J Food Sci Nutr
Vol 11, p 237~242 (2006)

J Food Science and Nutrition

Volatile Discrimination of Irradiated and Fumigated White Ginseng Powders at Different Storage Times and Temperatures Using the Electronic Nose

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Abstract

The pattern of volatile emissions from white ginseng powders (WGP) that were treated with selected preservatives was investigated during 5-months of storage (at -10 and 25°C) by an electronic nose system equipped with 12 metal-oxide sensors. WGP were treated with gamma radiation at 5 kGy, commercial methyl bromide (MeBr), and phosphine fumigations. Electronic nose differentiated the volatile patterns of the WGP with each different preservative treatment. In addition, each volatile pattern was affected by both storage time (1, 2 and 5 months) and temperature (-10 and 25°C). After 5-months of storage, the least change of volatile patterns was observed from WGP fumigated with phosphine at -10°C. The result also showed that volatile changes in WGP were much more affected by storage time than by storage temperature.

Key words: white ginseng powder, volatile profile, electronic nose, gamma irradiation, fumigation

INTRODUCTION

Korean ginseng, a traditional and medical herb, is widely used in ginseng-containing foods and dietary supplements for enhancing human health in Asia. The multifunctional effects of bioactive compounds, such as ginsenosides and phenolic acids, of ginseng have been studied (1,2). Ginseng has been reported to have pharmacological activities related to anti-fatigue, anti-stress and anti-tumor activities (3,4). Raw ginseng contains relatively high concentrations of bioactive compounds compared to processed products; many of the bioactive components easily deteriorate owing to the greater than 70% water content. Therefore, ginseng should be used as a dietary supplement after drying or steaming processes to increase the storage period. Usually, white ginseng is dried immediately after washing without any additional processing. Therefore, the protection of white ginseng from biological contamination is considered an important issue, because ginsengs and their products tend to be easily contaminated by insects and microorganisms during processing and storage. For that reason, chemical fumigants such as ethylene oxide, phosphine and methyl bromide have been extensively used to delay the deterioration. However, chemical fumigants may be potentially hazardous to human health and the environment because of their toxic remnants. Currently, irradiation is considered to an effective treatment for reducing microbial contamination. With the approval of the International Instrument (FAO/IAEA/WHO) in connection with Safety of Irradiation Food, some countries have allowed the irradiation of food with restrictions on irradiation dose and usable the type of foods. Many studies on the physiochemical characteristics of various irradiated foods have been performed (5,6), but very little is reported about the flavor characteristic of irradiated ginseng. Electronic nose has provided a rapid and non-destructive method of volatile compound analysis by using the combination of a gas sensor array with artificial neural networks. Electronic nose applications have included characterization of blended sesame oils (7,8), the habitat discrimination for agricultural products (9) and the volatile discrimination of red ginseng powder treated with irradiation and fumigation (10). In this study, ginseng powders (WGP) were respectively treated with chemical fumigants (methyl bromide and phosphine) and 5 kGy-irradiation. The volatile patterns of WGP with each preservative treatment were then observed during 5-months of storage at -10 and 25°C. For this purpose, the electronic nose system equipped with 12 metal-oxide sensors was used to differentiate volatile patterns during the 5-month storage period.

MATERIALS AND METHODS

Materials

Four-year old white ginseng roots (25 pieces) were purchased from a local market in Keumsan (Korea). The

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dried white ginseng was ground to pass through a 100-mesh sieve, and packed in a 150 mL polyethylene (PE) pail. The irradiation dosage of 5 kGy was reported to be a safe dose that can effectively eliminate microbes (11). Gamma-irradiation was carried out in a cobalt-60 irradiator equipped with 3.7 PBq (100 kCi) activity for the 5 kGy (±0.5 kGy) at room temperature (20±1°C), operated at a dose rate of 1 kGy hr^{-1}. The white ginseng powder (WGP) was fumigated with methyl bromide (MeBr, 12°C for 48 hrs at 28 g/m^3) or 40 g/m^3 phosphine (hydrogen phosphide) at 12°C for 114 hrs according to a commercial stipulation before packaging. The samples treated with irradiation and fumigation were stored, respectively at -10°C and 25°C for 1, 2 and 5 months, and then analyzed by electronic nose system equipped with 12 metal-oxide sensors (MOS) for the discrimination of their volatile compounds.

Discrimination of volatile profile by electronic nose system

The volatile discrimination analysis was performed with the FOX 3000 electronic nose system (Alpha M.O.S., Toulouse, France) which has an automatic headspace sampler, model HS 100 (Alpha M.O.S.) (12). The electronic nose is composed of twelve sensors with different metal-oxide coating such as SY/LG, SY/G, SY/AA, SY/Gh, SY/gCTl, SY/gCT, T30/1, P10/1, P10/2, P40/1, T70/2, and PA2. Among these sensors, P10/1, P10/2, SY/AA, and SY/gCT sensors especially detect non-polar volatile compounds, and PA2, T30/1 and SY/gCTl sensors are specific to organic solvents. P40/1 and SY/LG sensors detect fluoride and chloride compounds and SY/G sensor recognizes ammonia and sulfur compounds. Finally, the T70/2 sensor detects food aroma and volatile compounds in foods. Each 1 g of sample was weighed into a 20-mL vial, and sealed with a hole-cap and a silicon/PTFE septum. The vial was moved to an oven with the HS100 automated headspace sampler where it was incubated at 60°C for 30 min and simultaneously agitated at 500 rpm for headspace generation. At this time, an air conditioning unit (ACU) was used for maintaining a temperature of 30°C and 20% relative humidity. Flow rate and pressure of the carrier gas was set at 150 mL/min and 5 psi, respectively. A gas-tight syringe (2,500 μL) injected the headspace gasses into the sensors. After acquisition, the sensitivity (delta R_{gas}/R_{air}) of each sensor was entered into the data processing software connected with a computer. Principal component analysis (PCA) was performed on the collected data.

Statistical analysis

Principal component analysis (PCA) for the discrimination of volatile patterns of samples was conducted on the data obtained from the electronic nose system. Multivariate Analysis of Variance (MANOVA) using SAS software (SAS Institute Inc., USA) (13) based on Student-Newman-Keuls test was used to differentiate the volatile pattern of the data acquired from the electronic nose.

RESULTS AND DISCUSSION

Volatiles pattern by electronic nose system

White ginseng powders (WGP) treated with gamma-irradiation, phosphine and methyl bromide were stored at ambient temperature (25°C) or -10°C for 5 months. Then, their volatile changes were investigated by electronic nose. The volatiles of each treatment were grouped by principal component analysis techniques after analysis by the α-FOX 3000 electronic nose system in which volatile compounds from each sample were acquired from the headspace of each sample-containing vial while incubating under controlled temperature and agitation speed in the heating block. Then volatile compounds were passed through 12 different sensors with carrier gas and the interaction between the sensor and the various volatile compounds was exhibited as the response of each sensor. In general, samples containing similar volatile compounds have sensor responses which are similar in appearance, whereas samples containing different volatile compounds exhibits different sensor responses that can be analyzed by principal component analysis (PCA) of the electronic nose. Therefore, the volatile differences among samples can be classified by group. In this study, the responses (delta R_{gas}/R_{air}) of the sensors were obtained from the volatile compounds of WGP that had been irradiated or fumigated with phosphine or methyl bromide. Then, principal component analysis (PCA), explaining the interrelationships between different variables and the volatile patterns of grouped samples, was obtained from the sensor responses. Before storage, the PCA of control WGP (no treatment), the WGP irradiated at 5 kGy, and fumigated with MeBr or phosphine are plotted together in Fig. 1. The group distance between control and the WGP fumigated with phosphine was 0.0226. On the other hand, the volatile patterns of the WGP irradiated at 5 kGy and the WGP fumigated with MeBr are distinctly discriminated, exhibiting 0.7347 and 0.3694 group distances, respectively (Fig. 1). However, after 5-month storage at -10°C, group distances between the treatments showed smaller values to those in Fig. 1 (Fig. 2). Such results suggested that there were few residual volatile changes in the WGP

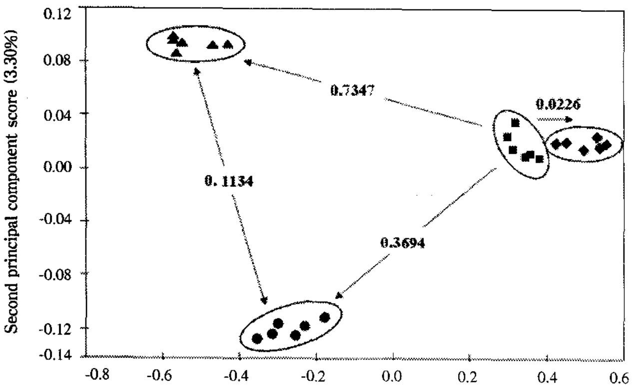

Fig. 1. Principal component analysis (PCA) plot from the electronic nose on white ginseng powder treated with gamma irradiation, methyl bromide and phosphine fumigation (before storage).
■, control; ▲, 5 kGy gamma-irradiation; ●, methyl bromide; ◆, phosphine.

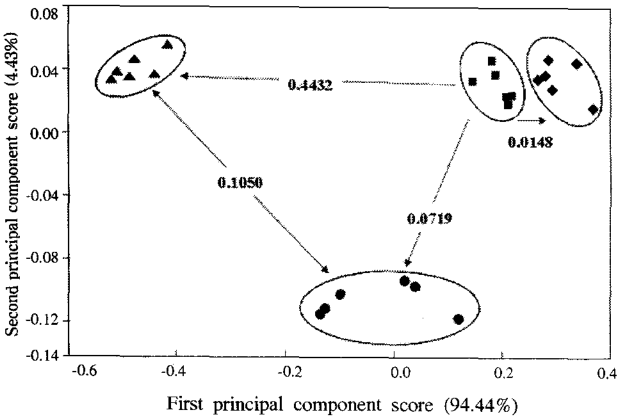

Fig. 2. Principal component analysis (PCA) plot from the electronic nose on white ginseng powder treated with gamma irradiation, methyl bromide and phosphine fumigation (stored for 5-month at -10°C).
■, control; ▲, 5 kGy gamma-irradiation; ●, methyl bromide; ◆, phosphine.

fumigated with phosphine after 5-month storage at -10°C; a similar result was obtained from red ginseng powder fumigated with phosphine (10).

Kwon et al. (14) reported that the contents of ginsenosides and free sugar in WGP were little changed during 6-months of storage when phosphine fumigation was applied, suggesting a need for further studies on volatile changes by each preservative treatment. The volatile change in WGP (control) according to the storage is illustrated in Fig. 3. The discrimination index, which explains degree of classification among samples, was 92 for the first principal component score and the second principal component scores were 70.69% and 22.51% respectively. The first principal component interprets the combination of variables that explains the greatest variance in the data while the second principal component defines the second largest variance independent of the first principal component in PCA. Therefore, it is plausible that volatile differentiation was not conclusively determined by such few sensors. Rather, many sensors responded to volatile changes in each WGP. Euclidean distance, the group distance which explains variation among samples within a group, tended to increase as storage time increased, a tendency that was clearly observed in samples stored at 25°C. In the multivariate statistical analyses performed with the data obtained from the electronic nose, a Wilks' lambda value was near zero and F-value, a quantitative number for the overall discrimination between classes, was 543.9 (Table 1). This indicated that there were significant volatile changes in WGP during 5 months of storage ($p<0.05$). Wilks' lambda is the most widely used method for testing the differences among more than two groups in MANOVA. The value is calculated from the inverse of eigenvalues of product, and accordingly is a kind of inverse measure. A Wilks' lambda value near zero indicates that there is high distinction among groups. F-value provides quantitative discrimination among samples for Wilks' lambda.

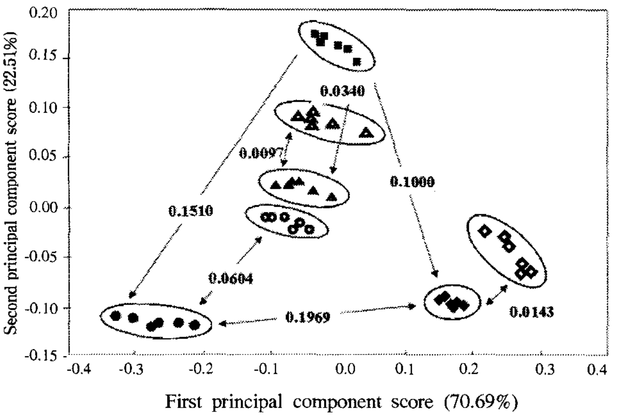

Fig. 3. Principal component analysis (PCA) plot from the electronic nose on white ginseng powder during storage.
■, before storage; ▲, 1-month at 25°C; △, 1-month at -10°C; ●, 2-month at 25°C; ○, 2-month at -10°C; ◆, 5-month at 25°C; ◇, 5-month at -10°C.

The volatile change in WGP stored for 5 months after MeBr fumigation is shown in Fig. 4. The discrimination index was greater than 90. The flavor pattern of the stored WGP was significantly different, with an F-value of 655.9 and a Wilks' lambda of 0 ($p<0.05$) (Table 1). The proportions of the first principal component and the second principal component were 85.73% and 9.86%, respectively. The group distance demonstrated that volatiles of MeBr fumigated WGP were more distinctly discriminated by storage time than by storage temperature. Also, the volatiles of posphine fumigated WGP were sig-

Table 1. Criteria of MANOVA test and discrimination index of white ginseng powder with different treatments

Treatments[1]	Wilks' Lambda	F-value	Pr>F	Discrimination index[2]
Control	0.00	543.9	<0.0001	92
MeBr	0.00	655.9	<0.0001	92
Phosphine	0.00	641.1	<0.0001	91
5 kGy-irradiation	0.00	464.7	<0.0001	90

[1] Control (no treatment): samples stored at 25°C or -10°C during 5-month.
MeBr (treated with methyl bromide): samples stored at 25°C or -10°C during 5-month.
Phosphine (treated with phosphine): samples stored at 25°C or -10°C during 5-month.
5 kGy-irradiation (treated with gamma irradiation): samples stored at 25°C or -10°C during 5-month.
All Wilks' lambda and F-value were significant at α-value of 0.05.

[2] Discrimination index is gained from principal component analysis of electronic nose system.

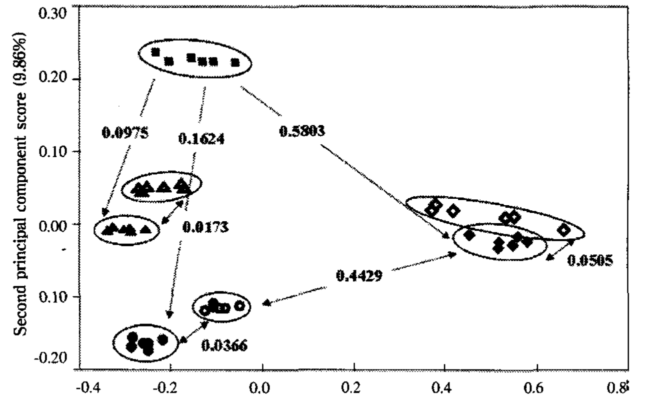

Fig. 4. Principal component analysis (PCA) plot from the electronic nose on white ginseng powder treated with methyl bromide.
■, before storage; ▲, 1-month at 25°C; △, 1-month at -10°C; ●, 2-month at 25°C; ○, 2-month at -10°C; ◆, 5-month at 25°C; ◇, 5-month at -10°C.

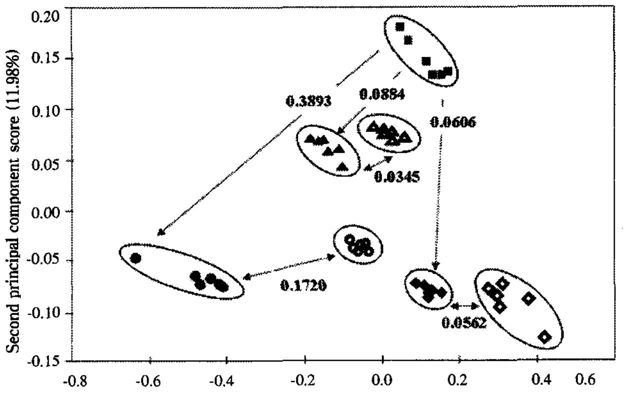

Fig. 5. Principal component analysis (PCA) plot from the electronic nose on white ginseng powder treated with phosphine.
■, before storage; ▲, 1-month at 25°C; △, 1-month at -10°C; ●, 2-month at 25°C; ○, 2-month at -10°C; ◆, 5-month at 25°C; ◇, 5-month at -10°C.

nificantly discriminated, showing similar volatile patterns of WGP with no treatment (Fig. 5). Again, the volatile pattern of the phosphine-fumigated WGP according to storage time and temperature was significantly different, with an F-value of 641.1 and a Wilks' lambda of 0 ($p<0.05$) (Table 1). Therefore, volatile patterns between control WGP (before storage and no treatment) and WGP with MeBr or phosphine fumigation were respectively differentiated by each storage time (1,2,5 months) as well as storage temperature (-10°C and 25°C). Furthermore, the volatile discrimination was much more affected by storage time than by storage temperature. Moreover, storage at 25°C rather than -10°C increased the Euclidean distance between groups, resulting in further volatile discrimination (Fig. 3, 4 and 5). Similar results were previously observed, in which red ginseng powder was used (10).

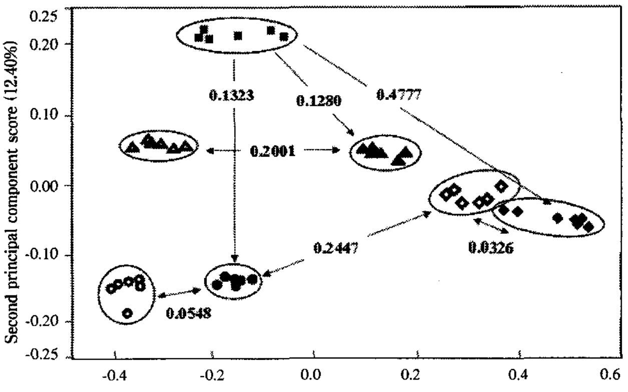

Fig. 6. Principal component analysis (PCA) plot from the electronic nose on 5 kGy gamma-irradiated white ginseng powder.
■, before storage; ▲, 1-month at 25°C; △, 1-month at -10°C; ●, 2-month at 25°C; ○, 2-month at -10°C; ◆, 5-month at 25°C; ◇, 5-month at -10°C.

The PCA of the WGP irradiated at 5 kGy is plotted in Fig. 6. It showed an F-value of 464.66, a Wilks' lambda of 0 (Table 1) and the first principal component of 85.47%, suggesting significant differences among samples ($p<0.05$). In this case, the responses of each sensor appeared significantly different from the 10 out of 12 sensors (except P10/1 and P40/1), when the irradiated WGP was stored for 1 month at -10°C (Table 2), while

Table 2. Response of each electronic nose sensor to 5 kGy gamma-irradiated white ginseng according to storage time

Sensor model	Response of each sensor			
	0 M[1]	1 M	2 M	5 M
SY/LG	0.41297±0.01[2]^{a}[3]	0.34575±0.00^{b}	0.31052±0.02^{c}	0.23942±0.01^{d}
SY/G	-0.96331±0.04^{b}	-1.11836±0.02^{c}	-1.26343±0.01^{d}	-0.79926±0.03^{a}
SY/AA	-0.63946±0.02^{d}	-0.59474±0.01^{c}	-0.54231±0.01^{b}	-0.44786±0.01^{a}
SY/Gh	-0.62184±0.03^{b}	-0.76299±0.02^{c}	-0.82618±0.01^{d}	-0.50436±0.02^{a}
SY/gCTl	-0.63454±0.03^{b}	-0.70585±0.02^{c}	-0.70100±0.01^{c}	-0.44408±0.01^{a}
SY/gCT	-0.50490±0.03^{b}	-0.55127±0.01^{c}	-0.57552±0.01^{d}	-0.38257±0.01^{a}
T30/1	0.66252±0.02^{a}	0.64101±0.01^{b}	0.63394±0.00^{b}	0.50496±0.01^{c}
P10/1	0.42868±0.01^{a}	0.42575±0.01^{a}	0.35776±0.01^{b}	0.28328±0.01^{c}
P10/2	0.33216±0.01^{a}	0.32233±0.01^{b}	0.27591±0.00^{c}	0.22560±0.00^{d}
P40/1	0.41966±0.01^{a}	0.41695±0.01^{a}	0.32478±0.00^{b}	0.26469±0.01^{c}
T70/2	0.64939±0.02^{a}	0.62671±0.01^{b}	0.62433±0.00^{b}	0.48518±0.01^{c}
PA2	0.74724±0.01^{b}	0.76189±0.01^{a}	0.70925±0.00^{c}	0.62205±0.01^{d}

[1] 0 M, before storage; 1 M, 1 month storage at -10°C; 2 M, 2-month storage at -10°C; 5 M, 5-month storage at -10°C.

[2] Response of each sensor is expressed by delta R_{gas}/R_{air}. R is resistance values of the sensors.

[3] Means within the same row with different superscripts are significantly different at $p < 0.05$ by MANOVA.

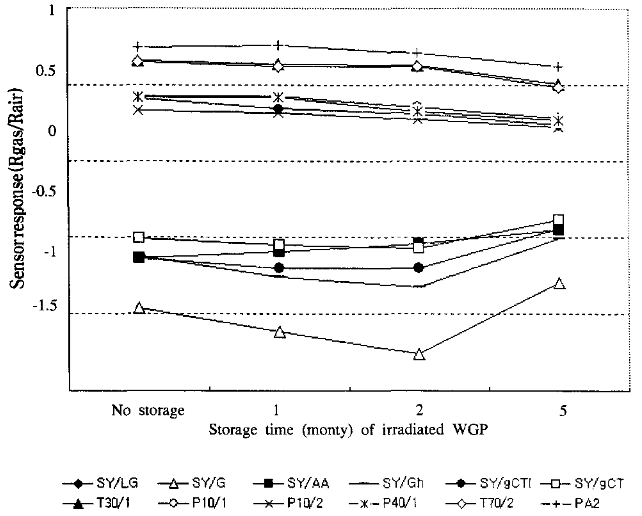

Fig. 7. The change of sensor response by the electronic nose on 5 kGy gamma-irradiated white ginseng powder according to storage time at -10°C.

all 12 sensors showed significant differences when the volatile patterns of irradiated WGP stored for 2 and 5 months were compared. The response variation of SY/G sensor was the highest during 5 months storage (Fig. 7). In conclusion, the volatile patterns of WGP with different preservative treatments were clearly discriminated by electronic nose. Among treatments in this study, phosphine fumigation was a better treatment for preventing volatile changes in WGP than 5 kGy-irradiation and MeBr fumigation during storages. In addition, the volatile patterns from each preservative treatment were more significantly affected by storage time than by storage temperature. Using electronic nose, it is possible to detect the volatile changes in WGP resulting from various preservative treatments and prolonged storage under different conditions in a relatively short analysis time, considering electronic nose as a convenient method for quality control.

ACKNOWLEDGMENTS

This work was supported in part by a grant from the Ministry of Science and Technology of Korea.

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(Received June 14, 2006; Accepted July 3, 2006)