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Determination of acetaldehyde, methanol and fusel oils in distilled liquors and sakès by headspace gas chromatography

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Abstract In this study, a headspace gas chromatography (HS-GC) method was carried out to determine the contents of acetaldehyde, methanol and fusel oils in distilled liquors and sakès from different countries. A DB-Wax column was adopted in HS-GC, which showed good linearity, high precision and accuracy and low LOQ and LOD on all the compounds. Results showed that distilled liquors contained higher levels of acetaldehyde with the values of 12.88–35.53 mg/L than sakès (0.83–29.13 mg/L). Methanol was only detected in a few distilled liquors with small amounts. Amyl alcohols, including isoamyl alcohol (2-methyl-1-butanol) and active amyl alcohol (3-methyl-1-butanol), isobutanol (2-methyl-1-propanol) and 1-propanol were the main fusel oils among the distilled liquors and sakès analyzed. Amyl alcohols contents were 2 to 4 times higher in Korean distilled liquors (203.01–428.66 mg/L) than that in Chinese distilled liquors (28.52–42.77 mg/L) and all the sakès (61.90–166.59 mg/L).

Keywords Volatile compounds · Distilled liquors · Sakès · Headspace gas chromatography · Validation

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Introduction

Acetaldehyde is a naturally occurring compound and found in diverse foods and beverages (such as vegetables, dairy products, fruits, and juices, etc.) as well as liquors (Kaseleht et al., 2011). In fact, acetaldehyde has long been employed as a flavor enhancer to provide a pleasant fruity bouquet at low concentrations (Miyake and Shibamoto, 1993; Paiano et al., 2014). Although it is widely used, high levels of acetaldehyde would produce an irritating odor of beverages. Also, acetaldehyde can exacerbate the hepatic, neurologic, and cardiac complications of alcoholism (Aberle and Ren, 2003).

Along with acetaldehyde, methanol and higher alcohols also can be found with various levels in liquors. For example, methanol is a byproduct produced due to the degradation of pectins during wine fermentation (Hantson, 2006). Excessive intake of methanol can lead to toxicosis manifesting as headache, vertigo, fatigue, vomiting, blurred vision, blindness and even death (Geroyiannaki et al., 2007). Higher alcohols such as propanol, isobutanol, and amyl alcohols are typically referred to fusel oils, which are widely present in variable concentrations of alcoholic beverages (Welsh and Williams, 1989). The presence of fusel oil below 300 mg/L contributes to the desired sensory in the liquors. However, if present in excess of about 400 mg/L, it contributes negatively to flavor of liquors (Rapp and Mandery, 1986) and might cause nervous hyperemia, headaches, and dizziness on human when exposed to large amounts (Nemestóthy et al., 2008; Woo, 2005). In addition, contents of fusel oils can be used to monitor the process malfunctions and to confirm fermentation substrate authenticity in liquors. Therefore, the quantification of acetaldehyde, methanol, and higher alcohols are essential for determining the qualities of

alcoholic beverages (Geroyiannaki et al., 2007; Gil et al., 2006; Lachenmeier et al., 2008).

Gas chromatography (GC) is conventionally used to quantify the volatile compounds. Among the available injection methods, direct injection is widely used. However, when samples containing high levels of water (such as liquors) are directly injected into a column repeatedly, there is a possibility to cause stationary phase degradation, which in turn lowers resolutions and reproducibility of the column (Peinado et al., 2004). On the contrary, the headspace GC (HS-GC) technique can eliminate the sample matrix effect and avoid column damage by water since HS-GC technique is limited to volatile compounds during GC injection (Fan and Qian, 2005).

Acetaldehyde, methanol and fusel oils are widely accepted hazardous volatile compounds in alcoholic beverages for human if over-consumed. In this study, HS-GC method was tested to verify the detection and quantification of these volatile components. In addition, method validation was conducted to confirm the acceptability of this method. Besides, the most representative alcoholic beverages from Asia countries were chosen to compare the content difference of these volatiles between countries and varieties, including Korean soju and sakès, Chinese distilled liquors, and Japanese sakès.

Materials and methods

Materials and chemicals

All chemicals used were of analytical grade: acetaldehyde (> 99.5%), ethanol (≥ 99.5%), methanol, 2-butanol, 1-propanol, 2-methyl-1-propanol (isobutanol), 3-pentanol, 3-methyl-1-butanol (isoamyl alcohol) and 2-methyl-1-butanol (active amyl alcohol) were obtained from Sigma-Aldrich Corp., (St. Louis, MO, USA). Commercial sakès and distilled liquors were purchased from a local supermarket in Korea.

Preparation of standard solution

Standard stock solution, that is, of acetaldehyde, methanol, 2-butanol, 1-butanol, 1-propanol, isobutanol, isoamyl alcohol, active amyl alcohol and 3-pentanol (internal standard, IS) were prepared individually at 10,000 mg/L in 15% ethanol solution. Then, 10 mL of each eight stock solutions (except IS) were added into a 100 mL volumetric flask and filled up to the volume by 15% ethanol solution, making the standard working solution with each substance at the concentration of 1000 mg/L. Thereafter, the standard working solution (1000 mg/L) was diluted into 10, 20, 50, 100, 200, and 500 mg/L, respectively. As for the IS stock solution, it was diluted to 500 mg/L. Finally, the diluted standard mixtures were mixed with IS solution (500 mg/L) at the ratio of 1:1 (v/v), making the final standard solutions with each component at concentrations of 5, 10, 25, 50, 100, 250 and 500 mg/L containing 250 mg/L IS. All the standard solutions were kept at − 4 °C before use.

Sample preparations

Pretreatment of liquor samples were different according to their ethanol contents. Among the commercial samples tested, Chinese distilled liquors contained highest ethanol contents of 32–50%. These samples were first diluted with an equal volume of distilled water, and then mixed thoroughly with IS solution (500 mg/L) by 1:1 (v/v). Other samples, such as Korean distilled liquors and sakès were directly mixed with IS solution (500 mg/L) at the same volume. All samples were maintained at − 4 °C before use. The content of each compound was determined according to individual standard calibration curve and the final concentration in liquors was calculated according to the dilution factor.

HS-GC conditions

Standard solutions and liquor samples were analyzed using a 7890B GC system (Agilent Technologies, Palo Alto, CA, USA) equipped with and a headspace sampling system (Yong Lin instrument Co., Ltd., South Korea). Separation was performed using a DB-Wax column (30 m × 250 μm × 0.25 μm, Agilent 122-7032) with an injection volume of 1000 μL at an injection speed of 30.0 mL/min, and a spilt ratio of 20:1. The initial oven temperature was held at 35 °C for 5 min, raised to 80 °C at 3 °C/min, raised to 250 °C at 10 °C/min and finally held at 250 °C for 10 min. Nitrogen (N_2) was used as the carrier gas at a constant flow of 0.7 mL/min. The inlet and FID temperatures were 200 °C and 250 °C, respectively. HS-GC method required sample incubation at 70 °C for 10 min before injected into the GC system.

Intra-day and inter-day test for validation of HS-GC method

Intra-day repeatability and inter-day precision were estimated over 3 days and calculated in terms of the relative standard deviations (RSD, %) of two different liquors (distilled liquor and sakè), performing three replicates of each sample in continuous 3 days.

LOQ and LOD

Limit of detection (LOD) and limit of quantitation (LOQ) are the lowest concentration of substrates that can be

detected and quantified. In this study, LOD and LOQ of acetaldehyde, methanol and fusel oils by HS-GC were calculated as three times and ten times of the signal-to-noise using the following equations (Armbruster et al., 1994):

$$\mathrm{LOD} = 3.3 \times \frac{\sigma}{\mathrm{S}} \quad (1)$$

$$\mathrm{LOQ} = 10 \times \frac{\sigma}{\mathrm{S}} \quad (2)$$

where σ is the standard deviation of determined lowest concentration of each ingredient in three independent tests, and S is the slope of the calibration curve.

Accuracy

Accuracy was estimated by recovery test with one distilled liquor and one sakè sample spiked with 25 or 250 mg/L of acetaldehyde, methanol and fusel oils. First, 100 mg/L and 1000 mg/L of the standard working solutions and 1000 mg/L IS solution were prepared as above. Then, 100 mg/L and 1000 mg/L solution mixtures were mixed separately with IS (1000 mg/L) at a ratio of 1:1 (v/v), thus making solutions containing 50 or 500 mg/L of each volatile compound and 500 mg/L of IS. Finally, distilled liquor and sakè samples were mixed with the 50 or 500 mg/L solutions in the same proportion and therefore making the final sample solutions that contained 25 or 250 mg/L of all the substrates and 250 mg/L of IS. Original contents of the volatile compounds in distilled liquor and sakè were measured by directly mixing liquors with IS solution (500 mg/L) at the ratio of 1:1 (v/v). All samples were prepared duplicated and stored at − 4 °C before use.

Statistical analysis

All analyses were conducted at least in duplicate and the results were expressed as mean ± standard deviation (SD) unless specifically stated. Results were analyzed by one-way analyses of variance (ANOVA) using the Statistical Package for Social Sciences (SPSS 24, Chicago, IL, USA) with Duncan's significance test at a $p < 0.05$ level.

Results and discussion

Separation of HS-GC method on the volatile compounds

Figure 1 shows the chromatograms of standard solution (A), sakè (B) and distilled liquor (C) obtained from HS-GC method in which acetaldehyde, methanol and fusel oils were separated. Identifications were performed by comparing the retention time with individual authentic standards. HS-GC method is commonly used for analyzing volatile compounds because of its fast, sensitive, and solvent-free characteristics (Zhang et al., 1994). Whereas, in some cases, direct injection is disadvantaged by the need of pretreatment, such as centrifugation, prior to GC analysis (Etievant et al., 1986). Further, when liquor samples are repeatedly injected directly into a column, low resolutions and reproducibility would be expected due to the water existed in the sample (Peinado et al., 2004). Therefore, because of its practical advantages and reliability, we adopted HS-GC method for analyzing levels of acetaldehyde, methanol and fusel oils in different alcoholic beverages.

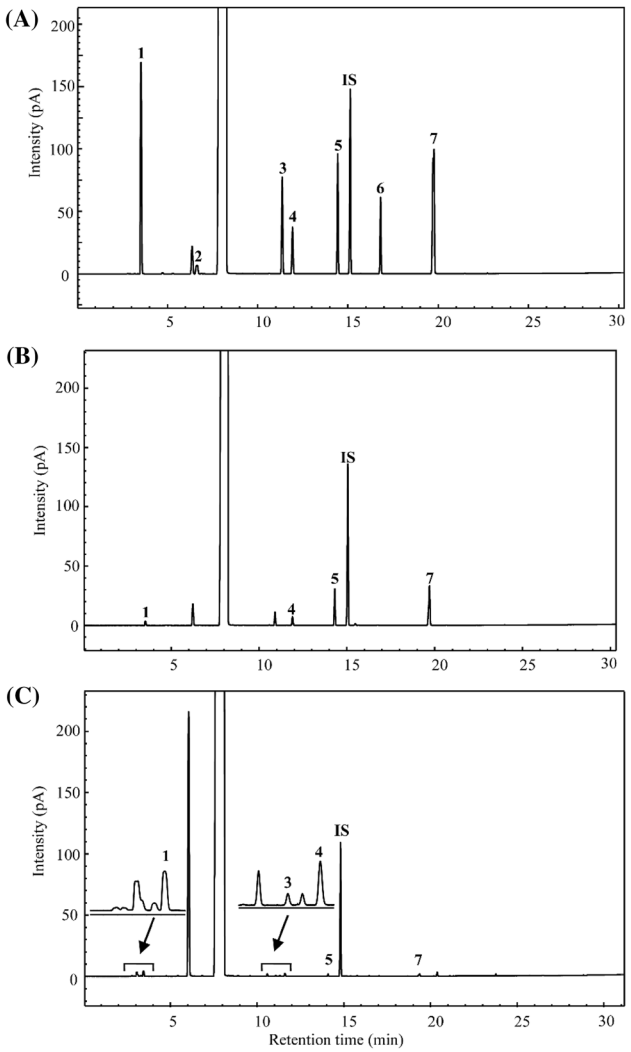

Fig. 1 Gas chromatograms of standard solution (250 mg/L) (**A**), sakè (**B**) and distilled liquor (**C**) by HS-GC method. 1, acetaldehyde; 2, methanol; 3, 2-butanol; 4, 1-propanol; 5, isobutanol; IS; 3-pentanol; 6, 1-butanol; 7, amyl alcohols

Method validation of HS-GC method

Method validation was conducted to confirm the acceptability of the HS-GC method in terms of its linearity, LOD, LOQ and accuracy. Linear equations, concentration ranges, and R^2 values are summarized in Table 1. During the experiment, it was found that peak areas of acetaldehyde and methanol were quite stable while IS areas varied between injections. This phenomenon intended that 3-pentanol might not be an appropriate internal standard for quantification of acetaldehyde and methanol. Therefore, calibration curves of acetaldehyde and methanol were conducted using external calibration curve by plotting peak area versus concentrations. Acetaldehyde and methanol showed excellent linearity with R^2 of 1.0000 and 0.9987 in the range of 5–500 mg/L (Table 1). In case of the fusel oils, 3-pentanol was in accordance to the peak area changes with them, indicating that 3-pentanol was the proper internal standard for those fusel oils, thus internal calibration curve was adopted for the quantification of the fusel oils. The internal calibration curves for fusel oils were constructed by plotting peak area ratios of fusel oils/IS versus concentrations of fusel oils. Results showed that HS-GC method exhibited good linearity of fusel oils with R^2 values more than 0.998 in 5–500 mg/L range (amyl alcohols in the range 10–1000 mg/L).

Method precision was evaluated by one distilled liquor and sakè, respectively. In this study, high precision of HS-GC was obtained in both intra-day and inter-day experiments. Table 2 shows that RSD% values in distilled liquor were lower than 5% in both intra-day and inter-day experiments, whereas less than 10% in sakè sample, exhibiting high precision and repeatability of HS-GC method in the determination of liquor samples.

LOD of acetaldehyde and methanol were 0.07 and 1.6 mg/L, respectively, and fusel oils ranged from 0.24 to 1.09 mg/L. Recovery rates of acetaldehyde, methanol and fusel oils were determined by spiking with 25 and 250 mg/L of each compound. Table 3 shows the recovery rate of each component in the distilled liquor and sakè sample. All the compounds showed acceptable performance with recovery rate (%) ranging from 85.2 to 117.9%, except methanol (77.9–121.7%).

Acetaldehyde and methanol contents in liquors

The HS-GC method was used to quantify acetaldehyde, methanol and fusel oil levels in commercial distilled liquors and sakès. During the experiment, it was found that peak areas of 3-pentanol (IS) decreased in distilled liquors (ranging from 32 to 50%), intending the instability of volatilization. These observations indicated that distilled liquors with high ethanol contents should be diluted before analysis. Similar results were previously reported by De la Calle García et al. (1996), who reported maximal adsorption of volatile compound (i.e. terpene) was obtained at low ethanol concentrations in samples. Hence, the distilled liquors were diluted (two times) before analysis.

In the present study, only Chinese distilled liquors were diluted two-fold prior to analysis with HPLC grade water, whereas Korean distilled liquors and all the sakès (ethanol content ranging from (13–25%) were directly mixed with IS solutions (500 mg/L). Table 4 shows the acetaldehyde contents in Korean distilled liquors and Chinese distilled liquors, which were 12.88–35.53 mg/L and 16.23–23.65 mg/L, respectively. In sakè samples, acetaldehyde contents ranged from 0.83 to 29.13 mg/L and most samples with the acetaldehyde contents below 10 mg/L. The data reveled that distilled liquors contains significantly higher ($p < 0.05$) concentrations of acetaldehyde than sakès except one sample with 29.13 mg/L, which might contribute to the raw materials or processes. Previous studies also measured the acetaldehyde contents in Korea distilled liquors and sakès by GC–MS, and found acetaldehyde contents ranged from 805 to 13,371 ng/g and 0 to 10,368 ng/g, respectively (Paiano et al., 2014; Park et al., 2006), which was in accordance with the data of our study. Acetaldehyde is a by-product of alcoholic

Table 1 Standard curve, linearity, LOQ and LOD of HS-GC method

Ingredient[a]	Retention time (min)	Range (mg/L)	Equations	Correlation coefficient (R^2)	LOQ (mg/L)	LOD (mg/L)
Acetaldehyde	3.52	5–500	y = 2.9363x − 0.1636	1.0000	0.2	0.07
Methanol	6.67	5–500	y = 0.2060x − 0.1517	0.9987	4.79	1.6
2-Butanol	11.36	5–500	y = 0.0024x + 0.0029	0.9995	1.81	0.6
1-Propanol	11.92	5–500	y = 0.0013x + 0.0016	0.9990	1.36	0.45
Isobutanol	14.36	5–500	y = 0.0025x + 0.0041	0.9997	0.72	0.24
1-Butanol	16.79	5–500	y = 0.0015x + 0.0011	0.9992	2.64	0.88
Amyl alcohols	19.70	10–1000	y = 0.0024x + 0.0007	0.9994	3.27	1.09

[a]All standards were dissolved in 15% (v/v) ethanol solution

Table 2 Intra-day and inter-day precision of HS-GC method of a distilled liquor and sakè sample[a]

Ingredient[a]	Distilled liquor (mg/L)		Sakè (mg/L)	
	Intra-day	Inter-day	Intra-day	Inter-day
Acetaldehyde	32.15 ± 0.30[b]	32.15 ± 0.83	17.51 ± 0.68	17.70 ± 0.73
Methanol	–	–	–	–
2-Butanol	11.28 ± 0.37	10.82 ± 0.16	–	–
1-Propanol	77.93 ± 3.62	73.75 ± 2.46	95.35 ± 8.52	93.74 ± 0.55
Isobutanol	26.02 ± 0.63	25.09 ± 0.15	182.06 ± 7.61	181.81 ± 1.28
1-Butanol	–	–	–	–
Amyl alcohols	80.97 ± 0.84	80.96 ± 1.00	203.07 ± 4.56	198.17 ± 11.37

[a]All standards were dissolved in 15% (v/v) ethanol solution

[b]Values are expressed as mean ± relative standard deviations (RSD) of three replicate determinations

–, represents not detected

Table 3 Recovery rate of acetaldehyde, methanol and fusel oils in distilled liquor and sakè by HS-GC method

Samples	Spiked amount (mg/L)	Recovery rate (%)						
		Acetaldehyde	Methanol	2-Butanol	1-Propanol	Isobutanol	1-Butanol	Amyl alcohols
Distilled liquor	25	108.1 ± 0.15[a]	77.9 ± 0.38	111.4 ± 0.02	98.5 ± 0.02	105.7 ± 0.02	98.6 ± 0.02	97.7 ± 0.03
	250	99.7 ± 0.03	121.7 ± 0.25	109.8 ± 0.02	104.3 ± 0.03	105.5 ± 0.01	90.6 ± 0.01	85.2 ± 0.00
Sakè	25	96.8 ± 0.01	102.0 ± 0.05	100.3 ± 0.02	94.2 ± 0.07	105.0 ± 0.02	107.0 ± 0.03	117.9 ± 0.07
	250	97.1 ± 0.00	91.8 ± 0.08	96.5 ± 0.02	92.7 ± 0.04	98.1 ± 0.01	108.1 ± 0.00	111.7 ± 0.01

[a]Values are expressed as mean ± standard deviation (SD) of duplicated determinations

production by yeast and a potent flavor compound with high volatility. During the fermentation process, conditions such as temperature, CO_2 level, types of yeast and raw materials may substantially affect acetaldehyde generation (Liu and Pilone, 2000). Low concentration of acetaldehyde in drinks provide a pleasant aroma, whereas high concentration imparts a harsh aroma (Miyake and Shibamoto, 1993) and enhanced exposure to acetaldehyde may have a negative effect on the upper digestive tract carcinogenicity and also in liver toxicity (Mello et al., 2008).

It is known that accidental consumption of methanol can lead to severe intoxication because its metabolites formaldehyde and formic acid are toxic to human (Cortés et al., 2005). Hence, accurate determination of methanol content in liquors is of great importance for manufacturers and consumers. In the present study, methanol was detected in only a few distilled liquors with the values of 14.6–22.36 mg/L and not detected in any sakè samples. Previous studies showed that methanol contents of Korean distilled liquors (Soju) and sakès ranged 9–106 ng/g and 0–27 ng/g, respectively (Chung et al., 2015; Park et al., 2006). The results in our present study were in accordance with the previous studies.

Fusel oils contents in liquors

Sakè is a traditional Japanese rice wine, and is widely consumed in Northeast Asia. It is brewed from steamed rice grains using *koji* (*Aspergillus oryzae*) or yeast (*Saccharomyces cerevisiae*) (Sugimoto et al., 2010). The flavor of sakè is mainly contributed by fusel oils (isoamyl alcohol, isobutanol, and n-propanol), esters and acids (Iwano et al., 2005).

Fusel oils are commonly referred to alcohols with more than two carbons and are considered important flavor compounds (Liu et al., 2002). Of the fusel oils, amyl alcohols are the most abundant and are produced from isoleucine and leucine by deamination and decarboxylation, respectively (Ferreira et al., 2013). In addition, amyl alcohols are considered predictors of sensory characters of distilled products (Soufleros et al., 2004). Besides, 1-propanol and isobutanol are the main components in liquors, and the former compound has been reported to confer a ripened fruit odor to wine (Giudici et al., 1993). In the present study, amyl alcohols were detected in Korean distilled liquors, Chinese distilled liquors, Korea sakès, and Japanese sakès at concentrations of 203.01–428.66 mg/L, 28.52–42.77 mg/L, 61.90–99.97 mg/L and 81.70–166.59 mg/L, respectively. Amyl alcohols in

Table 4 Acetaldehyde, methanol and fusel oils contents in distilled liquors and sakès from different countries by HS-GC method

	Origin	Concentration (mg/L)						
		Acetaldehyde (mg/L)[1]	Methanol (mg/L)	2-Butanol (mg/L)	1-Propanol (mg/L)	Isobutanol (mg/L)	1-Butanol (mg/L)	Amyl alcohols (mg/L)
Distilled liquor	Korea	12.88 ± 0.53^{h}	15.55 ± 2.06^{ab}	–	111.31 ± 6.46^{de}	203.08 ± 7.38^{d}	–	295.15 ± 8.01^{c}
		35.53 ± 0.48^{a}	15.07 ± 1.37^{ab}	–	74.83 ± 0.01^{hij}	135.94 ± 1.65^{f}	–	203.01 ± 3.87^{de}
		26.17 ± 0.29^{c}	–[2]	–	129.25 ± 13.06^{c}	249.80 ± 8.38^{b}	–	428.66 ± 14.24^{a}
		18.98 ± 0.67^{f}	–	–	98.22 ± 0.97^{ef}	233.19 ± 1.41^{c}	–	363.40 ± 59.95^{b}
		22.15 ± 0.43^{e}	–	–	231.56 ± 15.7^{a}	149.99 ± 5.65^{e}	–	231.56 ± 41.52^{d}
		15.16 ± 0.77^{g}	–	–	150.23 ± 2.23^{b}	269.12 ± 1.11^{a}	6.61 ± 0.46^{b}	395.60 ± 11.92^{b}
	China	16.23 ± 2.60^{g}	–	–	119.48 ± 4.22^{cd}	6.71 ± 0.77^{o}	17.12 ± 1.64^{a}	42.77 ± 9.96^{jkl}
		23.65 ± 0.19^{d}	22.36 ± 16.48^{a}	–	75.09 ± 0.69^{hij}	17.71 ± 0.49^{n}	–	30.29 ± 0.24^{kl}
		18.20 ± 0.00^{f}	14.60 ± 3.30^{b}	–	15.11 ± 1.19^{l}	5.32 ± 0.26^{o}	5.68 ± 0.80^{c}	28.52 ± 1.11^{l}
Sakè	Korea	10.53 ± 0.10^{i}	–	–	52.05 ± 3.12^{k}	39.83 ± 1.09^{kl}	–	78.35 ± 3.20^{hij}
		8.46 ± 0.05^{jkl}	–	–	62.94 ± 7.05^{jk}	21.13 ± 1.03^{n}	–	61.90 ± 1.96^{ijkl}
		7.84 ± 0.5^{jkl}	–	–	98.96 ± 6.34^{ef}	44.82 ± 1.53^{jk}	–	99.97 ± 4.87^{ghi}
		9.03 ± 0.87^{j}	–	–	57.31 ± 0.48^{k}	41.60 ± 0.59^{k}	–	74.39 ± 0.92^{hijk}
	Japan	7.06 ± 0.10^{lm}	–	–	93.32 ± 1.70^{fg}	72.88 ± 0.29^{g}	–	140.63 ± 13.36^{fg}
		0.83 ± 0.05^{o}	–	–	67.93 ± 5.18^{ijk}	42.42 ± 1.21^{k}	–	94.37 ± 4.55^{ghi}
		11.08 ± 0.10^{i}	–	–	64.82 ± 1.89^{ijk}	41.36 ± 0.52^{k}	–	94.41 ± 12.05^{ghi}
		6.21 ± 0.05^{m}	–	–	23.21 ± 1.81^{l}	34.50 ± 0.73^{lm}	–	90.88 ± 6.05^{hi}
		6.89 ± 0.05^{lm}	–	–	73.48 ± 0.82^{hij}	50.35 ± 0.09^{ij}	–	104.83 ± 1.83^{ghi}
		$29.13 \pm \pm 1.05^{b}$	–	–	89.02 ± 0.83^{fgh}	52.74 ± 0.10^{i}	–	81.70 ± 0.48^{hij}
		7.13 ± 0.48^{klm}	–	–	80.41 ± 13.81^{ghi}	50.57 ± 3.01^{ij}	–	110.61 ± 16.79^{gh}
		7.98 ± 0.05^{jkl}	–	–	26.95 ± 0.84^{l}	31.17 ± 0.39^{m}	–	96.81 ± 4.44^{ghi}
		15.81 ± 0.24^{g}	–	–	98.85 ± 1.54^{ef}	62.58 ± 0.81^{h}	–	116.57 ± 0.34^{gh}
		4.37 ± 0.05^{n}	–	–	87.20 ± 2.61^{fgh}	75.72 ± 1.77^{g}	–	166.59 ± 40.56^{ef}
		8.69 ± 0.87^{jk}	–	–	97.20 ± 18.96^{ef}	50.24 ± 4.40^{ij}	–	103.11 ± 35.26^{ghi}

[1]All values are expressed as mean ± standard deviation (SD) of duplicated determinations; means within a column followed by different letters are significantly different at $p < 0.05$ level by Ducan's multiple range test

–, represents not detected

Korean distilled liquors were almost 10 times higher than that in Chinese distilled liquor. 1-propanol levels ranged widely in distilled liquors and sakès from 15.11 to 231.56 and 23.21 to 98.96 mg/L, respectively. Isobutanol in Korea distilled liquor was the most abundant with the values of 135.94–269.12 mg/L, which was significantly higher ($p < 0.05$) than that in Chinese distilled liquors and all the sakè samples. Other trace substance, such as 1-butanol, was present in small amounts at 5.68–17.12 mg/L in distilled liquors, and was not detected in sakè samples. 2-butanol was not detected in any liquor samples tested. Due to the types and origins of liquors, the levels of fusels were significantly different.

In conclusion, volatile compounds such as acetaldehyde, methanol and fusel oils are important indicators to determine the quality of liquors, and thus the accurate determination of these volatiles is of great significance. In this study, HS-GC method exhibited excellent linear responses with R^2 values of > 0.9980 on the determination of acetaldehyde, methanol and fusel oils. LOQ of acetaldehyde, methanol, 2-butanol, 1-propanol, isobutanol, 1-butanol, and amyl alcohols in this method were 0.2, 4.79, 1.81, 1.36, 0.72, 2.64, and 3.27 mg/L, respectively. In addition, levels of acetaldehyde, methanol and fusel oils varied significantly due to liquor types and origins, for example, Korean distilled liquors contained highest amyl alcohols with the values of 203.01–428.66 mg/L, while Chinese distilled liquors only contained 28.52–42.77 mg/L.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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