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Analysis of Volatile Compounds Released during the Grinding of Roasted Coffee Beans Using Solid-Phase Microextraction

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A dynamic solid-phase microextraction (SPME) method to sample fresh headspace volatile compounds released during the grinding of roasted coffee beans was described and the analytical results using gas chromatography/mass spectrometry (GC/MS) and GC/olfactometry (GC/O) were compared to those of the conventional static SPME sampling methods using ground coffee. Volatile compounds released during the grinding of roasted coffee beans (150 g) were obtained by exposing the SPME fiber (poly(dimethylsiloxane)/divinylbenzene, PDMS/ DVB) for 8 min to nitrogen gas (600 mL/min) discharged from a glass vessel in which the electronic coffee grinder was enclosed. Identification and characterization of volatile compounds thus obtained were achieved by GC/MS and GC/O. Peak areas of 47 typical coffee volatile compounds, separated on total ion chromatogram (TIC), obtained by the dynamic SPME method, showed coefficients of variation less than 5% ($n = 3$) and the gas chromatographic profile of volatile compounds thus obtained was similar to that of the solvent extract of ground coffee, except for highly volatile compounds such as 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone and 4-ethenyl-2-methoxyphenol. Also, SPME dilution analysis of volatile compounds released during the grinding of roasted coffee beans showed linear plots of peak area versus exposed fiber length ($R^2 > 0.89$). Compared with those of the headspace volatile compounds of ground coffee using GC/MS and GC/O, the volatile compounds generated during the grinding of roasted coffee beans were rich in nutty- and smoke-roast aromas.

KEYWORDS: Solid-phase microextraction; gas chromatography/olfactometry; dynamic headspace; coffee; volatiles

INTRODUCTION

Using mainly solvent extraction and headspace sampling methods, numerous analytical studies have detected more than 800 volatile compounds in brewed and ground coffee (*1*). Also, gas chromatography/olfactometry (GC/O) has been used to determine which of these are the most odor potent compounds, which are likely to contribute to the characteristic aroma of brewed and ground coffee (*2*−*6*). Some studies of the headspace volatile compounds released from ground coffee used a gastight syringe to sample and GC/O to analyze (*7*) while others used a static headspace sampler to investigate the effects of time and temperature on the volatile compounds released from roasted ground coffee (*8*). The changes in volatile composition above ground coffee, sampled by collecting the headspace on Tenax traps from a novel sampling apparatus, has also been reported (*9*). Solid-phase microextraction (SPME) (*10*) involving both exposure to the gas phase above a sample and submersion in the liquid phase of a liquid sample has been applied to the flavor analysis of both brewed and ground coffee under the static, no gas flow, condition (*11*−*13*).

The pleasant aromas released during the grinding of roasted coffee beans are as attractive as the aromas of fresh brewed coffee. However, because fresh and pleasant aromas are highly volatile and unstable compounds, these are lost easily during industrialized processing such as the grinding of roasted coffee beans and storage of ground coffee. For this reason, the study of fresh and pleasant aromas released during the grinding of roasted coffee beans could help food chemists and flavorists make new and more desirable coffee flavors for processed foods. Therefore, we attempted to sample these aromas that are increasingly released during the grinding of roasted coffee beans using the SPME fiber. This paper reports the development of a new SPME based dynamic headspace sampling method useful for the investigation of volatile compounds released during the

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grinding of roasted coffee beans, and analytical results obtained by GC/MS and GC/O using this sampling method.

EXPERIMENTAL PROCEDURES

Coffee Sample. Coffee beans (*Coffea arabica*, Mocha Grade 2) originating from Ethiopia were medium roasted (L 23) using a Probat G-12 roaster (Germany). After being roasted, the coffee beans were allowed to stand at room temperature, packed in 1 kg portions, and stored at −20 °C until used. Before grinding, roasted coffee beans were held for 2 h to reach room temperature. Roast degree was represented as an *L* value. The *L* value was determined by measuring ground coffee (particle sizes: <500 μm) using a color difference meter (Nippon Denshoku, Tokyo, Japan). Ground coffee (particle sizes: 400−800 μm) suitable for the so-called paper drip mode was hermetically stored in a polyester/aluminum/polyethylene package at −20 °C after sealing under vacuum and used within 24 h for headspace sampling. Before analysis, the package containing ground coffee was allowed to stand for 2 h at room temperature.

SPME Device. The SPME fibers and the manual holder were purchased from Supelco Co. (Bellefonte, PA). The following types of SPME fiber were used: (i) poly(dimethylsiloxane) (PDMS) with 100 μm thickness, (ii) PDMS/divinylbenzene (DVB) with 65 μm thickness, and (iii) Carboxen/PDMS (CAR/PDMS) with 75 μm thickness. Unless otherwise noted, PDMS/DVB fiber was used for sampling headspace volatile compounds. Also, the actual thickness of the PDMS/DVB fiber was measured using the digital microscope model VH6300 (Keyence Co., Osaka, Japan) at 175× magnification.

GC/MS Parameters. GC/MS analysis was performed on a mass selective detector model 5973 coupled to a gas chromatograph model 6890 (Hewlett-Packard (HP), Palo Alto, CA). The fused silica capillary column DB-WAX (60 m × 0.25 mm, 0.25 μm film thickness, J&W Scientific, Folsom, CA) was used. The flow of the carrier gas helium was 1.6 mL/min. The temperature program was set at an initial 50 °C for 2 min, followed by an increase of 3 °C /min to 220 °C, and held at 220 °C for 20 min. The injection port, equipped with a 0.75 mm i.d. liner (Supelco Co., Bellefonte, PA), was maintained at 250 °C. The inlet was operated in the splitless mode, and the injection purge on the GC was off for an initial 1 min for the manual SPME injection, and for an initial 4.5 min in the case of the injection of solvent extract using an HP 6890 series injector (Palo Alto, CA). GC/MS analysis was conducted under the same MS conditions in which quantitative comparisons of data were necessary.

GC/O Parameters. GC/O (CharmAnalysis) was performed on a gas chromatograph model 6890 (HP, Palo Alto, CA) modified by DATU, Inc. (Geneva, NY) (*15*). The fused silica capillary column DB-WAX (60 m × 0.32 mm, 0.25 μm film thickness, J&W Scientific, Folsom, CA) was used. The flow of the carrier gas helium was 3.2 mL/min. The temperature program was set at an initial at 40 °C, followed by an increase of 6 °C/min to 230 °C, and held at 230 °C for 20 min. The injection and detector ports were maintained at 250 °C and the injection purge on the GC was off for the initial 1 min. The retention time of each odorant was converted to Kovats indices using C_6−C_{28} *n*-alkanes (Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan).

Identification of Volatile Compounds. Many compounds used as standards for identification were purchased commercially from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan), CTC Organics (Atlanta, GA), and Oxford Chemicals Ltd. (Hartlepool, England). Volatile compounds were identified by comparing their mass spectra and Kovats indices using C_6−C_{28} *n*-alkanes to those of authentic compounds and with those from literature (*14*). Also, compounds found only by GC/O analysis were tentatively identified by comparing their Kovats indices and aroma properties to those of authentic compounds and with those from literature (*2*).

Isolation of Volatile Compounds from Sample. *Solvent Extraction of Ground Coffee.* A mixture of freshly distilled diethyl ether and *n*-pentane (2:1, v/v, 150 mL, Kishida Chemical Co., Ltd., Osaka, Japan) (*3*) was poured over ground coffee (50 g) on a paper filter (no. 131, Advantec, Co., Tokyo, Japan). The filtrate (20 mL) was concentrated to approximately 2 mL using a nitrogen gas stream (300 mL/min), and the concentrate was centrifuged at 12000 rpm for 5 min at 5 °C.

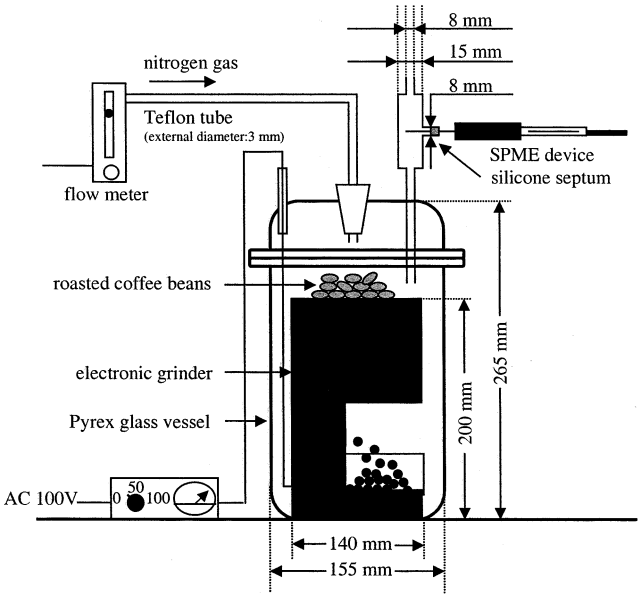

Figure 1. Sampling apparatus used to collect volatile compounds released during the grinding of roasted coffee beans.

General SPME Procedure. Before headspace sampling, the SPME fiber was reconditioned according to the SPME data sheet (T794123I, Supelco Co., Bellefonte, PA) in the GC injection port. After sampling, the fiber was placed into the injection port of the GC/MS or GC/O, and thermally desorbed for 10 min at 250 °C. Each SPME sampling was carried out at room temperature (25 °C) and conducted in triplicate.

Static Headspace SPME Sampling Using Different Types of SPME Fibers. The headspace volatile compounds were collected using the following different three fibers, PDMS, PDMS/DVB, and CAR/PDMS, under the same static conditions for the choice of fiber suitable for coffee volatiles sampling. Ground coffee (200 g) was transferred into a Pyrex glass bottle (volume ca. 1 L, Asahi Techno Glass, Co., Chiba, Japan), sealed with a Teflon-coated silicone cap (Supelco, Co., Bellefonte, PA), where it equilibrated for 1.5 h at room temperature (25 °C) prior to 8 min of SPME headspace sampling. After sampling, the fiber was placed into the injection port of the GC/MS, and thermally desorbed for 10 min at 250 °C.

Apparatus Used for Dynamic SPME Sampling. The Pyrex glass vessel (volume ca. 5 L, Asahi Techno Glass, Co., Chiba, Japan, **Figure 1**) was designed and built for analysis. The electronic grinder (model CG-4B, Melitta Japan, Tokyo) was purchased from the commercial market and modified for continuous grinding.

Measurement of the Actual Airflow Rate in Humans. For determination of the appropriate nitrogen gas flow rate for the SPME sampling during the grinding of roasted coffee beans using the apparatus mentioned above, the actual airflow rate in humans in a state of tranquility was measured using a digital flow meter (Agilent Technology, Inc., Palo Alto, CA) ($n = 5$).

General Dynamic SPME Sampling. Roasted coffee beans were placed on the hopper of the electronic grinder in the sampling apparatus. After the stainless steel housing of the SPME device was inserted into the sampling port, the nitrogen gas was passed into the glass vessel. The SPME fiber was pushed out of its stainless steel housing immediately after starting the grinding, and exposed to the effluent gas. Grinding speed of the electronic grinder in the sampling apparatus was controlled by varying the voltage to obtain ground coffee (particle sizes: 400−800 μm) suitable for the so-called paper drip mode.

Dynamic SPME Sampling with Variation of the Nitrogen Gas Flow Rate. The SPME fiber was exposed to the effluent nitrogen gas from the apparatus mentioned above while grinding roasted coffee beans (150 g) at 200, 400, 600, 800, and 1000 mL/min for 8 min, respectively. After sampling, the fiber was placed into the injection port of the GC/MS, and thermally desorbed for 10 min at 250 °C.

Dynamic SPME Sampling with Variation of the Sampling Time. For determination of the appropriate SPME sampling time, the SPME fiber

was exposed to the effluent gas (600 mL/min) for 1, 2, 4, 8, and 12 min, respectively, during the grinding of roasted coffee beans (220 g) using the apparatus mentioned above. After sampling, the fiber was placed into the injection port of the GC/MS, and thermally desorbed for 10 min at 250 °C.

SPME Sampling with Different Fiber Exposure Length. For investigation of the linearity of GC/MS peak area versus exposure length, volatile compounds were collected with four different fiber exposure lengths ((fully exposed (10 mm), approximately half exposed (5 mm), approximately one-fourth exposed (2.5 mm), and approximately one-eighth exposed (1.3 mm)) to the headspace of ground coffee (static headspace sampling) and the effluent nitrogen gas discharged during the grinding of roasted coffee beans (dynamic headspace sampling), respectively. Exposure length was controlled by creating three additional notches in the SPME holder (*16*). After sampling, the fiber was placed into the injection port of the GC/MS, and thermally desorbed for 10 min at 250 °C.

SPME-GC/O Evaluation of Volatile Compounds. Volatile compounds were collected with four different SPME fiber lengths mentioned above under the static and dynamic conditions, respectively. After sampling, the fiber was placed into the injection port of the GC/O, and thermally desorbed for 10 min at 250 °C. Odor activities of volatile compounds obtained by GC/O dilution analysis were represented as Charm values and the relative importances of component odorants were represented as odor spectrum value (OSV) (*17*). Each Charm value was rounded off to two significant figures to reflect the actual resolution of the dilution analysis. Acidic, buttery-oily, green-black currant, green-earthy, nutty-roast, phenolic, smoke-roast, soy sauce, sweet-caramel, and sweet-fruity were the aroma profiles used in all GC/O experiments to describe potent odorants. These profiles were chosen from the results of a single preliminary free choice GC/O analysis using a lexicon of commonly used words for coffee evaluation.

RESULTS AND DISCUSSION

Parameters for Headspace SPME Sampling. Many sample preparation methods have been developed to analysis volatile compounds of various food matrixes. Purge-and-trap, solid phase extraction, or direct sampling by a gastight syringe has often been used for the isolation and concentration of headspace volatile compounds on sample matrixes, respectively. However, these methods have various drawbacks including establishment of special instruments for GC such as the thermal desorption injector, excessive preparation time, loss of volatile compounds during solvent removal, or discrimination by slow injection. Extracts obtained using appropriate organic solvents can easily be evaluated for their aroma qualities by comparing with those of original samples, but, in general, these extracts also contain various kinds of less volatile and nonvolatile compounds. For this reason, the solvent extraction method is very time-consuming for flavor analysis using GC and GC/MS.

The SPME technique is well-known as a simple, rapid, sensitive, and high reproducible sampling method for liquid or gaseous volatile samples. The pleasant aromas of ground coffee begin to appear when roasted coffee beans are ground mechanically. Although there are many variables such as purge flow rate, sampling time, and fiber affinity, it is possible to collect volatile compounds contained in an inactive gas by placing the SPME fiber in the effluent discharged from samples. If a similar chromatographic profile to that of the conventional sampling method such as solvent extraction is obtained by the SPME sampling method, it should be useful for the investigation of volatile compounds of freshly ground coffee released during the grinding of roasted coffee beans.

Recently, a comparison of three fibers (PDMS, PDMS/DVB, and CAR/PDMS) for brewed coffee headspace volatiles was reported, and PDMS/DVB gave the overall best sensitivity, especially for phenols such as 2-methoxyphenol, 4-ethyl-2-methoxyphenol, 4-ethenyl-2-methoxyphenol, and polar compounds such as 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone and 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (*13*). Therefore, at first, static headspace samplings using three different fiber types (PDMS, PDMS/DVB, CAR/PDMS) were conducted to select the optimum fiber type for the analysis of ground coffee. A comparison of the adsorption capabilities of these three fibers was shown in **Table 1**, which clearly showed the differing adsorption affinities of volatile compounds. The CAR/PDMS fiber showed the most sensitivity for molecules such as 2-methylfuran, 2- and 3-methylbutanals, 2,3-butanedione, 2,3-pentanedione, pyridine, 2-methylpyrazine, 1-methyl-1*H*-pyrrole, and 1*H*-pyrrole, but its sensitivity for molecules such as 2-methoxyphenol, 4-ethenyl-2-mehoxyphenol, 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone were lower than other two type of fibers (PDMS, PDMS/DVB). The traditional nonpolar fiber, PDMS, is known to have good stability and it has its many applications for flavor analysis. However, the PDMS showed the lowest sensitivity to typical coffee volatile compounds. The PDMS/DVB fiber showed higher sensitivities for the following compounds than other type of fibers (PDMS, CAR/PDMS): pyrazines such as 2-ethyl-5- and 6-methylpyarzines, sulfur compounds such as 2-furanmethanethiol and 2-((methylthio)-methyl)furan, phenols, such as 2-methoxyphenol and 4-ethenyl-2-methoxyphenol, and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone. From these analytical results, PDMS/DVB fiber was selected for determination of the dynamic headspace sampling during the grinding of roasted coffee beans.

The amount of volatile compounds adsorbed on the SPME fiber was assumed to depend on the nitrogen gas flow rate (*18*). Therefore, the SPME fiber was exposed to the effluent nitrogen gas from the apparatus (**Figure 1**) while grinding roasted coffee beans at 200, 400, 600, 800, and 1000 mL/min for 8 min, respectively. The analytical results showed very similar total ion chromatograms (TICs), and the coefficients of variation of

Table 1. Comparison of the Adsorption Capabilities of Typical Volatile Compounds of Ground Coffee Sampled by Different Types of SPME Fibers under the Static Condition

peak no.[a]	compounds	peak area ($\times 10^5$) PDMS	PDMS/DVB	CAR/PDMS
2	2-methylfuran	85.48	130.26	9865.79
3	2-methylbutanal	184.86	430.64	4720.44
4	3-methylbutanal	158.80	329.30	6649.28
5	2,3-butanedione	67.89	256.11	6870.28
6	2,3-pentanedione	177.49	815.21	10546.94
9	1-methyl-1*H*-pyrrole	23.68	142.35	1736.27
12	pyridine	1301.42	1681.98	11663.00
16	2-methylpyrazine	1291.58	1701.25	7656.85
19	2,5-dimethylpyrazine	980.11	1325.87	1140.61
20	2,6-dimethylpyrazine	1029.54	1411.58	1329.76
24	2-ethyl-6-methylpyrazine	493.16	581.23	243.95
25	2-ethyl-5-methylpyrazine	352.15	518.52	217.95
29	2-furanmethanethiol[b]	1.86	11.21	0.86
35	2-ethyl-3,5-dimethylpyrazine	39.96	40.83	7.00
37	2-((methylthio)methyl)furan	13.12	80.06	43.99
42	1*H*-pyrrole	7.46	83.06	509.69
46	furfuryl acetate	491.27	1909.15	1680.21
47	5-methyl-2-furancarboxaldehyde	817.37	3564.12	2343.55
51	2-furanmethanol	1086.56	6288.11	9056.48
53	3-methylbutyric acid	387.56	1382.61	1517.84
57	2-methoxyphenol	26.75	41.36	24.59
64	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	12.59	20.87	7.13
65	4-ethenyl-2-methoxyphenol	58.12	80.89	7.61

[a] Peak numbers correspond to those of TICs shown in **Figures 2** and **3** and of **Table 3**. [b] Peak area of selected ion chromatogram (*m/z* 81).

Table 2. Effect of SPME Extraction Time for Typical Volatile Compounds Released during the Grinding of Roasted Coffee Beans under the Dynamic Conditions

peak no.[a]	compounds	time of adsorption, peak area ($\times 10^5$)				
		1 min	2 min	4 min	8 min	12 min
2	2-methylfuran	59.37	51.98	52.32	49.39	49.53
3	2-methylbutanal	218.99	181.49	161.15	153.35	153.50
4	3-methylbutanal	161.31	141.72	121.60	111.95	110.64
5	2,3-butanedione	129.80	120.15	110.06	104.33	105.25
6	2,3-pentanedione	461.29	417.32	362.31	349.45	347.03
9	1-methyl-1*H*-pyrrole	51.88	49.78	45.92	42.34	42.12
12	pyridine	585.43	862.13	906.48	904.19	905.88
16	2-methylpyrazine	640.15	927.98	1009.18	1081.09	1095.77
19	2,5-dimethylpyrazine	241.43	543.70	780.69	829.87	830.93
20	2,6-dimethylpyrazine	265.80	586.13	844.54	905.44	914.26
24	2-ethyl-6-methylpyrazine	62.22	170.22	306.70	422.57	432.59
25	2-ethyl-5-methylpyrazine	58.87	151.43	254.11	332.76	352.47
29	2-furanmethanethiol[b]	1.98	5.33	8.01	10.21	10.52
35	2-ethyl-3,5-dimethylpyrazine	3.66	11.01	26.57	53.04	69.71
37	2-((methylthio)methyl)furan	9.03	22.11	35.23	40.48	42.02
42	1*H*-pyrrole	35.40	39.81	43.95	47.82	51.23
46	furfuryl acetate	235.39	580.78	1061.55	1415.09	1423.51
47	5-methyl-2-furancarboxaldehyde	506.66	1200.84	1999.65	2459.76	2509.05
51	2-furanmethanol	1309.93	2776.42	3871.77	4195.93	4198.82
53	3-methylbutyric acid	127.22	421.27	697.30	977.90	983.32
57	2-methoxyphenol	5.67	17.06	37.83	78.36	108.57
64	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	3.14	16.40	48.05	122.13	199.35
65	4-ethenyl-2-methoxyphenol	4.40	17.93	55.67	137.25	228.48
	total peak area of 47 volatile compounds[a]	6967.37	11952.09	16156.92	18711.16	19339.46

[a] Peak numbers and 47 volatile compounds correspond to those of TICs shown in **Figures 2** and **3** and of **Table 3**. [b] Peak area of selected ion chromatogram (*m/z* 81).

total peak area of 47 volatile compounds, listed in **Table 3**, separated on TIC were under 5%. However, in the case of the small molecules such as 2-methylfuran, 2- and 3-methylbutanals, 2,3-butanedione, and 2,3-pentanedione, each peak area gradually decreased with increasing nitrogen gas volume flow rate, and with relative polar molecules such as 1-(2-furanylmethyl)-1*H*-pyrrole, 2-hydroxy-3-methyl-2-cyclopenten-1-one, 1*H*-pyrrole-2-carboxaldehyde, 4-hydroxy- 2,5-dimethyl-3(2*H*)-furanone, and 4-ethenyl-2-methoxyphenol, each peak area increased with increasing nitrogen gas flow rate, but their coefficients of variation were under 12%. These results show that the adsorption of volatile compounds by the fiber depends very little on the nitrogen gas flow rate within the range of 200−1000 mL/min. This fact was probably due to the existence of abundant volatile compounds released from the surface of a large number of coffee grains. On the other hand, the airflow rate during inhaling through the external nares has been reported to be 100 mL/s (*19*). To conduct the SPME sampling under conditions near to those of sniffing volatile compounds released during the grinding of roasted coffee beans, we measured the actual airflow rate in a state of tranquility using a digital flow meter. The average actual airflow rate in this state proved to be about 665 mL/min. On the basis of these results, the operating nitrogen gas flow rate was determined to be 600 mL/min.

To determine appropriate exposure time, the SPME fiber was exposed to the nitrogen gas effluent (600 mL/min) from the apparatus (**Figure 1**) at 1, 2, 4, 8, and 12 min, respectively, during the grinding of roasted coffee beans (220 g) to determine appropriate exposure time. As shown in **Table 2**, typical coffee volatile compounds, except for highly volatile compounds such as 2- and 3-methylbutanals, 2,3-butanedione, and 2,3-pentanedione, increased gradually at several proportions with increasing sampling time, and average total peak area of 47 volatile compounds, listed in **Table 3**, detected as separated peaks on TIC after 8 min reached about 97% of the total peak area obtained after 12 min, which corresponded to the time taken to finish grinding 150 g of roasted coffee beans. However, the highly volatile compounds mentioned above decreased after showing their maximum peak areas at 1 min sampling and showed almost similar peak areas at 2, 4, 8, and 12 min samplings. Compounds with low fiber-to-air equilibrium constants and those with high fiber-to-air equilibrium constants are contained in the headspace volatile of roasted coffee. These phenomena found in these experiments were estimated to be caused by compounds that have high fiber-to-air equilibrium constants. Also, it has been reported that competition phenomena occurred when the concentration exceeded the upper limit of the linear range, and short sampling times were an effective way to reduce fiber overloading and resulting biases, especially when both compounds of low and high affinity for the fiber were analyzed (*13*, *20*). However, if a similar chromatographic profile to that of the conventional extraction method such as solvent extraction is obtained by the SPME sampling, it should be possible to investigate aroma profiles of freshly ground coffee using GC/MS and GC/O. Therefore, we conducted the solvent extraction of freshly ground coffee using diethyl ether and *n*-pentane (2:1, v/v). As shown in **Figure 2**, although GC/MS responses of volatile compounds were different between the dynamic headspace SPME samplings (A: 1 min sampling, B: 8 min sampling) and solvent extract (C), the chromatographic profile of the solvent extract showed greater similarity to that of the dynamic SPME sampling at 8 min than at 1 min, except for less volatile compounds such as acetic acid, 3-methylbutyric acid, 4-ethenyl-2-methoxyphenol, and methyl hexadecanoate. The results suggest that volatile compounds obtained by careful SPME sampling under the dynamic conditions reflect fresh aromas of coffee grains just ground.

According to these results, the dynamic SPME sampling conditions were determined to be as follows: roasted coffee beans: 150 g, nitrogen gas flow rate: 600 mL/min, SPME (PDMS/DVB) sampling time: 8 min. Under these sampling conditions, we conducted three repeat sampling and found that

Table 3. Volatile Compounds Found in the Headspace of Ground Coffee under the Static and Dynamic Conditions

peak no.	compounds	peak area (× 10^5) static	peak area (× 10^5) dynamic	peak no.	compounds	peak area (× 10^5) static	peak area (× 10^5) dynamic
I	2-methylpropanal	56.49	91.62	35	2-ethyl-3,5-dimethylpyrazine	4.92	36.43
2	2-methylfuran	35.89	73.68	36	*cis*-linalool oxide (furanoid)	13.74	80.05
3	2-methylbutanal	113.80	170.76	37	2-((methylthio)methyl)furan	22.50	65.88
4	3-methylbutanal	95.41	134.33	38, 39[a]	2-methyl-5-vinylpyrazine, furfuryl formate	201.33	355.29
5	2,3-butanedione	71.41	119.39	40, 41[a]	2-acetylfuran, 2,5-dimethyl-3(2*H*)-furanone	521.55	1023.69
6	2,3-pentanedione	407.57	448.84	42	1*H*-pyrrole	38.67	50.62
7	2,3-hexanedione	62.12	59.92	43	1-(2-furyl)-2-propanone	62.24	177.85
8	3,4-hexanedione	50.86	44.43	44, 45[a]	2,4,5-trimethyl-3(2*H*)-furanone, 1-(acetyloxy)-2-butanone	184.42	569.52
9	1-methyl-l*H*-pyrrole	65.64	60.55	46	furfuryl acetate	588.23	1638.28
10	2-vinyl-5-methylfuran	95.19	80.95	47	5-methyl-2-furancarboxaldehyde	1065.89	2599.84
11	myrcene	66.61	136.17	48	1-methyl-1*H*-pyrrole-2-carboxaldehyde	133.53	360.16
12	pyridine	992.14	1280.28	49, 50[a]	acetylpyrazine, dihydro-2(3*H*)-furanone	226.96	586.77
13	limonene	88.38	144.96	51	2-furanmethanol	2019.36	4213.11
14	pyrazine	63.36	63.36	52	3-mercapto-3-methyl-2-butanol	11.29	88.50
15	dihydro-2-methyl-3(2*H*)-furanone	986.83	787.95	53	3-methylbutyric acid	441.60	1316.80
16	2-methylpyrazine	1184.87	1118.24	54	1-(1*H*-pyrrol-1-yl)-2-propanone[b]	56.26	199.60
17	3-hydroxy-2-butanone	284.97	255.93	55	1-(2-furanylmethyl)-1*H*-pyrrole	20.22	112.65
18	1-hydroxy-2-propanone	526.85	406.03	56	2-hydroxy-3-methyl-2-cyclopenten-1-one	20.68	148.75
19	2,5-dimethylpyrazine	470.14	844.05	57	2-methoxyphenol	10.16	71.80
20	2,6-dimethylpyrazine	583.66	973.10	58	2,3-dihydro-5-hydroxy-6-methyl-4*H*-pyran-4-one	6.53	84.07
21	2-ethylpyrazine	288.10	442.43	59	1-(5-methyl-2-furanyl)-1,2-propanedione	10.40	49.63
22	2,3-dimethylpyrazine	81.77	152.99	60	3-ethyl-2-hydroxy-2-cyclopenten-1-one	4.27	37.07
23	1-hydroxy-2-butanone	146.38	117.30	61, 62[a]	1-(1*H* -pyrol-2-yl)-ethanone, 3-hydroxy-2-methyl-4*H* -pyran-4-one	20.41	183.45
24	2-cthyl-6-methylpyrazine	164.96	424.71	63	1*H*-pyrrole-2-carboxaldehyde	26.96	97.97
25	2-ethyl-5-methylpyrazine	146.47	392.74	64	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	4.10	73.60
26, 27[a]	2-methyl-3(2*H*)-furanone, trimethylpyrazine	219.73	617.36	65	4-ethenyl-2-methoxyphenol	22.43	92.85
28, 29[a]	5-methyl-2(3*H*)-furanone, 2-furanmethanethiol	23.36	76.06	66	methyl hexadecanoate	n.d.[c]	n.d.
30, 31, 32[a]	acetic acid, *trans*-linalool oxide (furanoid), 3-ethyl-2,5-dimethylpyrazine	815.20	889.23	67	1-(2-furanylmethyl)-1*H*-pyrrole-2-carboxaldehyde[b]	trace	13.14
33, 34[a]	1-(acetyloxy)-2-propanone 2-furancarboxaldehyde	1994.40	3223.88				

[a] Volatile compounds detected as overlapping peaks on TIC. [b] Tentative identifications were achieved by comparing mass spectra and retention indices with data from ref *14*. [c] Not detected in the headspace volatiles.

the coefficients of variation of peak area of 47 typical coffee volatile compounds, listed in **Table 3**, detected as separated peaks on TIC, which corresponded to about 68% of total area detected on GC/MS analysis, were under 5%. These variations did not influence aroma evaluations by GC/O.

GC/MS Analysis of Static and Dynamic SPME Sampling. Typical TICs of the headspace volatile compounds adsorbed on the SPME fiber under dynamic and static conditions are shown in **Figure 3** and peak areas of typical volatile compounds found in these chromatograms are listed in **Table 3**. The dynamic SPME sampling resulted in acceptable peak intensity and chromatographic profile, and the ratios of components adsorbed were quite different to those obtained by the static SPME sampling. Total peak area of 47 volatile compounds obtained by the dynamic SPME sampling was about 1.8 times as much as the static condition. Also, besides major compounds, minor compounds reported as potent odorants of coffee, such as 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, 2-methoxyphenol, 4-ethenyl-2- methoxyphenol, and 2-ethyl-3,5-dimethylpyrazine, were found to be much increased in the dynamic headspace than the static headspace. Although we could not entirely discount some possibilities such as the rising temperature during the grinding of roasted coffee beans, the chromatographic differences mentioned above seemed to have resulted from the contribution of volatile compounds liberated into the atmosphere and carried away during the grinding of roasted coffee beans, and additional volatilization of compounds induced by flowing inert gas above the sample (*18*).

GC/MS Analysis with Variation of SPME Fiber Length. The application of the static headspace SPME sampling for GC/O based on dilution analysis of varying thickness and length of three types of the SPME fibers (PDMS: 95, 30, and 7 μm) has been developed using common flavor compounds, such as benzaldehyde, octanol, 1,8-cineol, 2-acetyl-3-methylpyrazine, decanal, neral, and geranial, and showed that the GC peak areas were reproducible at under 5% standard deviation for each fiber thickness, and these flavor compounds produced linear plots of GC peak area versus exposed fiber volume ($R^2 > 0.90$). Also, GC/O-SPME data have been shown to be very similar to the data produced by solvent extraction (*16*).

Actual SPME fiber (PDMS/DVB) used in this study was 10 mm long and the thickness was 65 μm. Measurement of this fiber with a Keyence Digital microscope at 175× magnification showed an actual thickness of 67 μm, giving a fiber volume of 0.396 mm^3. Thus, when exposure lengths were 10, 5, 2.5, and 1.3 mm, the resulting exposed volumes were 0.396, 0.198, 0.099 and 0.051 mm^3, respectively. For each fiber length, we conducted three repeat sampling under the static and dynamic conditions, and found that the coefficients of variation of peak area of 47 volatile compounds, listed in **Table 3**, separated on TIC were under 5%. As shown in **Table 4**, 15 typical volatile compounds including potent odorants of coffee (*2*−*6*, *13*) with different SPME exposure lengths under the static and dynamic conditions showed linear plots of peak area versus exposed fiber length (static condition: coefficient of determination (R^2) > 0.90, dynamic condition: $R^2 > 0.89$). Although the range of dilutions was limited by the fiber length and was only four steps (2^0, 2^1, 2^2, and 2^3), this GC/O-SPME sampling method could be useful to know odor potencies and profiles of fresh volatile compounds released during the grinding of roasted coffee beans.

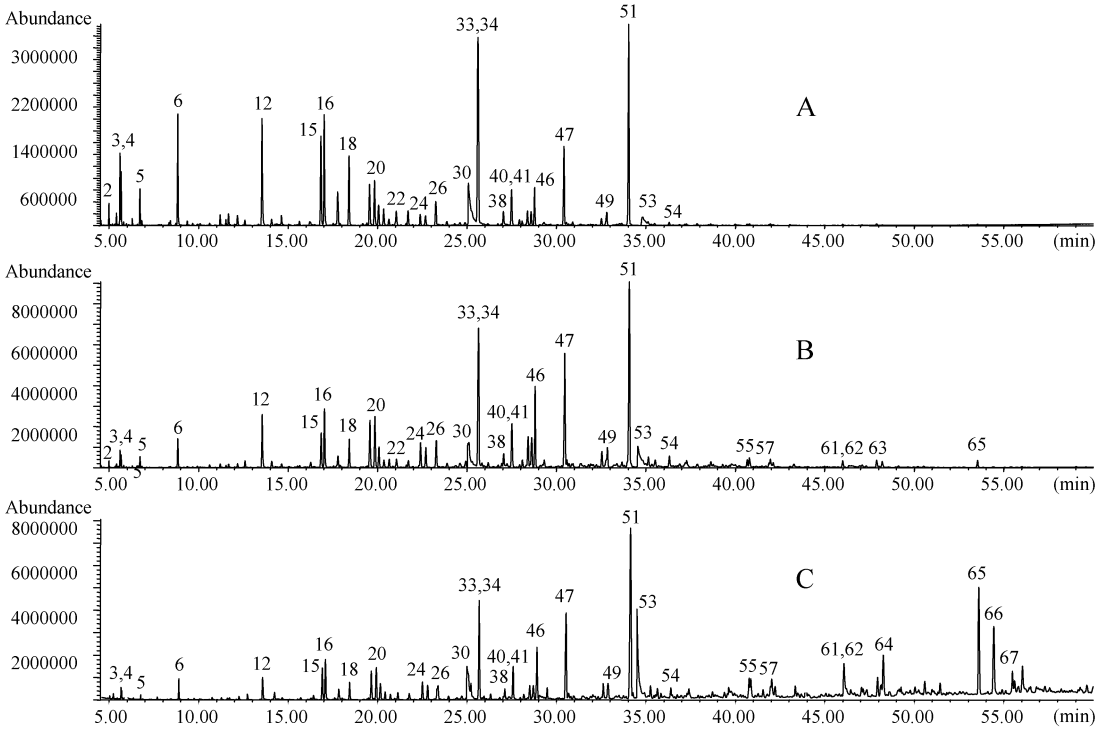

Figure 2. Comparison of total ion chromatograms (TICs) of volatile compounds released during the grinding of roasted coffee beans under the dynamic conditions (A, B) and the solvent extract of fresh ground coffee (C). (A) Dynamic conditions, SPME (PDMS/DVB) sampling time: 1 min. (B) Dynamic conditions, SPME (PDMS/DVB) sampling time: 8 min. (C) Solvent extract (diethyl ether:*n*-pentane = 2:1, v/v).

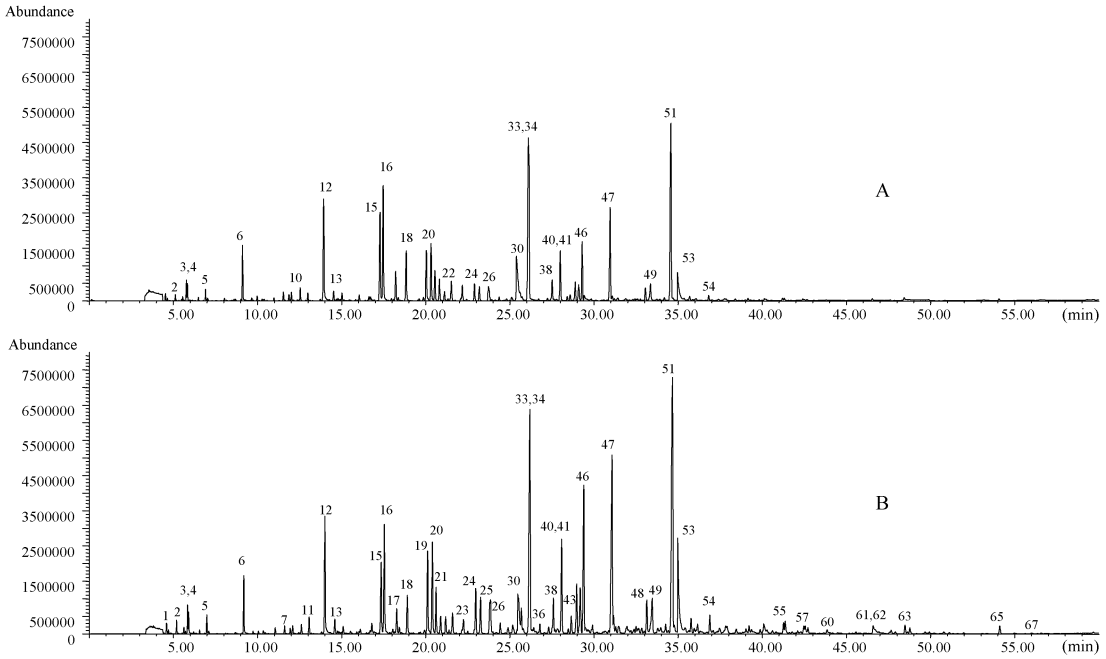

Figure 3. Typical total ion chromatograms (TICs) of volatile compounds of roasted coffee obtained using the SPME sampling method under the static (A) and dynamic (B) conditions. Peak numbers correspond to those of **Tables 1**–**4**.

GC/O Evaluation of Static and Dynamic SPME Sampling. The chromatographic differences observed by GC/MS analysis of coffee volatile compounds absorbed on the SPME fiber under the static and dynamic conditions may not accurately reflect the differences in aroma between such sampling conditions. Therefore, to objectively evaluate the characteristic coffee aromas obtained under the static and dynamic conditions, we conducted an olfactory test using GC/O. GC/O results of volatile compounds obtained using dynamic and static SPME headspace sampling methods were shown in **Figure 4**. Charm values (*15*) and OSVs (*17*) of 20 potent odorants with an OSV (above 50% OSV) detected in the headspace under dynamic and static condition are listed in **Table 5**. The total of the Charm values for these most potent odorants comprise 72% (dynamic condition) and 88% (static condition), respectively, of the sum total of Charm values. OSVs are independent of concentration and approximate the relative importance of odorants by accounting for the exponential nature of olfactory psychophysics, while Charm values indicate the true odor activity measurement and are linear functions of concentration (*15*). As shown in **Table**

Table 4. Average Peak Area ($\times 10^5$) of Typical Coffee Volatile Compounds with Different SPME Exposure Lengths

		static condition SPME exposure length (mm)					dynamic condition SPME exposure length (mm)				
peak no.[a]	compounds	10	5	2.5	1.3	R^2[b]	10	5	2.5	1.3	R^2[b]
3	2-methylbutanal	145.50	90.16	55.20	33.62	0.90	198.32	132.35	77.32	37.25	0.89
4	3-methylbutanal	165.91	101.82	58.94	41.13	0.91	189.32	125.11	69.32	42.56	0.89
5	2,3-butanedione	80.34	46.41	28.07	21.57	0.91	130.98	85.00	48.25	26.99	0.91
12	pyridine	958.99	501.54	275.68	177.32	0.99	1185.89	652.58	387.78	249.13	0.92
19	2,5-dimethylpyrazine	621.32	345.66	172.23	95.07	0.99	1061.60	641.91	308.36	170.65	0.95
24	2-ethyl-6-methylpyrazine	215.95	118.75	66.26	38.70	0.98	504.50	273.44	169.50	95.68	0.95
29	2-furanmethanethiol[c]	0.91	0.50	0.26	0.14	0.99	12.33	6.85	4.01	2.55	0.96
35	2-ethyl-3,5-dimethylpyrazine	9.22	4.36	3.06	2.06	0.96	65.31	38.66	22.29	12.36	0.96
37	2-((methylthio)methyl)furan	20.17	8.65	4.68	2.68	0.99	50.26	25.78	17.96	7.50	0.97
46	furfuryl acetate	651.35	366.09	201.97	119.94	0.98	1730.51	910.56	511.02	297.01	0.97
51	2-furanmethanol	2501.73	1480.71	815.45	480.56	0.96	4802.23	2761.04	1597.63	941.81	0.98
53	3-methylbutyric acid	432.69	230.32	120.68	70.13	0.99	1201.23	774.64	363.07	198.85	0.91
57	2-methoxyphenol	14.55	7.48	4.78	2.49	0.98	95.76	52.36	30.58	19.98	0.97
64	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	7.91	4.51	2.63	1.21	0.98	138.56	72.98	47.36	25.11	0.97
65	4-ethenyl-2-methoxyphenol	38.06	21.66	12.67	7.26	0.97	149.25	80.21	45.87	28.98	0.95

[a] Peak numbers correspond to those of TICs shown in **Figures 2** and **3** and **Table 3**. [b] Coefficient of determination. [c] Peak area of selected ion chromatogram (*m/z* 81).

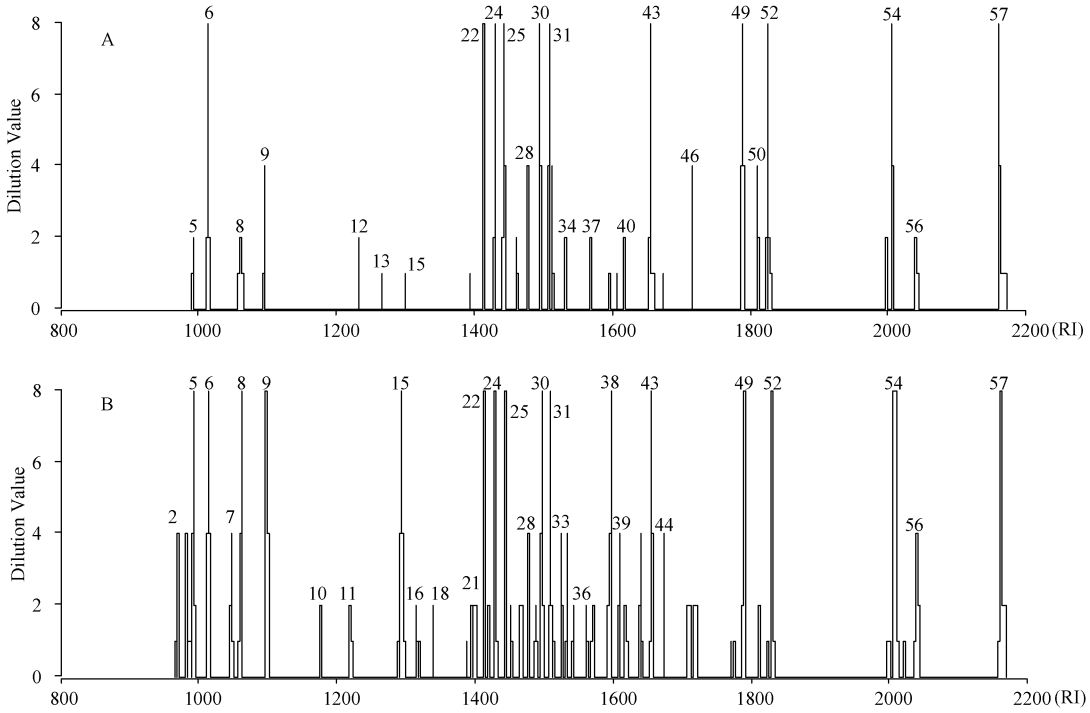

Figure 4. Aroma chromatograms of volatile compounds of roasted coffee obtained using the SPME sampling method under the static (A) and dynamic (B) conditions. Peak numbers correspond to those of **Table 5**.

6, compared with the results of GC/O of coffee volatile compounds obtained by the static SPME headspace sampling, the sum of Charm values of the dynamic sampling showed higher release of all aroma profiles and greater differences were particularly found between the profiles of nutty-roast and smoke-roast aromas as compared to all the others.

Highly volatile compounds, 2- and 3-methylbutanals, 2,3-butanedione, and 2,3-pentanedione (nos. 5, 6, and 8 in **Figure 4** and **Table 5**), which have buttery-oily aroma, were more abundant in the dynamic headspace than the static headspace as expected from GC/MS analysis. 3-(Methylthio)propanal (no. 24, soy sauce aroma), 3-mercapto-3-methylbutyl formate (no. 30, green-black currant aroma), and 2-methoxy-3-2-methylpropylpyrazine (no. 31, green-earthy aroma, which were difficult to detect in this GC/MS analysis, indicated high OSVs in both static and dynamic conditions, but these compounds were more abundant in the dynamic headspace than the static headspace. In the nutty-roast aroma, 2-methyl-3-furanthiol (no. 15), 2-ethyl-3,5-dimethylpyrazine (no. 25), and 6,7-dihydro-5-methyl-5*H*-cyclopentapyrazine (no. 38) were more abundant in the dynamic headspace than in the static condition as indicated by their Charm values. Especially, 2-methyl-3-furanthiol (no. 15), which was difficult to detect in this GC/MS analysis, and 2-ethyl-3,5-dimethylpyrazine (no. 25) indicated high OSVs in the dynamic condition and were significant candidates for the nutty-roast aroma released during the grinding of roasted coffee beans. In the smoke-roast aroma, 2-furanmethanethiol (no. 22) had high Charm values in both static and dynamic headspace and was significant odor active compound as indicated by its OSVs. Also, 3-methyl-2-butene-1-thiol (no. 9) was abundant in the dynamic condition as indicated by its Charm values, and this odorant had high OSV and seemed to contribute strong smoke aroma

Table 5. SPME-GC/O Results of 20 Potent Odorants (above 50% OSV) of Volatile Compounds of Roasted Coffee Obtained under the Dynamic and Static Conditions

no.[c]	retention indices	profiles	Charm values[a]		OSVs[b]		compounds
			dynamic condition	static condition	dynamic condition	static condition	
5	994	buttery-oily	240	47	70	37	2- and 3-methylbutanals
6	1016	buttery-oily	340	210	83	79	2,3-butanedione
8	1062	buttery-oily	180	96	61	53	2,3-pentanedione
9	1098	smoke-roast	360	95	86	53	3-methyl-2-butene-1-thiol[d]
15	1296	nutty-roast	230	16	69	22	2-methyl-3-furanthiol[d]
22	1415	smoke-roast	320	340	81	100	2-furanmethanethiol
24	1431	soy sauce	310	160	80	69	3-(methylthio)propanal[d]
25	1445	nutty-roast	230	150	69	66	2-ethyl-3,5-dimethylpyrazine
28	1478	nutty-roast	120	90	49	51	2,3-diethyl-5-methylpyrazine
30	1497	green-black currant	190	130	62	62	3-mercapto-3-methylbutyl formate[d]
31	1510	green-earthy	200	99	64	54	2-methoxy-3-(2-methylpropyl)pyrazine[d]
32	1514	buttery-oily	39	93	28	52	(*E*)–2-nonenal
38	1596	nutty-roast	170	18	59	23	6,7-dihydro-5-methyl-5*H*-cyclopentapyrazine
43	1656	acidic	280	180	76	73	3-methylbutyric acid
49	1789	sweet-fruity	340	340	83	100	(*E*)-beta-damascenone
51	1824	sweet-caramel	38	90	28	51	unknown
52	1831	phenolic	210	110	65	57	2-methoxyphenol
54	2008	sweet-caramel	410	210	91	79	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone
56	2039	sweet-caramel	170	57	59	41	2-ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone
57	2163	phenolic	490	290	1l0	92	4-ethenyl-2-methoxyphenol

[a] Each Charm value is rounded off to two significant figures to reflect the actual resolution of the dilution analysis, and represented as average value of three measurements. [b] Odor spectrum value (OSV) is the normalized Charm value modified with an approximate Stevens' law exponent ($n = 0.5$). [c] Peak numbers correspond to those of **Figure 4**. [d] Identifications were made by comparing Kovats indices and aroma properties to those of standard compounds and with data from ref 2.

Table 6. Odor Profiles Based on the SPME-GC/O Results of Volatile Compounds of Roasted Coffee Obtained under the Dynamic and Static Conditions

profiles	sum of Charm values[a]	
	dynamic condition	static condition
acidic	280	180
buttery-oily	927	446
green-black currant	271	130
green-earthy	262	99
nutty-roast	1203	518
phenolic	759	422
smoke-roast	1592	505
soy sauce	310	160
sweet-caramel	749	427
sweet-fruity	448	353

[a] Charm values are mean values of triplicate.

released during the grinding of roasted coffee beans. (*E*)-β-Damascenone (no. 49, sweet-fruity aroma) had high Charm values in both static and dynamic headspace, while the polar compounds, 3-methylbutyric acid (no. 43, acidic aroma), 2-methoxyphenol, and 4-ethenyl-2-methoxyphenol (nos. 52 and 57, phenolic aroma), and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone and 2-ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone (nos. 54 and 56, sweet-caramel aroma) were also abundant in the dynamic condition, as predicted by the GC/MS analytical results. However, 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (sotolone) and 5-ethyl-3-hydroxy-4-methyl-2(5*H*)-furanone (abhexone), found in the solvent extracts of roasted powder and brewed Arabica coffee as potent odorants possessing seasoning-like aroma quality (*3*), were not detected in this study.

CONCLUSIONS

Parameters for the dynamic-SPME (PDMS/DVB) sampling of headspace volatile compounds released during the grinding of roasted coffee beans were investigated. The chromatographic profile of the solvent extract (diethyl ether:*n*-pentane = 2:1, v/v) of ground coffee showed greater similarity to that of volatile compounds sampled dynamically (nitrogen gas flow rate: 600 mL/min, sampling time: 8 min) using the SPME fiber during the grinding of roasted coffee beans. This headspace sampling technique proved to be simple, rapid, and reproducible for GC/MS analysis. Comparing to the conventional static SPME sampling, volatile compounds adsorbed on SPME fiber under the dynamic condition were more abundant. GC/MS analysis with variation of the SPME fiber length showed that typical volatile compounds including potent odorants of coffee showed linear plots of peak area versus exposed fiber length ($R^2 > 0.89$) under the dynamic condition. Also, GC/O-SPME dilution analysis showed the nutty- and smoke-roast aromas were more potent under the dynamic conditions. These GC/MS and GC/O results indicated which odorants to use to make new flavors for coffee products such as beverages that would be more attractive to consumers.

ABBREVIATIONS USED

SPME, solid-phase microextraction; PDMS, poly(dimethylsiloxane); DVB, divinylbenzene; GC/MS, gas chromatography/mass spectrometry; GC/O, gas chromatography/olfactometry; CAR, Carboxen; OSV, odor spectrum value; TIC, total ion chromatogram; R^2, coefficient of determination.

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