing gas
S2	LY2/G	Ammonia, carbon monoxide
S3	LY2/AA	Ethanol
S4	LY2/GH	Ammonia/organic amine
S5	LY2/gCTL	Hydrogen sulfide
S6	LY2/gCT	Propane/butane
S7	T30/1	Organic solvents
S8	P10/1	Hydrocarbons
S9	P10/2	Methane
S10	P40/1	Fluorine
S11	T70/2	Aromatic compounds
S12	PA/2	Ethanol, ammonia/organic amine

value. The response value of each of the 12 sensors for every sample was recorded, and response curves were generated. When the measurement finished, the clean phase was activated, and lasted 400 s. The main purpose was to clean the test chamber and return the sensors to baselines.

2.4. Statistical processing

There are many different multivariate statistics methods available such as PCA, LDA, HCA, and ANN. Principal component analysis (PCA) and linear discriminant analysis (LDA) are applied to determine whether the metal oxide sensor array is able to extract sufficient relevant features used for monitoring the test materials. PCA is a chemometric, linear, unsupervised, and pattern recognition technique used for analyzing, classifying, and reducing the dimensionality of numerical datasets in a multivariate problem [11]. LDA is one of the most popular techniques of data classification and dimensionality reduction. This method maximizes the variance among categories and minimizes the variance within categories by discriminant functions. It looks for a sensible rule to discriminate categories by forming linear functions of data, and by maximizing the ratio of the between-group sum of squares to the within-group sum of squares. Hierarchical clustering analysis (HCA), a standard statistical procedure, provides a better alternative of accurate representation and classification of high-dimensional data, and it used the full dimensionality of the data to create a classification dendrogram [12]. HCA is a more direct tool to find sub-classes than PCA. We utilized HCA to study the connection among factors and the scale of each factor. To counteract the cross-sensitivity of metal oxide gas sensors, artificial neural network (ANN) is introduced to classify and predict unknown samples, and multilayer perceptron (MLP) and radial basis function (RBF) neural network are commonly used in the data analysis of metal oxide gas sensors [13].

3. Results and discussion

3.1. Electronic nose response to samples

Fig. 1 shows the typical responses of 12 sensors with sample No. 1. Each curve represents one sensor's conductivity induced by electro-valve action, when volatiles reach the measurement chamber. The EN sensor responses of samples are calculated using the following expression [14]:

$$R = \frac{R_0 - R_t}{R_0}$$

where R is the EN sensor response, R_t is the value of the conductance of metal oxide sensors, and R_0 is the value of metal oxide sensors at time 0 s. After low level in initial period, the conductivity increased continuously, and then stabilized after a few seconds. In this study, the maximum responses of sensors were extracted and analyzed.

3.2. Repeatability

The repeatability of the sample (No. 1) was measured and analyzed in six parallel tests. The relative standard deviation (RSD, $n = 6$) for each sensor was calculated, and the results were all less than 2%.

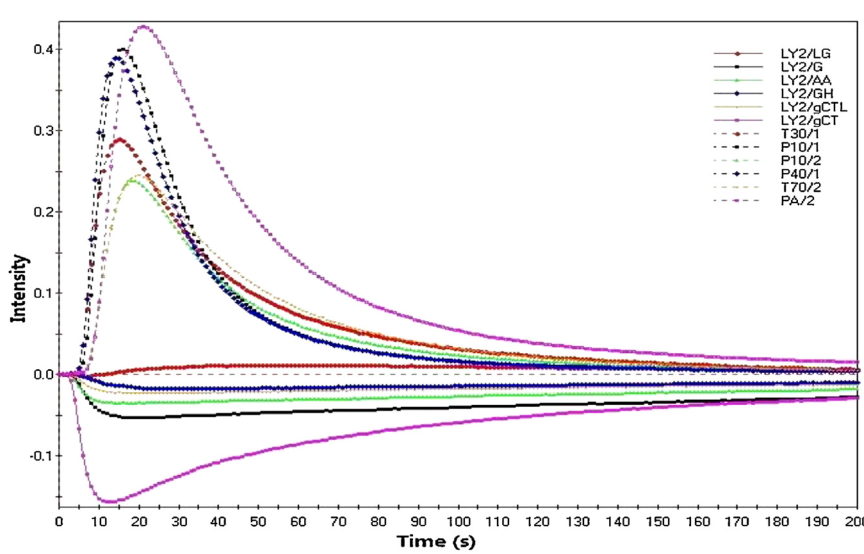

Fig. 1. A typical response of 12 gas sensors during the measurement of samples (No. 1).