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ARTICLE

Evaluation of volatile organic compounds in alcoholic beverages consumed in Korea

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Abstract Volatile organic compounds including acetaldehyde, methanol, and higher alcohols such as 1-propanol and 3-methyl-1-butanol in 75 domestic and imported alcoholic beverages consumed in Korea were investigated and evaluated using a gas chromatograph equipped with a mass spectrometer. The acetaldehyde contents in the studied samples ranged from 0.02 to 11.73 mg/L, and were highest in refined rice wines and fruit wines. Only the wine and fruit wine samples contained methanol, at concentrations in the range of 1.42–23.81 mg/L. The 1-propanol content was highest in whisky, while the 3-methyl-1-butanol content ranged from 4.45 to 280 mg/L in all samples other than Korean distilled liquor.

Keywords Volatile organic compounds · Acetaldehyde · Methanol · Higher alcohols · Alcoholic beverages · GC–MS · Method validation

Introduction

The major volatile organic compounds (VOCs) of alcoholic beverages are aldehydes such as acetaldehyde, low-molecular-weight alcohols such as methanol, and higher alcohols (Geroyiannaki et al. 2007; Lachenmeier and Sohuius 2008a; Lachenmeier et al. 2008b). Acetaldehyde and higher alcohols exert strong effects on the sensory qualities of various foods and alcoholic beverages (Miyake and Shibamoto 1993; Gil et al. 2006).

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Acetaldehyde is one of the important flavor compounds found in many alcoholic beverages and foods including fruit juice, beer, wine, and spirits (Adams and Moss 1995; Tao et al. 2008; Tian 2010; Uebelacker and Lachenmeier 2011). The concentration of acetaldehyde in various alcoholic beverages has recently been determined to be within the ranges of 0–63 mg/L in beer, 0–211 mg/L in wine, 12–800 mg/L in fortified wines, and 0–1159 mg/L in spirits (Lehtonen et al. 1999; Liu and Pilone 2000; Lachenmeier and Sohuius 2008a). Acetaldehyde is derived from the fermentation of raw materials and develops during the distillation and aging of spirits (Silva and Malcata 1998). It is also produced by microbe-mediated oxidation (Silva et al. 1996; Silva and Malcata 1999). In addition, sugar, which is the primary substrate of acetaldehyde formation, and amino acids (including alanine) can also contribute to the formation of this compound in alcoholic beverages Boulton et al. (1996, Henschke and Jiranek 1993). The International Agency for Research on Cancer (IARC) has designated acetaldehyde as a possible carcinogen in humans (Group 2B; IARC 1999), and acetaldehyde associated with the consumption of alcoholic beverages also being evaluated as carcinogenic to humans (Group 1; IARC 2012).

Methanol in alcoholic beverages is formed by pectinolytic enzymes that split the methoxyl group from the pectin present in crushed fruits (Silva and Malcata 1998). However, its toxicity is of concern since the ingestion of large amounts can produce blindness or even death Cortés et al. (2005). On the other hand, higher alcohols—which are formed by yeast metabolism from amino acids—occur naturally in the highest concentrations in distillates of alcoholic beverages and can act as a flavoring aroma with a characteristic odor note (Silva and Malcata 1999; Ehrlich 1913). For example, they commonly constitute about 50 %

of the aromatic constituents of wine, excluding ethanol (Jackson 2000). The major higher alcohols found in alcoholic beverages are 1-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 3-methyl-1-butanol (Lachenmeier et al. 2008b). Specifically, 2-methyl-1-propanol, 3-methyl-1-butanol, and 1-propanol can be produced by yeast through either the anabolic pathway from glucose or the catabolic pathway from their corresponding amino acids such as valine, leucine, isoleucine, and phenylalanine (Tao et al. 2008). The Joint FAO/WHO Expert Committee on Food Additives (JECFA) included higher alcohols (i.e., 1-propanol, 1-butanol, and 2-methyl-1-propanol) in the functional class of 'flavoring agent' due to the absence of any safety concerns at normal intake of intake levels (JECFA 2003); however, previous studies revealed the possible toxicity of higher alcohols in illegally and home-produced alcoholic beverages (Lachenmeier 2007).

European Council Regulation already limits the levels of VOCs including acetaldehyde, methanol, and higher alcohols in alcoholic beverages as follows: 0.5 g/hectoliter (hL) of absolute alcohol (AA) for acetaldehyde and 50 g/hL AA for methanol in neutral alcohol (98 % alcohol; EEC 1989). However, for certain groups of spirits there are defined limits for the minimum contents of volatile compounds (i.e., the quantity of volatile compounds, mainly higher alcohols, other than ethanol and methanol). For example, the minimum contents of volatile compounds specified for brandy, fruit spirits, and rum are 125, 200, and 225 g/hL AA, respectively (EC 2000).

Several analytical methods have been developed in order to determine VOCs in alcoholic beverages. The EC Regulations propose a method for determining the volatile congeners involving injecting the spirit sample directly into a gas chromatography (GC) system equipped with a WAX column and a flame ionization detector (FID; EC 2000). However, various analytical methods that employ different extraction methods, columns, and GC detectors have been developed for determining the contents of VOCs in alcoholic beverages (Vesely et al. 2003; Gerogiannaki-Christopoulou 2008; Geroyiannaki et al. 2007; Tao et al. 2008).

The levels of aldehydes, methanol, and higher alcohols in alcoholic beverages have been obtained following liquid–liquid extraction (Tressl et al. 1978), distillation (Gerogiannaki-Christopoulou 2008; Geroyiannaki et al. 2007), dynamic and static headspace sampling (Kallio 1991), and solid-phase microextraction (SPME) with on-fiber derivatization (Vesely et al. 2003; Tao et al. 2008). These compounds have also been analyzed using GC–FID as well as GC–mass spectrometry (MS) equipped with polyethylene glycol line columns such as WAX, CARBOWAX, and FFAP columns (Lang et al. 2006; Wang et al. 2004; Vesely et al. 2003; Gerogiannaki-Christopoulou 2008; Geroyiannaki et al. 2007; Tao et al. 2008). For examples, acetaldehyde and methanol in Greek traditional alcoholic beverages from varietal fermented grape pomaces (*Vitix vinifera* L.) were determined using GC–FID after distillation (liquid distillate; Gerogiannaki-Christopoulou 2008; Geroyiannaki et al. 2007). Volatile compounds—including higher alcohols—in red wines were extracted by SPME and detected by a GC–MS system equipped with a CB-WAX column (Tao et al. 2008). The contents of methanol in wine, beer, spirits, and Chinese medicinal liqueur were determined using GC–FID with a WAX column (Wang et al. 2004). Higher alcohols including 1-propanol, 1-butanol, 3-methyl-1-butanol, and methanol in illegally produced alcoholic beverages in Estonia were identified using a GC–MS system equipped with a FFAP column (Lang et al. 2006). A method for the rapid determination of the principal volatile compounds (acetaldehyde, methanol, 2-butanol, 1-butanol, and higher alcohols) via the direct injection of the spirit samples has been developed with a CP-WAX column (López-Vázquez et al. 2010).

In this study, the volatile compounds in alcoholic beverages were determined by direct injection into a GC system based on the methods for the analysis of spirits described in the European Commission Regulation (EC 2000). In addition, the direct injection of liquid samples was used to determine the contents of alcohols with a wide range of molecular weights present in alcoholic beverages (Woo 2005; López-Vázquez et al. 2010; Lachenmeier and Sohuius 2008a). The overall objective of this study was to use qualitative and quantitative analysis methods based on GC–MS combined with direct injection to determine the VOCs in various alcoholic beverages consumed in Korea.

Materials and methods

Reagents, standards, and samples

Acetaldehyde, 1-propanol, 1-butanol, 3-methyl-1-butanol, 4-methyl-2-pentanol, and 3-octanol were purchased from Sigma-Aldrich (St. Louis, MO, USA). Formaldehyde solution was purchased from Duksan (Gyungkido, Korea). Water, methanol, and ethanol were all HPLC grade and obtained from J. T. Baker (Phillipsburg, NJ, USA).

The contents of VOCs in 75 samples of alcoholic beverages distributed in Korea (42 samples domestic and 33 samples imported) were analyzed. All samples were purchased from local markets located in Seoul, Korea. Of manufactured in Korea, 10 samples of distilled liquor, 14 of beer, 8 of fruit wine, and 8 of Korean rice wine, and 2 of refined rice wine were studied. Of imported samples, 10 samples of beer, 8 of whisky, 5 of red wine, 3 of white

wine, and 3 of sparkling wine, and 4 of Chinese spirit were analyzed. All samples were stored at 4 °C prior to analysis.

Sample preparation

Alcoholic beverage samples, stored at 4 °C in a refrigerator, were kept at room temperature for 1 h prior to the analysis. All authentic compounds and internal standard solutions (IS) were prepared prior to the analysis each day. Alcoholic beverage or standard solution samples (1 mL) were prepared by mixing 800 μL of each alcoholic beverage or standard solution and 100 μL of each IS, 2-methyl-4-pentanol (500 mg/L in 6 % ethanol, w/v) for aldehyde and 3-octanol (500 mg/L in 6 % ethanol, w/v) for methanol and higher alcohol analysis (1 mL of total volume).

Analysis of volatile organic components

VOCs including acetaldehyde, formaldehyde, methanol, 1-propanol, 1-butanol, and 3-methyl-1-butanol were analyzed using an Agilent 7890A gas chromatograph connected to 5975 mass selective detector (GC–MSD; Agilent Technologies Inc., Palo Alto, CA, USA) equipped with a CP WAX-57 capillary column (50 m length × 0.32 mm i.d. × 0.2-μm film thickness, Varian, Lake Forest, CA, USA).

The carrier gas was helium at a constant flow rate of 1.0 mL/min. One microliter of the samples was directly injected using splitless injection mode. The oven temperature was initially held at 40 °C for 3 min, and then raised to 75 °C at a rate of 6 °C/min and to 200 °C at a rate of 9 °C/min.

For GC–MS analysis, the injector and transfer line temperatures were 250 and 200 °C, respectively. The MS was operated in the electron impact ion source mode at 70 eV, an ion source temperature of 230 °C, and a scanning range of 25–550 mau with a scanning rate of 2.86 s^{-1}. For the analysis of methanol, the MS was operated in the selected ion monitoring (SIM) mode and the following ions were monitored: *m/z* 15, 28, 29, 30, 31, and 32 and 31 for qualification and quantification of methanol, respectively.

The identification of VOCs was positively confirmed by comparing its mass spectral data and retention time with those of authentic standard compounds. The quantification of volatile organic components was obtained on the base of the relative areas of volatile compounds identified, which were determined by comparing their peak areas to that of 2-mehtyl-4-pentanol for aldehyde and 3-octanol for methanol and higher alcohols, their internal standard compounds, on total ion chromatograms of GC–MS. The calibration curve of each standard solution in the range was used for the calculation of each compound based on the relative peak area versus concentration ration of organic volatile compound/internal standard.

Method validation

In order to evaluate the validation of GC–MS analysis, a series of each standard solution including acetaldehyde, formaldehyde, methanol, 1-propanol, 1-butanol, and 3-methyl-1-butanol in the concentrations of 2–1000 mg/L in 6 % ethanol with IS was subjected to analysis. Linear least squares regression calibration curves were constructed by plotting the peak area ratios of the analyte to that of the IS versus the expected concentrations of the working solutions.

Precision was determined by injecting one sample of each standard solution (100 mg/L) three times on the same day (repeatability, within-day precision). The intermediate precision (inter-day) was established by analyzing one sample (100 mg/L) of each standard solution three times a day at 3 successive days. The value was determined by a percentage of relative standard deviations (% RSD).

The limit of detection (LOD) and the limit of quantification (LOQ) for each standard solution were defined as the lowest detectable concentration yielding a signal versus noise (S/N) of 3 and an S/N of 10, respectively. In order to determine LOD and LOQ, the values were calculated using the formula: LOD = 3 S_{blank}/Slope of calibration graphs, which is the standard deviation of the seven blank values for the individual standard; LOQ = 9 S_{blank}/Slope of calibration graphs, which is the standard deviation of the seven blank values for the individual standard. Each test was conducted in triplicate.

Results and discussion

Method validation

The validation of GC–MS method involves a procedure testing the linearity, precision (repeatability and intermediate precision metrics), LOD, and LOQ as recommended according to previous studies (Thompson et al. 2002; Taverniers et al. 2004).

A linear relationship between the relative peak area and the concentration ratio of VOCs/internal standards in the standard solutions was obtained, based on analysis of the equation slope, intercept, and correlation coefficient (r^2; Table 1). The correlation efficient ranged from 0.9599 to 0.9983 in the GC–MS analysis. Formaldehyde analysis showed 0.9599 as the correlation efficient using GC–MS analysis. The determination of formaldehyde in alcoholic beverages has been performed using GC or high-performance liquid chromatography (in particular) after derivatization (Nascimen et al. 1997; Park

Table 1 Regression equations for volatile organic compounds analyzed using GC–MS

Compounds	Equation[a]	R^2	Precision (% RSD)			
			Repeatability intraday	Intermediate inter-day	LOD (mg/L)	LOQ (mg/L)
Acetaldehyde	Y = 0.0089x − 0.0823	0.9953	2.25	9.96	0.43	1.28
Formaldehyde	Y = 0.0002x − 0.0074	0.9599	4.75	7.91	5.00	15.00
Methanol[b]	Y = 0.0036x − 0.087	0.9959	4.05	3.06	3.31	9.94
1-Propanol	Y = 0.0034x − 0.1619	0.9939	1.31	3.41	8.46	25.38
1-Butanol	Y = 0.047x − 1.0589	0.9983	1.75	6.97	0.77	2.31
3-Methyl-1-butanol	Y = 0.0865x + 1.0964	0.9973	2.79	2.20	0.89	2.67

The concentration of each standard solution was 100 mg/L

R^2, correlation coefficient

[a] The linearity range of each standard solution was 50–1000 mg/L

[b] For the analysis of methanol, the MS was additionally operated in the selected ion monitoring (SIM) mode and the following ions were used: *m/z* 15, 28, 29, 30, 31, 32 and 31 for qualification and quantification of methanol, respectively

et al. 2006; Sowiński et al. 2005). However, limited data on formaldehyde were available when studying the volatiles in alcoholic beverages due to the analytical difficulties associated with its high volatility and polarity, and low selectivity and sensitivity in typical GC methods (EC 2000).

The precision was tested by injecting the same standard solution (at 100 mg/L) containing each authentic compound three times using GC–MS (Table 1). The repeatability (intraday) and intermediate (inter-day) were determined by analyzing each standard solution with the same concentration in triplicate on three successive days. The standard deviations of repeatability and intermediate precision of each standard solution ranged from 1.31 to 5.67 % and from 2.20 to 9.96 %, respectively. In addition, the standard deviations of the repeatability and intermediate precision for methanol were 4.05 and 3.06 % in SIM mode, respectively. Although the precision (repeatability and intermediate) of methanol in scan mode was acceptable, the SIM mode for methanol analysis was chosen for the current study since the LOD and LOQ values were not stable. The standard deviation values of all standard solutions except acetaldehyde were also acceptable (<8 %).

The LOD and LOQ values of the VOCs are listed in Table 1. The LOD [with a signal-to-noise (S/N) ratio of 3:1] and LOQ (S/N of 9:1) values of VOCs in GC–MS were calculated. The LOD and LOQ values of acetaldehyde, methanol, 1-butanol, 1-propanol, and 3-methyl-1-butanol analyzed on GC–MS were determined, which indicated similar patterns for the LOQ and LOD values.

VOCs in alcoholic beverages

The concentrations of acetaldehyde, methanol, and higher alcohols including 1-propanol and 3-methyl-1-butanol determined in alcoholic beverages using GC–MS are listed in Table 2, and summarized data are given in Table 3. The levels of formaldehyde and 1-butanol are not included in Tables 2 and 3 since they were not detected from all alcoholic beverage samples tested in the current study.

Acetaldehyde

All of the alcoholic beverage samples except for Korean rice wine, beer, and wine contained acetaldehyde, at levels ranging from 0.02 to 11.73 mg/L (Table 3). The mean values of acetaldehyde of refined rice wine and fruit wine samples were 8.28–4.16 mg/L, respectively. Miyake et al. (1993) reported that the content of methanol analyzed in sake samples ranged from 14.8 to 60.2 mg/L (Miyake and Shibamoto 1993). Lachenmeier and Sohuius 2008a) found that wine samples contained acetaldehyde in the range of 0–211 mg/L. The current study found that the mean levels of acetaldehyde in whisky, Korean distilled liquor, and Chinese spirit samples were 1.95, 0.48, and 1.79 mg/L, respectively. The acetaldehyde levels ranged from 0 to 77 mg/L in whisky and from 33 to 721 mg/L in Chinese spirit samples (Lachenmeier and Sohuius 2008a).

Acetaldehyde is known to be a potent flavor compound in many alcoholic beverages and foods such as wines and apple ciders (Miyake and Shibamoto 1993). This compound is a byproduct of alcoholic fermentation by yeasts, acetic acid bacteria, and combined auto-oxidation of ethanol and phenolic compounds in alcoholic beverages It has been demonstrated that both sugars—which are the primary substrate of acetaldehyde formation—and amino acids such as alanine contribute to the formation of acetaldehyde Boulton et al. (1996; Liu and Pilone 2000). Acetaldehyde can also form from spontaneous or microbe-mediated oxidation (Soufleros et al. 2004). However, it is highly reactive and readily binds to proteins, peptides, and amino acids to generate various flavor compounds (Liu and

Table 2 Concentration of volatile organic compounds in domestic alcoholic beverages analyzed using GC–MS

Group of alcoholic beverage	Sample no.	Concentration (mg/L)[a]			
		Acetaldehyde	Methanol[b]	1-Propanol	3-Methyl-1-butanol
Korean rice wine	1	–[c]	–	163.97 ± 0.08	61.41 ± 0.31
	2	–	–	162.91 ± 0.04	66.33 ± 0.17
	3	–	–	232.57 ± 0.02	77.00 ± 0.25
	1	–	–	288.03 ± 0.05	50.41 ± 0.25
	5	–	–	140.26 ± 0.02	21.50 ± 0.04
	6	–	–	199.99 ± 0.08	60.02 ± 0.38
	7	–	–	185.04 ± 0.15	86.15 ± 0.94
	8	–	–	156.09 ± 0.46	62.08 ± 2.32
Refined rice wine	9	11.57 ± 0.23	1.51 ± 0.01	–	9.08 ± 0.07
	10	4.99 ± 0.23	–	–	4.45 ± 0.26
Beer	11	–[c]	–	–	34.02 ± 0.10
	12	–	–	–	35.65 ± 0.30
	13	–	–	–	30.13 ± 0.04
	14	–	–	–	39.45 ± 0.10
	15	–	–	–	21.92 ± 0.07
	16	–	–	–	40.73 ± 0.14
	17	–	–	–	25.06 ± 0.14
	18	–	–	–	30.96 ± 0.13
	19	–	–	–	40.96 ± 0.20
	20	–	–	–	40.93 ± 0.11
	21	–	–	–	39.71 ± 0.09
	22	–	–	–	37.42 ± 0.13
	23	–	–	–	35.05 ± 0.40
	24	–	–	–	35.79 ± 0.34
	25	–	–	–	31.12 ± 0.03
	26	–	–	–	42.70 ± 0.25
	27	–	–	–	30.79 ± 0.12
	28	–	–	–	45.55 ± 0.55
	29	–	–	–	22.84 ± 0.19
	30	–	–	–	45.70 ± 0.44
	31	–	–	–	43.30 ± 0.11
	32	–	–	–	22.56 ± 0.13
	33	–	–	–	40.83 ± 0.49
	34	–	–	–	43.24 ± 0.25
Wine	35	–	1.42 ± 0.25	–	30.25 ± 0.02
	36	–	–	295.41 ± 0.02	143.97 ± 0.13
	37	–	–	47.62 ± 0.00	119.07 ± 0.02
	38	–	–	119.07 ± 0.02	47.62 ± 0.00
	39	–	–	141.35 ± 0.09	141.35 ± 0.09
	40	–	–	507.29 ± 0.03	80.94 ± 0.36
	41	–	–	193.65 ± 0.08	66.90 ± 0.22
	42	–	–	153.89 ± 0.11	61.96 ± 0.11
	43	–	–	138.44 ± 0.00	51.38 ± 0.08
	44	–	–	47.62 ± 0.00	60.69 ± 0.37
	45	–	–	121.74 ± 0.05	40.21 ± 0.26

Table 2 continued

Group of alcoholic beverage	Sample no.	Concentration (mg/L)[a]			
		Acetaldehyde	Methanol[b]	1-Propanol	3-Methyl-1-butanol
Fruit wine	46	1.33 ± 0.04	10.78 ± 0.01	–	30.76 ± 0.53
	47	–	23.81 ± 0.01	–	20.09 ± 0.27
	48	–	–	–	29.15 ± 0.16
	49	2.73 ± 0.04	22.78 ± 0.00	–	34.46 ± 0.53
	50	3.75 ± 0.06	–	–	94.79 ± 2.10
	51	–	–	–	15.56 ± 0.03
	52	3.37 ± 0.21	–	–	56.63 ± 0.13
	53	11.73 ± 0.21	17.14 ± 0.04	–	97.63 ± 3.09
Whisky	54	1.90 ± 0.00	–	486.71 ± 1.99	53.19 ± 0.11
	55	0.58 ± 0.02	–	1041.13 ± 0.29	174.65 ± 0.63
	56	1.68 ± 0.03	–	449.80 ± 0.09	76.35 ± 0.10
	57	1.70 ± 0.02	–	489.89 ± 0.63	80.10 ± 0.12
	58	1.75 ± 0.02	–	524.87 ± 0.24	71.76 ± 0.36
	59	0.81 ± 0.03	–	692.24 ± 0.45	129.93 ± 0.80
	60	1.63 ± 0.03	–	1055.77 ± 0.57	205.52 ± 0.66
	61	3.59 ± 0.56	–	869.52 ± 0.34	154.60 ± 0.99
Korean distilled liquor	62	–	–	–	–
	63	0.02 ± 0.01	–	–	–
	64	0.28 ± 0.01	–	–	–
	65	1.43 ± 0.10	–	–	–
	66	0.40 ± 0.02	–	–	–
	67	–	–	–	–
	68	–	–	–	–
	69	–	–	–	–
	70	0.26 ± 0.00	–	–	–
	71	–	–	–	–
Chinese spirit	72	2.42 ± 0.02	–	198.95 ± 0.05	228.77 ± 0.14
	73	1.85 ± 0.20	–	255.87 ± 0.00	280.79 ± 0.32
	74	1.09 ± 0.01	–	121.12 ± 0.12	204.99 ± 0.22
	75	–	–	178.57 ± 0.00	178.40 ± 0.03

Sample no 35–39 red wine, *40–42* white wine, *43–45* sparkling wine

[a] Values are means ($n = 3$) ± standard deviation (SD)

[b] For the analysis of methanol, the MS was additionally operated in the selected ion monitoring (SIM) mode and the following ions were used: *m/z* 15, 28, 29, 30, 31, 32 and 31 for qualification and quantification of methanol, respectively

[c] Not detected

Pilone 2000; Miyake and Shibamoto 1993). Moreover, its extreme reactivity and binding activity to DNA leading to genotoxicity in vitro and in vivo have prompted concerns that it is harmful to human health (IARC 2010). According to IARC reported that it could be carcinogenic to humans (Group 2B; IARC 1999), and recently acetaldehyde associated with the consumption of alcoholic beverages has been classified into Group 1 as a human carcinogen (IARC 2012). The level of acetaldehyde is restricted to 0.5 g/hL AA only for neutral alcohol—which is ethyl alcohol of agricultural origin and used in spirits such as gin or liqueurs—according by EC regulation No. 1576/89. In addition, the US FDA and the JECFA refer to the use of acetaldehyde as a flavoring agent as 'generally recognized as safe' and with no safety concerns at normal levels of intake, respectively (FDA 2003; JECFA 2001). Although the acetaldehyde concentrations in the alcoholic beverages tested in the current study were found to be lower than in previous studies, it should still be noted that its consumption might be linked to carcinogenicity in humans.

Methanol

The refined rice wine, wine, and fruit wine samples were the only samples containing methanol in this study (Table 3). In particular, one sample of refined rice wine contained 1.51 mg/L methanol, and 1 out of 11 wine samples contained 1.42 mg/L methanol. The methanol concentrations in fruit wine samples were in the range of 10.78–23.81 mg/L. A previous study found that the methanol concentrations in Thai rice wine samples were in the range of 0.96–5.15 mg/L of methanol concentration (Sirisantimethakom et al. 2008). Wang et al. (2004) reported that the methanol contents of wine and fruit wine samples were in the ranges of 76–202 and 63–320 mg/L, respectively (Wang et al. 2004). Cabaroglu (2005) reported that the methanol contents in Turkish varietal wine samples were in the range of 30.5–207.0 mg/L Cabaroglu (2005). The alcoholic beverage samples tested in the present study were found to have lower methanol concentrations than those reported previously (Sirisantimethakom et al. 2008; Wang et al. 2004; Cabaroglu 2005). Methanol detected in wines and grape pomace spirits is formed from the enzymatic degradation of natural pectic substances (pectin) present in crushed grapes by pectinesterase, and its formation in wines is dependent upon several factors such as the grape variety, grape skin containing a high pectin content, grape condition, and processing conditions (e.g., maceration condition and fermentation temperature; Ribereau-Gayon et al. 2000; Geroyiannaki et al. 2007). Methanol consumption is highly toxic to humans, leading to blindness or even death at high levels Cortés et al. (2005), and so the methanol concentration in distillates is regulated by EC regulations No. 1576/89 to a maximum level of 50–1000 g/hL AA (50 g/hL AA for neural alcohol and 1000 g/hL AA for fruit spirits). In addition, the levels of methanol in alcoholic beverages can be elevated due to the use of incorrect or insufficient distillation conditions during their manufacture (Anli et al. 2007).

Higher alcohols

The contents of higher alcohols including 1-propanol and 3-methyl-1-butanol detected from alcoholic beverages are listed in Table 3. None of alcoholic beverage samples studied contained 1-butanol. The mean values of 1-propanol in Korean rice wines, wine, whisky, and Chinese spirits samples were 170.57, 176.61, 701.24, and 178.57 mg/L, respectively. Previous studies found wide ranges in the 1-propanol contents of alcoholic beverages: 11–29 mg/L for Korean rice wines, 17.0–100.97 mg/L for Thai rice wine, 26.5 mg/L for rose wine, 29.5–71.5 mg/L for red wine, 17.2–61.4 mg/L for white wine, 6.0–10.7 mg/L for sparkling wine, and 340–1380 mg/L for Scotch whisky (Lee et al. 1994; Woo 2005; Chuenchomrat et al. 2008; Cao et al. 2010; Aylott and MacKenzie 2010; Mateo et al. 2001; Lilly et al. 2000; Mamede et al. 2005; Gil et al. 2006). The mean 3-methyl-1-butanol contents in the present study (excluding Korean distilled liquor) varied from 6.77 mg/L for refined rice wine samples to 223.24 mg/L for Chinese spirit samples. As indicated in Table 3, 3-methyl-1-butanol was present in Korean rice wine, refined rice wine, whisky, and Chinese spirit samples at 21.50–86.15, 4.45–9.08, 53.19–205.52, and 178.40–280.79 mg/L, respectively. A previous study found 3-methyl-1-butanol in America

Table 3 Volatile organic compound concentration in alcoholic beverages

Group of beverage	N[b]	Concentration (mg/L)											
		Acetaldehyde			Methanol[a]			1-Propanol			3-Methyl-1-butanol		
		n[c]	Mean	Range	n	Mean	Range	n	Mean	Range	n	Mean	Range
Korean rice wine	8	–[d]	–	–	–	–	–	8	170.57	140.26–288.03	8	74.12	21.50–86.15
Refined rice wine	2	2	8.28	4.99–11.57	1	1.51	1.51	–	–	–	2	6.77	4.45–9.08
Beer	24	–	–	–	–	–	–	–	–	–	24	38.44	21.92–45.70
Wine	11	–	–	–	1	1.42	1.42	10	176.61	47.62–507.29	11	76.79	30.25–143.97
Fruit wine	8	5	4.16	1.33–11.73	4	18.14	10.78–23.81	–	–	–	8	47.39	15.56–97.63
Whisky	8	8	1.95	0.58–3.59	–	–	–	8	701.24	449.80–1055.77	8	118.26	53.19–205.52
Korean distilled liquor	10	5	0.48	0.02–1.43	–	–	–	–	–	–	–	–	–
Chinese spirits	4	3	1.79	1.09–2.42	–	–	–	4	178.57	121.12–255.87	4	223.24	178.40–280.79

[a] For the analysis of methanol, the MS was additionally operated in the selected ion monitoring (SIM) mode and the following ions were used: *m/z* 15, 28, 29, 30, 31, 32 and 31 for qualification and quantification of methanol, respectively

[b] The number of samples tested

[c] The number of samples detected for each volatile organic compound

[d] Not detected

bourbon whisky (1060 mg/L), rose wine (178 mg/L), and red wine (133 mg/L) (Poisson and Schieberle 2008). Gil et al. (2006) reported that white wines, rose wines, and red wines contained 3-methyl-1-butanol at 180, 200, and 230 mg/L, respectively (Gil et al. 2006). Moreover, Chinese rice wine and Thai rice wine had 3-methyl-1-butanol at 91.5–195.32 and 79.06–155.90 mg/L, respectively Cao et al. (2010; Chen and Xu 2010; Sirisantimethakom et al. 2008). In addition, sake also contained 196–247 mg/L of 3-methyl-1-butanol (Asano et al. 1999). Furthermore, Park et al. (2013) recently reported that the concentration of 3-methyl-1-butanol in Korean rice wine increased from 25.08 to 183.01 mg/L during storage (Park et al. 2013).

Higher alcohols including 1-propanol and 3-methyl-1-butanol are formed in the first two stages of alcoholic fermentation, which contribute to the aroma of alcoholic distillates such as wine and whisky (Gil et al. 2006). For example, 1-propanol is described as a ripened fruit note in wine, and its content is affected by the yeast strains that are responsible for the fermentation (Giudici et al. 1993). In addition, the concentration of 1-propanol might be increased by microbial spoilage during storage under unfavorable conditions (Apostolopoulou et al. 2005). In addition, 3-methyl-1-butanol is also responsible for wine aroma with a fruity attribute and is usually found in alcoholic beverages with abundant concentration (Selli et al. 2004). This compound is formed from isoleucine and leucine during fermentation by deamination and decarboxylation reactions, respectively Boulton et al. (1996; Kana et al. 1988). However, a high content of 3-methyl-1-butanol could have a negative effect on the aroma of the distillate (Falqué et al. 2001).

Since these compounds—which are affected by various processing factors such as the fermentation condition, distillation techniques, and grape variety (in the case of wines)—can contribute to the characteristic aroma of alcoholic distillates (Giudici et al. 1993; Silva and Malcata 1998; Apostolopoulou et al. 2005), their total content is required by EU legislation to be a minimum of 12–225 g/hL AA, depending on the type of distillate (Lachenmeier et al. 2008b; EC 2000). However, a higher concentration of these compounds might negatively affect these alcoholic beverages, including concern about them being a possible cause of liver disease (Lachenmeier et al. 2008b; Apostolopoulou et al. 2005; Falqué et al. 2001).

This study used GC–MS combined with direct injection to investigate VOCs including acetaldehyde, methanol, and higher alcohols such as 1-propanol and 3-methyl-1-butanol in 75 domestic and imported alcoholic beverages consumed in Korea. These compounds are considered to be either flavoring compounds or toxic substances depending on their concentration. The acetaldehyde content was found to be highest in refined rice wines and fruit wines, while the methanol content was highest in fruit wines. All of the alcoholic beverages except for Korean distilled liquor contained higher alcohols, with their content being highest in whisky.

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