Analysis of the flavor of aged spirits made from sweet potato and rice by gas chromatography–mass spectrometry

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Abstract Flavor patterns of sweet potato spirits (SPS) made from *sul-deot* manufactured by sweet potato showed an increasing tendency for aging from 64 to 128 weeks. When the SPS was blended with spirits made from *sul-deot* manufactured by rice in a 7:3 ratio, showing an increase for aging from 16 to 60 weeks, using a gas chromatography–mass spectrometry with solid-phase microextraction. The main compounds showing increasing tendency of the SPS and blended spirits (BS) were isoamyl alcohol, n-propanol. Especially, ethyl caprylate, and ethyl acetate increased in SPS. The results were cross-checked by an electronic nose. For the results of SPS in the flavor pattern, a decrease was noted by main ion fragments. For the BS, a decrease was noted. These cross-checked results were useful for controlling quality of aging spirits, especially SPS. Based on these results, it was considered that further experiments are needed to identify key compounds for accurate correlation analysis.

Keywords Gas chromatography–mass spectrometry · Electronic nose · Distilled spirits · Aging · Sweet potato (*Ipomoea batatas*)

Introduction

Globally, famous distilled spirits such as whiskey, brandy, rum etc. occupy the majority of the domestic alcohol market because of recognition as high-quality products based on accumulated production skills such as fermentation and distillation [1–5]. In recent years, domestic liquor manufacturers have recognized the necessity for strengthening the domestic distilled spirits to compete against imported distilled spirits. There have been numerous studies regarding domestic production, such as the analysis of volatile compounds in liquor distilled from mash produced using Koji or *Nuruk* under reduced or atmospheric pressure by Yi et al. [6]. Cho et al. [7] analyzed the quality characteristics of fruit spirits from a copper distillation apparatus, and Lee et al. [8] analyzed the quality characteristics of fermented wine using *Nuruk* by aging containers and period of distilled liquor. However, for domestic spirits, there are few research regarding the flavor of distilled soju, particularly those made from sweet potato as one of the raw materials. Kim et al. [9] that analyzed properties of flavors and tastes of Koguma-soju prepared using the Korean sweet potato. Additionally, Kim et al. [10] analyzed the aromatic ingredients and distinct flavors of Koguma-soju produced from various Korean sweet potato varieties including Yeonmi, Jeungmi, Shincheonmi, and Shinyeulmi. Park et al. [11] analyzed the effects of sweet potato cultivars and koji types on general properties and volatile flavor compounds in sweet potato spirits. However, the accumulated researches are not sufficient for determining competitiveness against imported distilled spirits.

Japan has manufactured distilled spirits made from sweet potato (*Ipomoea batatas*) since the end of the eighteenth century from Kagoshima. Moreover, Japan has formed its own distinctive culture of distilled spirits from sweet potato and there have been lots of analysis data of

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long-aged spirits using various aging containers such as pottery, casks made from white oak, and those made from cedar [9, 10]. However, there are few studies analyzing the changes of flavor patterns of distilled spirits from sweet potato depending on long term aging. Additionally, no research exists regarding the analysis of blended distilled spirits while taking into account the effects of long-term aging. Also, there are few studies into the discriminating volatile compounds from distilled spirits for various aging periods as determined by an electronic nose (e-nose) combined with a mass spectrometer. Generally, flavor compounds of distilled spirits are analyzed via high-performance liquid chromatography (HPLC), gas chromatography (GC), and GC-mass spectrometry (GC-MS). However, these analysis methods cause loss of a small amount of component due to the pretreatment process. Also, when different types of columns are used, different compounds are analyzed. Hence, it is necessary to determine other analysis methods to overcome those variables. An e-nose combined with a mass spectroscope can be used to analyze whole components. In other words, volatile organic compounds (VOCs) derived from combined samples can be tested without a pretreatment process of the samples. This could reduce the loss of the flavor components and allow for faster analysis. Ion fragments ionized from the flavor components of the samples are used to discriminant the samples through the discriminant power of each ion fragments. Based on these methods, Kim et al. [12] performed flavor analysis of commercial Korean distilled spirits using an e-nose and electronic tongue. Additionally, Choi et al. [13] analyzed yeast selection for quality optimization of distilled spirits using an e-nose while Kim et al. [14] assessed physicochemical characteristics among different types of pale ale beer using an e-nose. Therefore, this study aims to understand the change in flavor patterns of distilled spirits from sweet potato including the effects of aging as well as blended spirits with sweet potato spirits and rice (*Oryza sativa*) spirits where long term aging also may be a factor. This study seeks to broaden the scope of distilled spirits, increase the quality, and better control the product by determining changes in flavor patterns that may occur during storage using both the GC-MS and an e-nose combined with a mass spectrometry.

Materials and methods

Nuruk and culture yeast

Manufacturing process of *Nuruk* is divided into two, pre-cultivation and main cultivation. At pre-cultivation, *Rhizopus oryzae* KSD-815 is used as a seed bacterium of

Nuruk and the cell is incubated for 24 h at pH 3.5, 30° and 150 rpm in a 10% wheat shorts culture medium. At main cultivation, the 30% pre-cultivation broth is inoculated in wheat bran (by weight of wheat bran) steamed at 100° and is incubated for 72 h at 30°. After incubating, the inoculated wheat bran is dried by hot air for 6 h at 40° and used as *Nuruk*.

Culture yeast is manufactured by *Saccharomyces cerevisiae* KYP. The cell is cultured for 24 h, 30° and 150 rpm in a 5% wheat shorts and 10% dextrose culture medium.

Spirits samples

A first seed mash, called *sul-deot*, was manufactured from raw material, sweet potato and rice. The mash was made from 30 kg of sweet potato and rice from Yeo-ju, respectively. After each sweet potato and rice was washed, the raw materials were then dipped, steamed and cooled. After cooling, 0.5 kg of *Nuruk* and 2×10^7 CFU of culture yeast were injected along with 45 L of water. The seed mash mixture was fermented at 25 °C for 1 day to produce *sul-deot*. A second seed mash was manufactured using 70 kg of sweet potato and rice from Yeo-ju, respectively. The process for making the second seed mash was the same as the first one; however, for the second stage, 1 kg of *Nuruk* was used and 105 L of water was added. The fermentation of the second seed mash mixture was performed at 25 °C for 5 days. After fermentation, each *sul-deot* manufactured by sweet potato and manufactured by rice was distilled using a distiller made of copper (20 L, Hoga Co., Salvaterra de Mino, Spain). When the spirits induced from each *sul-deot* were distilled, the spirits were blended with sweet potato and rice spirits at a 7:3 ratio and the sweet potato spirits made from *sul-deot* manufactured by sweet potato (SPS) were produced via atmospheric distillation. The rice spirits made from *sul-deot* manufactured by rice were distilled by distillation under reduced pressure. After distillation, the spirits produced by atmospheric distillation were diluted to 55%. Spirits produced by distillation under reduced pressure were diluted to 49.9%. The spirits were then aged in permeable pottery at 15 °C for different aging periods.

GC-MS analysis with solid-phase micro extraction method

To analyze volatile compounds of the spirits, extraction of volatile compounds was carried out by the solid phase micro extraction (SPME) method [15] using a 75 µm-carboxen-polymethylsiloxane fiber filter (Supelco, Bellefonte, PA, USA). A 15 mL sample was placed in a clear vial (Supelco, Bellefonte, PA, USA) and sealed using a cap

made from PTFE/Silicone septa (Supelco, Bellefonte, PA, USA). The vial was agitated on a hot plate at 40 °C for 30 min to equilibrate; then, the SPME fiber was exposed for 30 min to the headspace. After sampling the SPME fiber was introduced into the GC injector, and was left for 10 min to allow the analytes thermal desorption. Agilent 6893 gas chromatography with mass spectrometry (Agilent Technologies, Santa Clara, CA, USA) with an Agilent DB-WAX column was used to analyze the volatile compounds. Injector temperature, 200 °C; injection mode, splitless; column, 0.25 mm × 30 m; MS source temperature, 230 °C; MS quad temperature, 150 °C; ion voltage, 70 eV; scan range, 40–350 m/z. The oven temperature was programmed as follows: the temperature was maintained at 40 °C for 5 min, the ramped up at 5 °C/min to 230 °C and maintained for 9 min. Helium was used as a carrier gas with a flow rate of 1 mL/min (constant flow). Standard substances used in this study were n-propanol, iso-amyl alcohol, and isobutyl alcohol purchased from Sigma-Aldrich Co. (St. Louis, MO, USA).

Identification and quantification procedures

Identification is based on mass data. When more than 80% matching to library of Whill 5 mass spectrum database, it is regard to identify a substance. In case of quantification procedure, calibration curve and quantitative analysis are progressed after manufacturing standard reagents of volatile organic compounds by concentration.

Determination of volatile organic compounds by E-nose based on MS and DFA

A 0.5-g sample of spirits was taken in a 10-mL vial (La-Pha-PackTM GmbH, Langerwehe, Germany) then hermetically sealed using a cap with PTFE/silicone septum (Shimadzu, Kyoto, Japan). The vial was agitated at 350 rpm for 10 min at 70 °C. For the headspace analysis, 2.5 mL of volatile components were taken with a syringe placed on a temperature-controlled tray holder maintained at 110 °C (CombiPAL, CTC Analytics, Industriestrasse, Zwingen, Switzerland) and injected into an injection port of the e-nose (Smart Nose300; Smart Nose Inc., Marin-Epagnier, Switzerland) at 130 °C through an auto-sampler (CombiPAL; CTC Analytics, Zwingen, Switzerland). N₂ gas was used as a carrier gas with a flow rate of 230 mL/min. The e-nose was coupled with a mass spectrometer (ThermoStarTM GSD 320 T2, Balzers Instruments, Masin-Epagnier, Switzerland). The volatile substances derived from the samples were ionized at 70 eV. The ionized substances formed over a period of 180 s were passed through a quadrupole mass filter. The ion fragments ionized and filtered at 10–200 (m/z) were used as channels for an integer

unit. An air sample was used as the control and the test was repeated three times for each sample. The statistical program used for the analysis was the Smart NoseTM statistical analysis software (version 1.51, THOPAS Soft Creation, Marin-Epagnier, Switzerland). DFA was performed by the methods discussed in Kim et al. [16].

Results and discussion

Analysis of volatile organic compound of each distilled spirits using GC–MS

To understand the change in the flavor patterns of spirits and the effects of aging periods, the volatile compounds of distilled spirits made from sweet potato, rice, and the blended spirit were analyzed via GC–MS. The distilled spirits used in this study were as follows. One was a sweet potato spirits (SPS) made from *sul–dut* manufactured by sweet potato SP, another was a rice spirits (RS) made from *sul–dut* manufactured by rice, and the final spirit was blend with two types of spirits, SPS and BS at a 7:3 ratio. The results are shown in Table 1.

The SPS were aged in pottery for 76, 60, 14, and 1 weeks and named as samples D, E, F, and G, respectively. Each sample was analyzed through the headspace using GC–MS. Generally, fatty acid ester compounds and fusel oil were the primary compounds influencing the flavor of the spirits [17]. As shown in Table 1, iso-amyl alcohol, ethyl acetate, n-propanol, phenethyl alcohol, ethyl caprylate, and ethyl caprate were found. These results were not consistent with the study conducted by Park et al. [11]. The difference in the results of the volatile compounds was due either to different analysis methods of the GC–MS or the pretreatment methods of samples. Thus, a variety of specific volatile compounds derived from sweet potatoes, including fatty acid esters and monoterpene alcohols (MTAs) such as linalool, nerol, geraniol, and citronella, were not detected in this study. Considering the sensory threshold of the compounds derived from the general spirits, it was considered that sensory threshold of esters was relatively lower than those of the alcohols such as acetic acid ethyl ester (5.9 ppm), ethanol (1.4% ppm), n-propanol (600–800 ppm), n-butanol (50 ppm), active amyl alcohol (50–65 ppm), and β-phenethyl alcohol (40–75 ppm) [18]. Based on the sensory threshold, compounds having an influence on these samples were iso-amyl alcohol, ethyl acetate, ethyl caprate, and ethyl caprylate, in that order. In addition, the compounds increased based on the aging period to amounts that a person can perceive the iso-amyl alcohol, ethyl caprate, and ethyl caprylate compounds, with the exception of the 1-week aging period. The reason the 1 week period should be excluded as an aging period is that a number of low-volatility

Table 1 Volatile compounds of distilled spirits according to aging periods that were made from sweet potato and rice through GC-MS

Samples compounds (mg/L)	Spirits Blended with 70% sweet potato spirits with 30% rice spirits					100% sweet potato spirits					100% rice spirits				
	Aging day of each sample (weeks)														
	A 128 weeks	B 92 weeks	C 64 weeks	D 76 weeks	E 60 weeks	F 16 weeks	G 1 week	H 56 weeks	I 28 weeks						
Ethyl acetate	104.21 ± 7.23	100.29 ± 6.34	90.28 ± 4.72	85.0 ± 3.28	66.92 ± 1.45	83.15 ± 2.35	128.54 ± 4.78	84.01 ± 2.76	97.87 ± 3.05						
n-Propanol	114.36 ± 9.62	90.54 ± 4.21	55.13 ± 2.45	40.52 ± 1.78	20.46 ± 0.99	18.29 ± 0.41	27.52 ± 1.23	—	3.71 ± 0.08						
Iso-amyl alcohol	826.47 ± 23.22	757.2 ± 18.45	611.3 ± 17.45	772.5 ± 20.35	635.3 ± 12.51	592.82 ± 8.63	965.98 ± 10.43	435.33 ± 5.45	529.52 ± 4.86						
Isobutyl alcohol	—	—	—	—	—	—	—	—	—						
Ethyl caprylate	7.47 ± 1.45	7.16 ± 0.89	5.48 ± 0.65	5.21 ± 0.32	4.79 ± 0.07	3.90 ± 0.13	7.92 ± 0.09	—	—						
Ethyl caprate	14 ± 1.78	2.76 ± 0.12	14.36 ± 1.12	14.1 ± 0.09	12.91 ± 0.56	11.52 ± 0.89	16.09 ± 0.59	—	—						
Phenethyl alcohol	46.55 ± 2.05	50.77 ± 1.88	34.88 ± 2.70	40.2 ± 1.23	29.95 ± 0.79	35.94 ± 1.08	15.49 ± 0.72	23.47 ± 1.04	16.85 ± 0.94						

compounds are present just after distillation; hence, they caused the flavor of the distilled spirits to be sharp and strong [8]. It seemed that the SPS had a flavor pattern that increased slightly according to the aging period. The flavor of the sweet potato spirits, however, is composed of numerous complicated volatile compounds. Therefore, there is a need to determine the key compounds having an influence on the flavor of sweet potato spirits and to confirm the exact correlation between compounds and aging period through further experimentation in future studies.

The RS were aged in pottery for 56 and 28 weeks, then named as samples H and I, respectively. Each sample was analyzed through the headspace using GC–MS. As shown in Table 1, unlike sweet potato spirits, only iso-amyl alcohol, ethyl acetate, n-propanol, and phenethyl alcohol were detected. The results were not consistent with the study conducted by Lee et al. [8] despite the use of the rice as the raw material. The difference in results was considered due to different analysis methods of GC–MS, the pretreatment methods of the samples or the characteristics of the secondary ingredients such as yeast, *Nuruk*, and even rice's place of origin. Considering the sensory threshold of compounds derived from general spirits, it is considered that iso-amyl alcohol and ethyl acetate had a greater influence on the samples. The rice-based compounds exhibited a decreasing pattern relative to the aging period, unlike those of sweet potato spirits. As shown in the detection results, it can be confirmed that iso-amyl alcohol and ethyl acetate decreased during the aging period as the following values indicate: from 529.52 ± 4.86 to 435.33 ± 5.45 mg/L and from 97.87 ± 3.05 to 84.01 ± 2.76 mg/L, respectively. These changes were similar to a study conducted by Lee et al. [8]. Generally, fusel oils such as iso-amyl alcohol, n-propanol, and isobutyl alcohol were changed by various reactions of oxidation owing to the permeable pottery. Lee et al. [8] reported that iso-amyl alcohol had a decreasing flavor pattern during the aging period. Therefore, based on the results of this analysis, it seemed that the RS had a slight decreasing flavor pattern as aging period increased. The flavor of the rice spirits, however, was composed of numerous complicated volatile compounds and there were many variables, including the GC–MS method, pretreatments, and the origin of the rice. Hence, there is a need to perform further studies to determine the key compounds having an influence on the flavor of Yeo-ju rice and to confirm the exact correlation between the compounds and the aging period.

The distilled spirits blended with SPS and RS at a 7:3 ratio were aged in pottery pieces for 128, 92, and 64 weeks and named as samples A, B, and C, respectively. Each of the aged spirits was analyzed through the headspace using GC–MS. In this case, iso-amyl alcohol, ethyl acetate,

n-propanol, ethyl caprylate, and ethyl caprate were detected in that order. Among the detected compounds, when considering the sensory threshold of the compounds derived from the general spirits, iso-amyl alcohol, ethyl acetate, and n-propanol were considered the major compounds for this sample because of the detection value. Based on the increased aging period, the detection values for iso-amyl alcohol increased as follows: 611.3 ± 17.45 , 757.2 ± 18.45 , and 826.47 ± 23.22 mg/L. The values for ethyl acetate and n-propanol also increased as follows: 90.28 ± 4.72 , 100.29 ± 6.34 , 104.21 ± 7.23 and 55.13 ± 2.45 , 90.54 ± 4.21 , 114.36 ± 9.62 mg/L, respectively. These results were similar to those for the SPS and were considered due to the ratio of blended spirits, which was blended by using more SPS per the 7:3 ratio. That is, the blended spirits were more affected by the sweet potato spirits. The synergy effect of blending the two types of raw materials, sweet potato and rice, could not be exactly confirmed by this analysis. This is because there were a number of variables, especially the different aging times of each spirit, making the comparison difficult for each result of compounds of spirits. Therefore, based on the results of this analysis, it is considered that the flavor pattern of blended spirits with SPS and RS at a 7:3 ratio seemed to increase; however, there is a need to study these results further owing to the number of variables.

The difference of the results was considered due to the aging time of the spirits. That is, the previous study used samples that were aged for 180 days during the initial aging stage. Whereas, this study used samples that were aged during 64, 92, and 128 weeks, included at the middle-aging stage. Due to the high permeability of air in the pottery pieces, it is known that some fusel oil was exchanged through various oxidation reactions [19]. Hence, the results of the change in patterns of the iso-amyl alcohol and n-propanol were different between the previous study and this study. Considering the sensory threshold of compounds induced from the spirits, it was considered that the sensory threshold of esters was relatively lower than those of the alcohols; also, the amount of volatile compounds increased by an amount that can lead a person to perceive the iso-amyl alcohol, ethyl acetate, ethyl caprylate, and ethyl caprate.

Analysis of change pattern of flavor of each distilled spirits by using E–nose based on MS

To cross-check the change in the pattern of the sample's flavor as analyzed by GC–MS according to the aging period, an e-nose based on the MS and DFA were used in this study. The independent variables of the discriminant function were the main ion fragments having high discrimination in the range of 10–200 (m/z). In the DFA, the

coefficients of determination were R^2 , indicating the success rate of the discrimination and F-value as well as the discriminant power of each ion fragment.

As shown in Fig. 1(A), the flavor of the sweet potato spirits (SPS) made from *sul-dut* manufactured by sweet potato showed a decreasing pattern according to the aging period of 1, 16, 60, and 76 weeks and named as samples G, F, E, and D, respectively. The coefficient of determination, R^2 , and F-values of DF1 and those of DF2 were as follows, 0.9998, 8109.00 and 0.9984, 932.64. For a ratio of the F-value, the DF1 was higher than the DF2 by approximately 9 times. That is, the samples in the Fig. 1(A) were discriminated mainly by DF1. The DF1 was set as the x-axis and the DF2 was set as the y-axis in order of having a high discrimination value. An air samples were used as the control due to being regarded as free of volatile components. Based on DF1 as plotted on the x-axis, the VOCs of the samples moved to the right side. In other words, they approached to the air samples plotted at the right side

according to an increase in the aging periods. In Fig. 1(B), it was confirmed that change amount of the VOCs decreased with an increase in the aging period as indicated by the bar graph, showing the relation between $\Delta DF1$ ($DF1_n - DF1_{air}$). Additionally, there are numerous VOCs after a 1-week aging period just after distillation, which was same as the GC-MS results and a previous study [8]. In these results, it was considered that the SPS had decreasing flavor pattern as the aging period increased. Furthermore, this flavor pattern was different from those of the GC-MS. In addition, it was considered the major compounds have a high influence on the e-nose analysis and were different from those of the GC-MS. The major ion fragments were 23, 61, 43, 44, 42, and 88 (m/z) in that order by the e-nose analysis. However, the major components in the GC-MS data were iso-amyl alcohol, ethyl acetate, n-propanol and those of the main ion fragments were 55, 42, 43, 41, 70, and 31 (m/z); 43, 61, 45, 29, and 70 (m/z); and 31, 29, 27, 42, and 52 (m/z), respectively. The

Fig. 1 (A) Discriminant function analysis of the obtained data by electronic nose based on mass spectrometry for sample D, E, F and G which were 100% sweet potato spirits according to aging period for

76, 60, 16 and 1 week. (B) Relationship between delta discriminant function first score of each of samples and aging period of spirits (DF1: $r^2 = 0.9998$, $F = 8109.00$ and DF2: $r^2 = 0.9984$, $F = 932.64$)

differences were thought to be due to variables such as the analysis temperature and the VOCs sampling method just like presence of the pretreatment process that could induce a loss of VOCs. The sensitive detection of the VOCs by the e-nose may not be detected by GC–MS as it depends on the column types of the GC–MS.

As shown in Fig. 2(A), the flavor of the rice spirits (RS) made from *sul-dut* manufactured by rice showed an increasing pattern according to the aging period where the period was 28 and 56 weeks and named as samples I and H, respectively. The coefficient of determination, R^2 , and F-values of DF1 and those of DF2 were as follows: 0.9996, 8500.20 and 0.9899, 294.39. For the ratio of the F-value, the DF1 was higher than the DF2 by approximately 29 times. That is, the samples in the Fig. 2(A) were discriminated mainly by DF1. The DF1 and DF2 were set as the x-axis and y-axis, respectively. Air samples were used as controls. Based on the DF1 as plotted on the x-axis, it was shown that

the VOCs of the samples moved to the left side. In other words, the VOCs moved away from the air samples as plotted on the right side according to the increase of aging periods. In Fig. 2(B), it was confirmed that change amount of the VOCs increased with increase in the aging period, but the amount was minimal as indicated by the bar graph showing the relation between $\Delta DF1$ ($DF1_n - DF1_{air}$) and the samples. This flavor pattern was different from those of the GC–MS. Also, it was considered the major compounds having a high influence on the e-nose analysis were different from those of the GC–MS. The major ion fragments were 61, 72, 88, 73, and 103 (m/z) in that order by the e-nose analysis. However, the major components in the GC–MS data were iso-amyl alcohol and ethyl acetate where the ion fragments were 55, 42, 43, 41, 70, and 31 (m/z) and 43, 61, 45, 29, and 70 (m/z), respectively. The differences were thought to be due to variables such as the analysis temperature and the VOCs sampling method similar to the presence of the pretreatment

Fig. 2 (A) Discriminant function analysis of the obtained data by electronic nose based on mass spectrometry for sample H and I which were 100% rice spirits according to aging period for 64 and 28 weeks.

(B) Relationship between delta discriminant function first score of each of samples and aging period of spirits (DF1: $r^2 = 0.9998$, $F = 8109.00$ and DF2: $r^2 = 0.9984$, $F = 932.64$)

process that could induce a loss of VOCs. The other reason the sensitivity of the VOCs detected by the e-nose may not have been detected by GC–MS was due to the column types of the GC–MS. Therefore, for cross-validation between GC–MS and the e-nose, it is considered that further research is necessary to determine the exact analysis methods considering the number of variables.

As shown in Fig. 3(A), the flavor of the blended spirits from the sweet potato and rice showed a decreasing pattern based on the aging periods of 64, 92, and 128 weeks and named as samples C, B, and A, respectively. The coefficient of determination, R^2 , and F-values of DF1 and those of DF2 were as follows: 0.9996, 5846.20 and 0.9994, 3691.10. For the ratio of the F-value, the DF1 was higher than the DF2 by approximately 1.6 times. That is, the samples in Fig. 3(A) were discriminated mainly by DF1. The DF1 and DF2 were set as the x-axis and y-axis, respectively. Air samples were used as the controls. Based on the DF1 as plotted on the x-axis, it was shown that the

VOCs of the samples moved to the right side. In other words, the air samples plotted on the right side according to an increase in the aging periods. In Fig. 3(B), it was confirmed that change amount of the VOCs increased with an increase in the aging period and the amount was relatively high by the bar graph, indicating a relation between $\Delta DF1$ ($DF1_n - DF1_{air}$) and the samples. This flavor pattern was different from those of the GC–MS. Also, it was considered the major compounds having a high influence on the e-nose analysis were different from those of the GC–MS. The major ion fragments were 15, 43, 44, 42, 41, and 29 (m/z) in that order by the e-nose analysis. However, the main components of the GC–MS data were iso-amyl alcohol and ethyl acetate where the ion fragments were 55, 42, 43, 41, 70, and 31 (m/z) and 43, 61, 45, 29, and 70 (m/z), respectively. The main ion fragments of the e-nose study were similar to acetaldehyde with 29, 44, 43, 42, and 15 (m/z) ion fragments. Based on the characteristics of acetaldehyde, it was considered that the irritating and sharp

Fig. 3 (A) Discriminant function analysis of the obtained data by electronic nose based on mass spectrometry for sample A, B and C which were blended spirits according to aging period for 128, 92

and 64 weeks. (B) Relationship between delta discriminant function first score of each of samples and aging period of spirits (DF1: $r^2 = 0.9996$, $F = 8500.20$ and DF2: $r^2 = 0.9899$, $F = 294.39$)

Fig. 4 (A) Discriminant function analysis of the obtained data by electronic nose based on mass spectrometry for sample A, B, C, D, E, F, H and I which were blended spirits (A, B, C), 100% sweet potato

spirits (D, E, F) and 100% rice spirits (H, I) (DF1: $r^2 = 0.9988$, $F = 1433.30$ and DF2: $r^2 = 0.9983$, $F = 1063.20$)

flavor of the sample decreased as the aging period increased. That is, the flavor of the distilled spirits softened with an increase in the aging period.

The flavor pattern of all samples, the blended spirits from the sweet potato and rice, SPS, and RS is showed at Fig. 4. The coefficient of determination, R^2 , and F-values of DF1 and those of DF2 were as follows: 0.9988, 1433.30 and 0.9983, 1063.20. For the ratio of the F-value, the DF1 was higher than the DF2 by approximately 1.3 times. That is, the samples in Fig. 4 were discriminated mainly by DF1. The DF1 and DF2 were set as the x-axis and y-axis, respectively. An air samples were used as the controls. Based on the DF1 as plotted on the x-axis, it was shown that blended spirits were platted between SPS and RS. It is considered that the blended spirits tended to be closer to the SPS due to the ratio SPS:RS = 7:3. The different results in the flavor patterns were caused by the difference in the primary compounds as a result of the significant number of variables. Compounds analyzed by GC–MS were changed depending on the types of column or pretreatment process utilized. It is considered that there were also other compounds from sweet potato distilled spirits besides the general primary compounds of distilled spirits. Therefore, for improving the methods for controlling long-term aging of the spirits and based on the results of the change pattern of flavor, it was considered that further experiments are needed to identify key compounds for accurate correlation analysis.

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