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RESEARCH NOTE

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Application of Mass Spectrometer-based Electronic Nose for Discrimination of *Angelicae gigantis radix*

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Abstract Potential of mass spectrometer-based electronic nose to discriminate habitat of *Angelicae gigantis radix* was evaluated using 24 and 86 Korean and non-Korean samples, respectively. Loading plot(s) of principal component analysis of data measured through this system revealed difference between Korean samples (probability; 100%) and non-Korean ones (probability; 95.3%), suggesting this technique could be used as efficient method to differentiate habitat of *A. gigantis radix*.

Keywords: *Angelicae gigantis radix*, electronic nose, mass spectrometer, principal component analysis

Introduction

Angelicae gigantis radix is the root of *A. gigas Nakai*, which has been reported to have immunostimulatory (1, 2), blood platelet cohesion inhibitory, anticancer (3), and other health-promoting activities. As a common material for making herbal medicinal tea, it can be purchased at local markets in Korea without any restrictions, and huge quantity has been imported from abroad and sold as domestically grown product .

Discrimination of the agricultural origin of products is very important, because contamination of heavy metal and undesirable pesticides has been found in the imported products. Traditionally, the flavor of agricultural products has been measured by means of sensory panels trained to recognize and score the flavor attributes. Because this procedure is subjective and expensive, as alternative, instrumental techniques such as GC/MS can be used to identify and quantify aroma compounds. However, these techniques also have several disadvantages such as being time-consuming and labor-intensive, and needing pretreatment. In addition, they require expensive instruments and considerable technical skills.

Recently, an electronic nose comprised of an array of electronic chemical sensors with partial specificity and an appropriate pattern-recognition system, capable of recognizing simple or complex odors, was introduced. Numerous applications of the electronic nose in the food industry for the prediction of shelf lives of soybean curd (4) and soymilk (5), detection of irradiated red pepper (6) and irradiated meat (7), lipid oxidation of soybean oil (8), and quality control of microencapsulated DHA (9) have been reported.

Electronic nose has also been used for the discrimination of habitats of agricultural products including *ginseng*, garlic, and carrot (10). Noh et al. reported that electronic nose with conducting polymer sensor was used for the discrimination of habitat for sesame, *Ganoderma lucidum*, and arrowroot (11). They also achieved good discrimination of Chinese and Korean ginseng using electronic nose with metal oxide sensor and conducting polymer sensor (12). The unknown sample data as determined by electronic nose were analyzed using the learned neural network analysis program for discrimination of black rice habitat after learning the input database by neural network system (13).

Previously, volatile components of domestic and imported *A. gigas Nakai* have been determined using GC based on the surface acoustic wave sensor (Z-Nose) (14). Discrimination between domestic and imported *A. gigas Nakai* was successfully achieved through the recognition of their visual patterns.

Saevels et al. evaluated the potential of the mass spectrometer-based electronic nose to monitor changes in apple fruit volatiles during shelf life for quality control of food (15).

The purpose of this study was to determine the origin of different samples of *A. gigantis radix* using the MS based on electronic nose as an alternative method to discriminate Korean samples from those of other countries.

Materials and Methods

Electronic nose system (SMart Nose300, SMart Nose®, Switzerland) fitted with an automatic headspace sampler (SMart Nose® Autosampler, SMart Nose, Switzerland) and a detector based on a mass spectrometer (Quadrupole Mass Spectrometer, Balzers Instruments, Switzerland) was used for analysis. The operating conditions are shown in Table 1. Dry powder (0.5 g) of each sample of *A. gigantis radix* was sealed in a 10-mL vial with an adequate septum closure (Pharma Fix. Chemmea, Slovakia). The syringe and the injector were purged and washed under a dry nitrogen flow after each sampling. The analysis was performed in bargraph mode to achieve a complete fingerprint of the sample.

Intensities of different channels were recorded in a matrix. The software reduces the raw data, and the comparison of the sets of values leads to the desired plot of the discriminated samples.

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Table 1. Operating condition of mass spectrometer based electronic nose for analysis of *Angelicae gigantis radix*

Number of channels :151 (bargraph mode, 10-160 amu)
Purge gas : Nitrogen 99.95% , 0.25 bar, 200 mL/min
Incubation :20 min, 120°C, with agitation
Injected volume and syringe temperature :2.5 mL , 130°C
Injector temperature :140°C
Acquisition after injection : 4 min (0.5 s / mass), 15s delay time
Syringe / injector purge time :3 min / 10 min

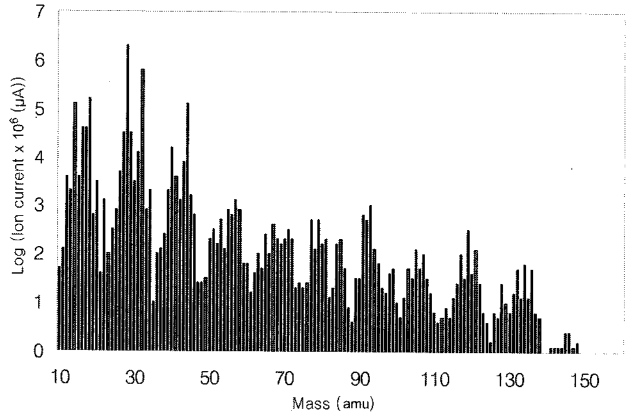

Fig. 1. Bargraph raw data of mass spectrometer based electronic nose for the 2nd measuring cycle on sample k21-1. The intensity of ion current (y axes) are log scale and x axes are mass.

Twenty-four Korean samples (k1 - k24) and eighty-six non-Korean samples (r1 - r86) were evaluated. All measurements were performed in duplicates (k1-1, k1-2,... r1-1, r1-2, ...r86-1, r86-2) and six repetitions for air sample (air-1, ... air-6) at the beginning of the experiment.

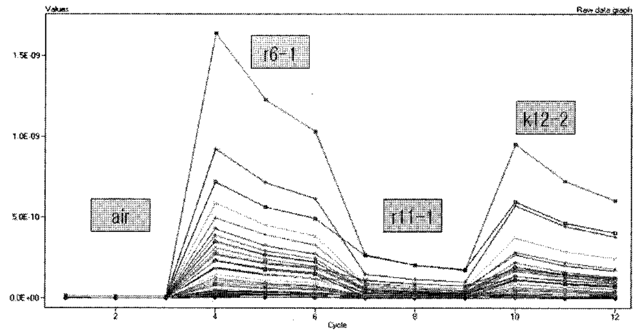

Fig. 2. Raw data plot of three sample measurements, with air reference using mass spectrometer based electronic nose.

Results and Discussion

The ion mass intensities coming from different selected channels were stored in a database. An average intensity was calculated for each variable, thus giving a set of values associated with each sample.

Figure 1 shows a bargraph measurement of sample k21-1. The processed data for each sample are the averages of three cycles. Figure 2 shows the plot of raw data; only the most significant variables were represented to clarify the graphic. Some differences in the intensities appeared immediately at the first look of Figure 2. Samples r6 and k12 showed highest intensities among the samples. The differences among other samples could only be determined through statistical calculations.

The collection of value sets allowed statistical Principal Component Analysis (PCA), which gave a 2-D map of the discriminated samples. The processed data for each sample led to PCA statistical analyses, in which the maximum distance between all samples was optimal (Fig. 3), and only the most discriminating variables have been used for the calculations.

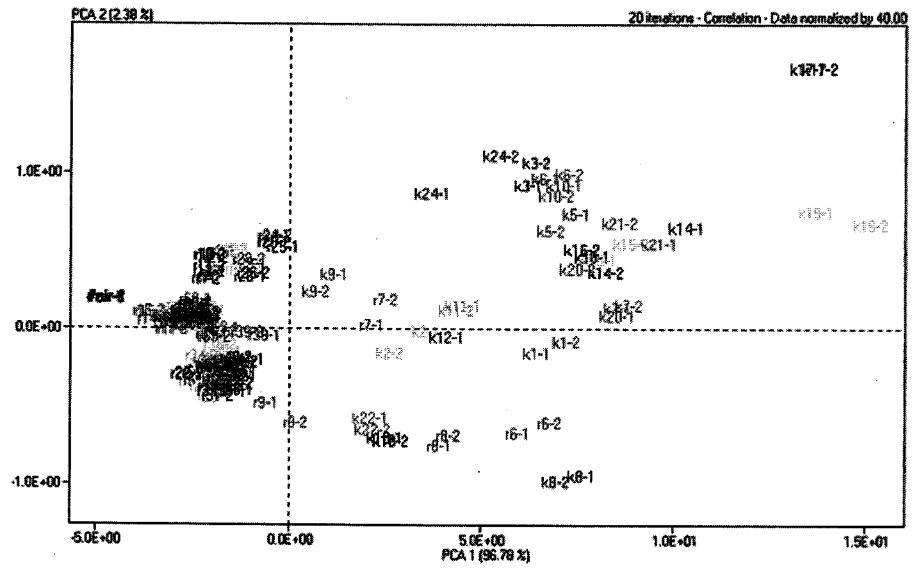

Fig. 3. PCA plot of the 226 measurements for *Angelicae gigantis radix* using mass spectrometer based electronic nose. The measurement of each sample is always close together, showing the high reproducibility. Group percent in place is 96.4%.

Table 2. Classification of discriminant analysis using the mass spectrometer based electronic nose for Korean *Angelicae gigantis radix* and non-Korean one

Actual ones	Predicted *A. gigantis radix*		Total
	Korean	Non-Korean	
Korean	24/24	0/24	24
	(100%)	(0%)	
Non-Korean	4/86	82/86	86
	(4.7%)	(95.3%)	
Total probability			106/110
			(96.4%)

Table 3. Discriminant power of variables for Korean *Angelicae gigantis radix* and non-Korean one

Mass (amu)	R2	Mass (amu)	R2
130	0.8131	132	0.8031
116	0.7958	131	0.7958
117	0.7940	115	0.7936
101	0.7843	118	0.7809
133	0.7777	102	0.7746
114	0.7723	129	0.7678
88	0.7676	89	0.7672
75	0.7671	103	0.7649
104	0.7631	120	0.7591
63	0.7589		

The analysis showed a good discrimination between the Korean and non-Korean samples. In particular, sample k4 was very different from the others, its position being outside of the Fig. 3 range. The Korean sample showed a higher intensity of volatile compounds and more intensive aroma and taste. Only the non-Korean samples r6, r7, and r8 were classified in the Korean zone. R9 was in the boundary between the Korean and the non-Korean zones, and thus was assumed as being a Korean sample. Therefore, four non-Korean samples including r9 were incorrectly discriminated.

We can estimate that the quality of these samples was also good. It is possible that these groups of non-Korean samples correlated with their origin. Table 2 exhibits the predictive probabilities of the samples. The probabilities for Korean and non-Korean samples were 100 and 95.3%, respectively, with 106 among 110 samples being correctly predicted for habitat of *A. gigantis radix*.

The major groups of mass (amu) to contribute for good discrimination is 130, 132, and 116 (Table 3), and the discriminant powers (R2) of the variables were 0.8131, 0.8031 and 0.7953, respectively. These differences could be due to the different harvest times. The imported samples were probably harvested earlier than the domestic ones. Nonetheless, our results thus suggest this technique could be used as an efficient method to differentiate habitat of *A. gigantis radix*, as well as discriminate agricultural products.

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