Optimization of Adsorption and Desorption Time in the Extraction of Volatile Compounds in Brewed Java Arabica Coffee Using the HS-SPME/GC-MS Technique

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Article Info

Abstract

The headspace solid phase microextraction (HS-SPME) technique has been recognized as a reliable technique for characterizing the aroma profile of Arabica coffee beans. The amount and content of the detected volatile compounds depend on the volatile analyte extraction process with HS-SPME, namely the adsorption and desorption processes. However, the optimal extraction time in applying coffee volatile compounds is still limited. This research aimed to obtain the optimum adsorption and desorption time in analyzing volatile compounds in brewed Java Arabica coffee. The adsorption time was optimized for 20 to 60 minutes with 5 minutes desorption time. The desorption time was optimized from 5 to 45 minutes with a 20 minutes of adsorption time. There are 14 volatile compounds with a peak area percentage of more than 2% from adsorption and desorption optimization. The optimal adsorption time was 50 minutes, where there were 5 of 7 compounds with the most significant area, such as 2-furfural (29%), 2-acetyl furan (3%), 2-furfuryl acetate (6%), 5-methyl furfural (12%), and 2-furfuryl alcohol (14%). Meanwhile, the most optimal desorption time was 5 minutes which detected 12 compounds, while the other desorption time only detected eight compounds. Furfuryl formate (2%), pyridine (12%), and 2-furfuryl alcohol (14%) had a higher peak area than the other compounds at a desorption time of 5 minutes. The results showed the same number of volatile compounds at each adsorption time. In conclusion, the adsorption time did not affect the number of compounds detected as in the optimization of desorption time. Adsorption and desorption time is crucial in analyzing volatile compounds from coffee using the HS-SPME/GC-MS technique.

1. Introduction

One of the plantation products with a high-value sale is coffee. The value of coffee exports from 2016 amounted to US\$ 1,008,549, an increase in 2017 reached US\$ 1,187,157 [1]. The increase in coffee export results is one of the advantages for society who have a livelihood as coffee farmers. This increase is because the coffee plantation business mostly comes from society's plantations. One of the most commonly cultivated coffees by the community is Arabica coffee, which has a distinctive taste and special market [2]. Arabica coffee is often used to improve the taste and aroma of instant coffee products [3]. One of the Arabica coffees that have become worldwide from Indonesia is Java Arabica which has a characteristic thin aroma of spices.

One of the qualities of coffee is determined by its aroma. Aroma is one factor that affects the sensory perception of food originating from the food product itself [4]. Compounds that determine coffee aroma can be identified by Gas Chromatography-Mass Spectrometry

(GC-MS) instrument [5]. Volatile compounds, such as 2,5-dimethyl pyrazine; 2,6-dimethyl pyrazine; acetic acid; 2-acetyl furan; and 1-furfuryl pyrrole are present in coffee [6]. Ribeiro *et al.* [7] succeeded in detecting coffee volatile compounds, such as dihydro-2-methyl 3(2H) furanone; methyl pyrazine; N-furfuryl pyrrole; 2-furfuryl alcohol; 5-methyl furfural; and 2-furfuryl acetate. These compounds give different aroma effects on coffee, such as 2,5-dimethyl pyrazine compounds, 2,6-dimethyl pyrazine, and methyl pyrazine gives a nutty aroma [5]. In contrast, the 2-furan alcohol compound affects the burning, sweet, and caramel aroma [8]. These studies used the Headspace Solid Phase Microextraction (HS-SPME) technique to extract volatile compounds from brewed coffee.

SPME is one of the best sampling methods in extracting and concentrating volatile compounds simultaneously from a sample [9] without using a solvent in the extraction process. The process of extracting volatile compounds in coffee using the SPME method includes compound absorption/adsorption and compound release (desorption) on SPME fiber adsorbents. The adsorption and desorption processes are essential in analyzing volatile compounds in brewed coffee. Therefore, the length of time required for both processes greatly determines the concentration and number of compounds that can be analyzed using GC-MS [10, 11]. Yang *et al.* [5] and Giacalone *et al.* [6] investigated the volatile compounds from brewed coffee using HS-SPME with 5 minutes of adsorption time and a desorption time of 15 minutes. While the research was conducted by Ribeiro *et al.* [7] has 20 minutes of adsorption time and a fast desorption time. The difference in the length of time for adsorption and desorption can also be seen in the research of Bressanello *et al.* [12], where the required adsorption time was 40 minutes and the desorption time was 5 minutes. Based on previous studies, the optimal length of time for adsorption and desorption in coffee analysis has not been studied; therefore, the purpose of this research is to acquire the optimal adsorption and desorption time when analyzing the volatile compounds in brewed Arabica coffee using HS-SPME/GC-MS.

2. Experimental Section

This research was conducted in the laboratory of the Ma Chung Research Center for Photosynthetic Pigments (MRCPP), Ma Chung University, Malang. The study focused on obtaining the optimal adsorption and desorption time in analyzing volatile compounds from arabica coffee using the HS-SPME/GC-MS method. Volatile compounds from detected arabica coffee will be selected based on the peak area larger than 2%. Identification of volatile compounds based on the mass spectrum compared to the library Wiley Registry of Mass Spectral data 9th Edition with a similarity percentage above 90%. In addition, the volatile compounds were compared with references from reference libraries [13, 14], the Mass Bank of North America (MoNA) database, and the National Institute of Standards and Technology (NIST). The flow chart of the research to be carried out can be seen in Figure 1.

2.1. Equipment and Materials

The main raw materials used were Java Arabica coffee beans, namely Banjarnegara coffee from Central Java for optimizing adsorption time, and Malang coffee from East Java for optimizing desorption time with a medium roast. The solvent used in this study was distilled water with chromatography-grade from Merck (Darmstadt, Germany). The tool used to grind coffee beans was the Philips Coffee Grinder HR2185 (China). The tools used in coffee extraction were the Labinco L32 Basic Hotplate and magnetic stirrer (Breda, The Netherlands) and the Hermle Z 160 M centrifuge (Wehingen, Germany). The volatile compounds were analyzed by SPME Fiber Assembly 50/30 m DVB/CAR/PDMS with Manual Holder Supelco (Bellefonte, USA) and GC-MS Shimadzu QP2010 Plus (Kyoto, Japan) with RTX-WAX column (30 m × 0.25 mm). × 0.50 m) (Bellefonte, USA).

2.2. Optimization of Adsorption and Desorption Time

The adsorption process is shown in Figure 1 (number 10), carried out by inserting SPME fiber into a 20 mL vial containing brewed Banjarnegara coffee. The adsorption time was optimized for 20, 30, 40, 50, and 60 minutes with 5 minutes desorption time. Then the desorption time optimization (Figure 1, number 11) was conducted by varying times (5, 15, 30, and 45 minutes) with 20 minutes of adsorption time using a sample of Malang coffee.
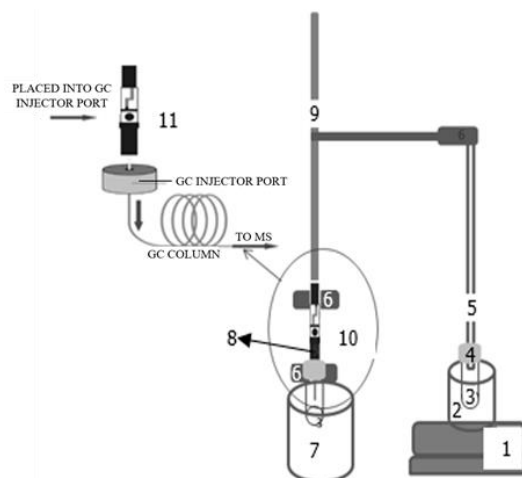

Figure 1. Schematic analysis stages of arabica coffee volatile compounds using HS-SPME/GC-MS. 1. Mechanical heater and magnetic stirrer, 2. 100 mL beaker glass filled with distilled water (70℃), 3. HS-SPME vial, 4. Septal cap, 5. Thermometer, 6. Clamp, 7. 500 mL beaker glass filled with distilled water (room temperature), 8. HS-SPME, 9. Stative, 10. Adsorption process, 11. Desorption process

2.3. Volatile Compounds Analysis Using GC-MS

Analysis of volatile compounds was conducted based on the modified method of Yang *et al.* [5] and Ribeiro *et al.* [7]. Ten grams of coffee beans were ground into powder using a grinder for 1 minute and used directly without a sifting process. After that, 0.1 grams of coffee powder was put into the HS-SPME vial, added 10 ml of boiling water, and then tightly closed with a septum. The coffee solution was homogenized using a magnetic stirrer and incubated at 70℃. After 10 minutes, the vial containing the sample

was immersed in a glass beaker filled with tap water for 10 minutes to lower the temperature. The schematic stages of the analysis of coffee volatile compounds can be seen in Figure 1. After the temperature of brewed coffee dropped to ±25℃, the adsorption process was carried out on the sample (number 10), then continued with the desorption process on the GC-MS injector (number 11).

GC-MS Shimadzu QP2010 Plus was set with the following parameters: injection temperature (235℃), ion source temperature (200℃), interface temperature (235℃), splitless mode, pressure (103 kPa), and flow rate of Helium gas is 9 mL/min. The oven column temperature was set at an initial temperature of 50℃ for 15 minutes, increased with a heating rate of 3℃/min to 220℃, then expanded with a heating rate of 8℃/minute to 240℃ held for 5 minutes. The column used was RTX WAX. Volatile compounds were detected by the scan mode with a range of 35 to 500 m/z and a 1,666 Da/sec scanning rate.

3. Results and Discussion

Adsorption and desorption processes were crucial in volatile compounds analysis from coffee. The amount of adsorbed volatile compounds can be increased by optimizing extraction time or, in other words, adsorption time [15]. The optimizing also applied to the desorption time, which affected the high yield [16]. Adsorption of volatile compounds from coffee using SPME was carried out on coffee grounds that have been brewed with hot water; thus, the types of volatile compounds identified by GC-MS correspond to the volatile compounds felt by coffee connoisseurs.
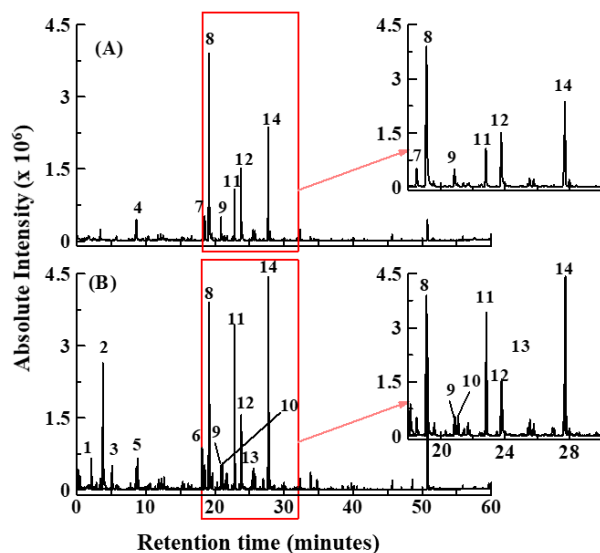

Figure 2. Total Ion Chromatogram (TIC) for volatile compounds of Java Arabica coffee from Banjarnegara (A) and Malang (B) with 20 minutes of adsorption time and 5 minutes desorption using the HS−SPME/GC−MS technique. Information on peak numbers is shown in Table 1

The separation results of volatile compounds from 2 types of Java Arabica coffee using GC-MS with 20 minutes of adsorption time and 5 minutes of desorption time are shown in Figure 2. Fourteen volatile compounds (Figure 3) have a peak area percentage of more than 2% from the optimization results adsorption and desorption times in coffee, where 5 of these compounds were found in the results of the two optimizations (Table 1). Identification of volatile compounds was also carried out by analyzing molecular ions and fragment ions compared with reference libraries and the fragmentation pattern of the structure of the compounds.

An illustration of its identification was exhibited at the second peak, pyridine (C_5H_5N), which gave a sour and roasted aroma [17]. Pyridine, with an exact mass of 79.0422 Dalton (Da), eluted at a retention time (t_R) 3.8 minutes (second peak) has precursor ion at m/z 79 [M]+ and fragment ions at m/z 63 [M−H$_2$N]+, 52 [M−HNC]+ [13]. The twelfth peak (t_R = 23.8 minutes) is the compound responsible for spices and caramel aroma [17] in coffee which was identified as 5-methyl furfural ($C_6H_6O_2$; with an exact mass of 110.0368 Da) has a molecular ion at m/z 110 [M]+ and fragment ions at m/z 95 [M−CH$_3$]+, 81 [M−COH]+, dan 53 [M− O$_2$C$_2$H]+ [14].
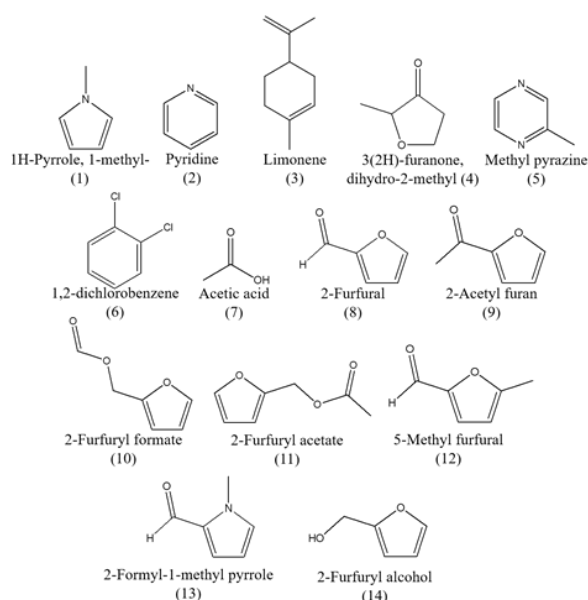

Figure 3. The structure of the volatile compounds has a peak area percentage of more than 2% from the results of adsorption and desorption optimization on Java Arabica coffee

Based on research conducted by Ribeiro *et al.* [7], analysis of volatile compounds from Arabica coffee was carried out using SPME with 20 minutes of adsorption time, followed by a desorption process of volatile compounds in a GC injector afterward. Therefore, the adsorption time was optimized in the 20−60 minutes range, with 5 minutes of desorption time in this study. The optimization of the adsorption time was carried out to determine whether the longer the adsorption time caused the content of the identified volatile compounds to increase or not. The optimization results of adsorption time based on the peak area value and the percentage of the peak area of the seven volatile compounds detected in Java Arabica coffee are served in Table 2.

Table 1. Identification of volatile compounds with a peak area percentage of more than 2% from the adsorption and desorption optimization results on Java Arabica coffee

Peak Number	Compound name	Molecular Formula	Exact Mass (Da)	t_R (minutes)	Molecular Ion (m/z)	Fragment Ions (m/z)	Similarity (%)	Adsorption	Desorption
1	1H-pyrrole, 1-methyl-	C_5H_7N	81	2.1	81[M]$^+$	53[M$-$H$_2$NC]$^+$	93	–	+
2	pyridine	C_5H_5N	79	3.8	79 [M]$^+$	52[M$-$HNC]$^+$; 63 [M$-$H$_2$N]$^+$	97	–	+
3	limonene	$C_{10}H_{16}$	136	5.1	136 [M]$^+$	68 [M$-$2CH$_3-$2CH$-$C]$^+$; 93 [M$-$2CH$_3-$CH]$^+$	96	–	+
4	3(2H)-furanone, dihydro-2-methyl-	$C_5H_8O_2$	100	8.6	100 [M]$^+$	43 [M$-$CH$_3-$2CH$-$O]$^+$; 72[M$-$CH$_3-$CH]$^+$	97	+	–
5	methyl pyrazine	$C_5H_6N_2$	94	8.8	94 [M]$^+$	40 [M$-$C$-$CH$-$CH$_3-$N]$^+$; 67 [M$-$C$-$CH$_3$]$^+$	96	–	+
6	1,2-dichlorobenzene	$C_6H_4Cl_2$	147	18.1	146 [M$-$H]$^+$	111 [M$-$H$-$Cl]$^+$	97	–	+
7	acetic acid	$C_2H_4O_2$	60	18.5	60 [M]$^+$	43 [M$-$OH]$^+$; 45 [M$-$CH$_3$]$^+$	99	+	–
8	2-furfural	$C_5H_4O_2$	96	19.2	96 [M]$^+$	39 [M$-$C$-$CH$-$2O]$^+$	97	+	+
9	2-acetyl furan	$C_6H_6O_2$	110	20.9	110 [M]$^+$	39 [M$-$2C$-$CH$_3-$2O]$^+$; 95 [M$-$CH$_3$]$^+$	95	+	+
10	furfuryl formate	$C_6H_6O_3$	126	21.1	126 [M]$^+$	53 [M$-$CH$-$2CH$_2-$2O]$^+$; 81 [M$-$CH$-$2O]$^+$	91	–	+
11	2-furfuryl acetate	$C_7H_8O_3$	140	22.8	140 [M]$^+$	43 [M$-$C$-$3CH$-$CH$_2-$2O]$^+$; 98 [M$-$2CH$-$O]$^+$	96	+	+
12	5-methyl furfural	$C_6H_6O_2$	110	23.8	110 [M]$^+$	53 [M$-$C$-$2CH$-$CH$_3$]$^+$; 81 [M$-$CH$-$O]$^+$; 95 [M$-$CH$_3$]$^+$	97	+	+
13	2-formyl-1-methyl pyrrole	C_6H_7NO	109	25.6	109 [M]$^+$	53 [M$-$2CH$-$O]$^+$; 80 [M$-$CH$-$O]$^+$;	91	–	+
14	2-furfuryl alcohol	$C_5H_6O_2$	98	27.7	98 [M]$^+$	39 [M$-$C$-$CH$_2-$OH$-$O]$^+$; 81 [M$-$OH]$^+$	96	+	+

Description: the minus (–) symbol is for not detected, and the plus (+) symbol is for detected

The detected volatile compounds had the same amount and type at the adsorption time of 20 to 60 minutes. There were similarities in the variation of the optimization time, where 2-furfural, 2-furfuryl alcohol, and 5-methyl furfural were the volatile compounds with the highest percentage in Java Arabica coffee, where this result was similar to the study of Zakidou et al. [18]. Research from Caporaso et al. [17] also mentioned that 2-furfuryl alcohol was the most abundant compound in arabica coffee.

The results (Table 2) also show that the longer the adsorption time, the greater the peak area of the compound for the adsorption time from 20 minutes to 50 minutes. The reason is that at the adsorption time of 20 minutes, the ability of the SPME adsorbent to bind compounds is still immense. Meanwhile, at the adsorption time of 50 minutes, the SPME adsorbent could maximally bind the volatile compounds. Therefore, at the adsorption time of 60 minutes, the content of volatile compounds detected was less than the adsorption time of 50 minutes because the volatile compounds were no longer able to be absorbed by the SPME adsorbent and were likely to be rereleased.

Figure 4(A) shows that seven compounds have a large area of more than 2%, where 2-furfural has the largest peak area percentage of 28–30%, while other compounds have ≤ 15% peak area. At 50 minutes of adsorption time, five of the seven compounds produced the largest volatile compounds compared to other adsorption times.

Table 2. Value of peak area and peak area percentage of volatile compounds from Java Arabica coffee using HS-SPME/GC-MS analysis for optimization of adsorption time with 5 minutes of desorption time

Peak No	Peak Area (x 10^5)					Percentage of Peak Area (%)					Volatile Compound
	20'	30'	40'	50'	60'	20'	30'	40'	50'	60'	
4	39.0	27.9	15.6	26.4	28.2	5	3	3	2	2	3(2H)-furanone, dihydro-2-methyl-
7	25.8	23.6	24.4	27.4	29.9	3	2	2	2	2	acetic acid
8	236.0	320.5	328.1	456.8	357.1	29	30	29	29	28	2-furfural
9	24.9	35.6	35.2	52.0	43.0	3	3	3	3	3	2-acetyl furan
11	46.3	67.1	55.9	102.5	77.7	6	6	6	6	6	2-furfuryl acetate
12	80.3	117.4	138.6	183.6	148.5	10	11	11	12	11	5-methyl furfural
14	118.9	146.7	155.7	227.7	186.4	15	14	13	14	14	2-furfuryl alcohol

Description: ' = minutes

These compounds were 2-furfural (8), 2-acetyl furan (9), 2-furfuryl acetate (11), 5-methyl furfural (12), and 2-furfuryl alcohol (14). While the volatile compounds 3(2H)-furanone, dihydro-2-methyl- (4) had a larger peak area with 20 minutes of adsorption time, in contrast, the largest peak area of acetic acid (7) was at 60 minutes. Meanwhile, volatile compounds had the largest area for 50 minutes the adsorption time; thus, the most optimal adsorption time was 50 minutes. These results were similar to the optimization of the extraction time of volatile compounds in Arabica coffee using static headspace gas chromatography (SH-GC), where all compounds were detected within 30 minutes, while many compounds had a higher content (in %) at 45 minutes of extraction process [19].
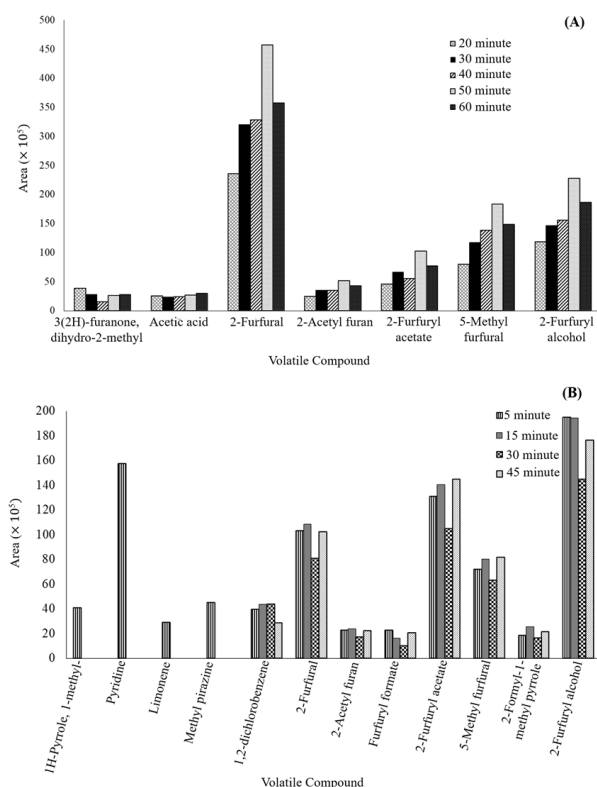
Figure 4. Value of peak area for Java Arabica coffee volatile compounds from the optimization results of adsorption time (A) and desorption time (B). Peak numbers, names of volatile compounds, and peak area as mentioned in Table 2 and Table 3

In contrast to the adsorption time, which only affects the amount of volatile compounds content, the difference in desorption time also affects the number of compounds identified. Desorption times of 5, 15, 30, 45 minutes were chosen to determine the best time for the volatile compounds to be released from the SPME adsorbent and detected by GC-MS. The use of 5 minutes of desorption time refers to Bressanello *et al.* [12], Mondello *et al.* [20], and Zakidou *et al.* [18], as well as standard coffee cupping, where the aroma is tested at 4 minutes after coffee being brewed with hot water. In addition, Shimadzu's application notes on analyzing coffee volatile compounds using SPME desorption for 2 minutes [21]. Yang *et al.* [5] and Laukaleja and Kruma [22] used 15 minutes of desorption time to analyze volatile compounds from discrepancies in the coffee bean roasting process. In addition to the two desorption times, two long periods of 30 and 45 minutes were used in testing the optimization of desorption time.

The results of the desorption time optimization of the volatile compounds of Java Arabica coffee are illustrated in Figure 4 (B) and Table 3. Fourteen volatile compounds were detected at 5 minutes of desorption time and eight compounds at 15, 30, and 45 minutes with the percentage of peak area above 2%. Three volatile compounds, such as pyridine, furfuryl formate, and 2-furfuryl alcohol, have 10−19% of peak area percentage, the largest compared to other compounds, where other compounds only have <10% peak area. Four volatile compounds (peaks 1, 2, 3, and 5) that appeared at less than 10 minutes retention time were not detected at

desorption times of 15, 30, and 45 minutes. This result indicated that the longer the desorption time caused some compounds to be wasted into the sewer in the GC-MS, such as the compound 1H-Pyrrole, 1-methyl-(1); pyridine (2); limonene (3); methyl pyrazine (5).

Table 3. The value of peak area and peak area percentage of volatile compounds from Java Arabica coffee using HS-SPME/GC-MS analysis for desorption time optimization with 20 minutes of adsorption time

Peak Number	Peak Area (x 10⁵)				Percentage of Peak Area (%)				Volatile Compound
	5'	15'	30'	45'	5'	15'	30'	45'	
1	40.7	–	–	–	3	–	–	–	1H-pyrrole, 1-methyl -
2	157.6	–	–	–	12	–	–	–	pyridine
3	28,9	–	–	–	2	–	–	–	limonene
5	45.2	–	–	–	3	–	–	–	methyl pyrazine
6	39.7	43.9	43.8	28.7	3	4	6	3	1,2-dichlorobenzene
8	103.0	108.5	80.7	102.3	8	10	10	11	2-furfural
9	22.7	24.0	17.4	22.2	2	2	2	2	2-acetyl furan
10	22.6	16.5	9.9	20.4	2	2	1	2	furfuryl formate
11	131.1	140.4	104.8	144.7	10	12	13	15	2-furfuryl acetate
12	72.0	80.2	63.2	81.8	5	7	8	9	5-methyl furfural
13	18.5	25.5	16.3	21.2	1	2	2	2	2-formyl-1-methyl pyrrole
14	195.0	194.5	144.9	176.3	14	17	19	18	2-furfuryl alcohol

Description: ' = minutes

Nonetheless, at the peaks of 6, 8, 9, and 13, the highest area was at 15 minutes desorption. While at 5 minutes desorption, the peaks of 10 and 14 were the most significant area. The highest area at peaks 11 and 12 was at 45 minutes. These results indicated that a rapid desorption time allowed more volatile compounds to be detected. Long desorption time served to obtain the full content of certain volatile compounds. However, the analysis of volatile compounds in coffee required complete data. Therefore, the most optimal desorption time was 5 minutes because it could detect more compounds, and there were two volatile compounds with the most significant area compared to other desorption times. The optimizing result of 5 minutes desorption time in this study was in accordance with the information on the desorption time in the research regarding the identification of volatile compounds in coffee [12, 20] for 5 minutes and application notes Shimadzu [21] for 2 minutes.

4. Conclusion

Coffee volatile compounds were extracted using the HS-SPME technique, which included an adsorption process for compound extraction and desorption to release compounds into GC-MS. The optimization results of adsorption and desorption time detected 14 volatile compounds in Java Arabica coffee with a peak area percentage of more than 2%. Seven of 14 compounds were found at each variation of the adsorption time. It could be done for 20 minutes of adsorption to detect coffee volatile

compounds. However, the most optimal adsorption time was 50 minutes because five of volatile compounds, namely 2-furfural (456.8×10^5), 2-acetyl furan (52.0×10^5), 2-furfuryl acetate (102.5×10^5), 5-methyl furfural (183.6×10^5), 2-furfuryl alcohol (227.7×10^5) had the most prominent peak area. In contrast, the desorption time affected the number of detected volatile compounds. The optimal desorption time in this study was 5 minutes which detected 12 compounds, while at the other desorption time, only eight compounds were detected. This optimal adsorption and desorption time is vital in analyzing volatile compounds in coffee because it determines the concentration and number of compounds that can be analyzed using GC-MS effectively.

Acknowledgments

References

[1] Direktorat Statistik Tanaman Perkebunan, in, Badan Pusat Statistik, Jakarta, 2018, p. 17-69

[2] Elsera Br Tarigan, Tajul Iflah, Dibyo Pranowo, Tingkat kesukaan konsumen terhadap kopi campuran robusta dengan arabika, *Jurnal Teknologi dan Industri Pertanian Indonesia*, 7, 1, (2015), 12-17

[3] Peter Capek, Ema Paulovičová, Mária Matulová, Danica Mislovičová, Luciano Navarini, Furio Suggi-Liverani, Coffea arabica instant coffee—chemical view and immunomodulating properties, *Carbohydrate Polymers*, 103, (2014), 418-426 https://doi.org/10.1016/j.carbpol.2013.12.068

[4] Kristianto Pradipta, Kiki Fibrianto, Perbedaan Air Seduh Terhadap Persepsi Multisensoris Kopi: Review Jurnal, *Jurnal Pangan dan Agroindustri*, 5, 1, (2017), 85-91

[5] Ni Yang, Chujiao Liu, Xingkun Liu, Tina Kreuzfeldt Degn, Morten Munchow, Ian Fisk, Determination of volatile marker compounds of common coffee roast defects, *Food Chemistry*, 211, (2016), 206-214 https://doi.org/10.1016/j.foodchem.2016.04.124

[6] Davide Giacalone, Tina Kreuzfeldt Degn, Ni Yang, Chujiao Liu, Ian Fisk, Morten Münchow, Common roasting defects in coffee: Aroma composition, sensory characterization and consumer perception, *Food Quality and Preference*, 71, (2019), 463-474 https://doi.org/10.1016/j.foodqual.2018.03.009

[7] J. S. Ribeiro, F. Augusto, T. J. G. Salva, M. M. C. Ferreira, Prediction models for Arabica coffee beverage quality based on aroma analyses and chemometrics, *Talanta*, 101, (2012), 253-260 https://doi.org/10.1016/j.talanta.2012.09.022

[8] Ze Song, Qian Jia, Miaomiao Shi, Tao Feng, Shiqing Song, Studies on the Origin of Carbons in Aroma Compounds from [13C6] Glucose-Cysteine-(E)-2-Nonenal Model Reaction Systems, *Polymers*, 11, 3, (2019), 521 https://doi.org/10.3390/polym11030521

[9] J. S. Ribeiro, R. F. Teófilo, F. Augusto, M. M. C. Ferreira, Simultaneous optimization of the microextraction of coffee volatiles using response surface methodology and principal component analysis, *Chemometrics and Intelligent Laboratory Systems*, 102, 1, (2010), 45-52 https://doi.org/10.1016/j.chemolab.2010.03.005

[10] Yi-Ni Yang, Miao Liang, Yan Yang, Fu-Ping Zheng, Xing-Ping Wang, Ai-Nong Yu, Optimization of a headspace solid-phase microextraction method for the gas chromatography-mass spectrometry analysis aroma compounds of *Litsea mollis* Hemsl. immature fruit, *Food Science and Technology*, 40, 4, (2020), 786-793 https://doi.org/10.1590/fst.20319

[11] Mauricio Aguirre-González, Gonzalo Taborda-Ocampo, Carmen Dussan-Lubert, Cristina Nerin, Milton Rosero-Moreano, Optimization of the HS-SPME technique by using response surface methodology for evaluating chlorine disinfection by-products by GC in drinking water, *Journal of the Brazilian Chemical Society*, 22, 12, (2011), 2330-2336 https://doi.org/10.1590/S0103-50532011001200013

[12] Davide Bressanello, Erica Liberto, Chiara Cordero, Patrizia Rubiolo, Gloria Pellegrino, Manuela R. Ruosi, Carlo Bicchi, Coffee aroma: Chemometric comparison of the chemical information provided by three different samplings combined with GC−MS to describe the sensory properties in cup, *Food Chemistry*, 214, (2017), 218-226 https://doi.org/10.1016/j.foodchem.2016.07.088

[13] M. A. Elsayed, Successive advanced oxidation of pyridine by ultrasonic irradiation: effect of additives and kinetic study, *Desalination Water Treatment*, 53, 1, (2015), 57-65 https://doi.org/10.1080/19443994.2013.837003

[14] Haider Mashkoor Hussein, Analysis of trace heavy metals and volatile chemical compounds of Lepidium sativum using atomic absorption spectroscopy, gas chromatography-mass spectrometric and fourier-transform infrared spectroscopy, *Research Journal of Pharmaceutical Biological and Chemical Sciences*, 7, 4, (2016), 2529-2555

[15] Stefania Vichi, Extraction techniques for the analysis of virgin olive oil aroma, in: V.R. Preedy, R.R. Watson (Eds.) *Olives and olive oil in health and disease prevention*, Elsevier, 2010, https://doi.org/10.1016/B978-0-12-374420-3.00066-8

[16] Sibylle Mothes, Rainer Wennrich, Coupling of SPME and GC-AED for the determination of organometallic compounds, *Microchimica Acta*, 135, 1, (2000), 91-95 https://doi.org/10.1007/s006040070023

[17] Nicola Caporaso, Martin B. Whitworth, Chenhao Cui, Ian D. Fisk, Variability of single bean coffee volatile compounds of arabica and robusta roasted coffees analysed by SPME-GC-MS, *Food Research International*, 108, (2018), 628-640 https://doi.org/10.1016/j.foodres.2018.03.077

[18] Panagiota Zakidou, Fotini Plati, Anthia Matsakidou, Evdoxia-Maria Varka, Georgios Blekas, Adamantini Paraskevopoulou, Single Origin Coffee Aroma: From Optimized Flavor Protocols and Coffee Customization to Instrumental Volatile Characterization and Chemometrics, *Molecules*, 26, 15, (2021), 4609 https://doi.org/10.3390/molecules26154609

[19] Cristina Sanz, Diana Ansorena, Jose Bello, Concepción Cid, Optimizing Headspace

Temperature and Time Sampling for Identification of Volatile Compounds in Ground Roasted Arabica Coffee, *Journal of Agricultural and Food Chemistry*, 49, 3, (2001), 1364-1369 https://doi.org/10.1021/jf001100r

[20] Luigi Mondello, Rosaria Costa, Peter Quinto Tranchida, Paola Dugo, Maria Lo Presti, Saverio Festa, Alessia Fazio, Giovanni Dugo, Reliable characterization of coffee bean aroma profiles by automated headspace solid phase microextraction ‐ gas chromatography ‐ mass spectrometry with the support of a dual ‐ filter mass spectra library, *Journal of Separation Science*, 28, 9 ‐ 10, (2005), 1101-1109 https://doi.org/10.1002/jssc.200500026

[21] Shimadzu Corporation, *High Sensitivity Analysis of Coffee Aroma Components Using the SPME Arrow*, 2019

[22] Ilze Laukaleja, Zanda Kruma, Evaluation of a headspace solid-phase microextraction with different fibres for volatile compound determination in specialty coffee brews, *Research for Rural Development*, 1, (2019), 215-221 https://doi.org/10.22616/rrd.25.2019.032