Effect of different aroma extraction methods combined with GC-MS on the aroma profiles of coffee

Effect of different aroma extraction methods combined with GC-MS on the aroma profiles of coffee

S S Yuwono, N Hanasasmita, W B Sunarharum and Harijono

Sensory and Applied Food Science Research Group, Faculty of Agricultural Technology, Universitas Brawijaya, Malang, Indonesia

E-mail: wbsunarharum@ub.ac.id

Abstract. Aroma is arguably the most important factor in the determination of coffee quality. The aroma profiles of coffee could be evaluated by application of gas chromatography-mass spectrometry (GC-MS). Prior to GC-MS analysis, those aroma compounds need to be extracted. This extraction method can be carried out with or without solvent. This research is aimed to know the effect of different aroma extraction methods combined with Gas Chromatography-Mass Spectrometry (GC-MS) on the aroma profiles of medium-roasted coffee (Java Arabica and Java Robusta). The solvent extraction applied Ultrasonic Assisted Extraction (UAE) method with three different solvents (dichlorometane, ethyl acetate, hexane), while Headspace-solid phase microextraction (HS-SPME) was employed as a solvent-free extraction method. The results showed that different solvents used for extraction produce significantly different yield of aroma extracts ($\alpha = 0.05$). Aroma compounds extracted using solvents combined with GC-MS consisted of 3 groups, i.e. acid, ester, and alcohol, where acid group dominated in all treatments. Meanwhile, HS-SPME GC-MS analysis resulted in an identification of 12 groups, such as aldehyde, pyrazine, pyrrole, pyrimidine, ketones, phenol, esther, acid, furan, alcohol, hydrocarbon, and sulfur compound. Aroma compounds of Java Arabica coffee was dominated by aldehydes, while phenolswas found to be the major compounds identified in Robusta.

1. Introduction

Coffee production in the world reached 155.4 million of 60 kg bags in 2017 [1]. Meanwhile in Indonesia, coffee consumption reached 0.896 kg/capita/year in 2015 [2]. These markets certainly demand good quality coffee. Aroma is one of the determinants of coffee quality. Aroma has a large impact on the perceived flavour. Good quality coffee flavour has been described as a pleasant sensation, a balanced combination on flavour, body, and aroma in the absence of faults [3].

More than 800 volatile components have been identified through extensive research on coffee. Volatile components in coffee have been studied extensively using gas chromatography-mass spectrometry (GC-MS), such as in Lee and Shibamoto [4], Fisk et al. [5], Sunarharum [6], and Yang et al. [7]. In Indonesia, there are only few reports on the identification of volatile components from local coffee, especially from Malang's coffee, Indonesia.

Before being analyzed, aroma compound has to be extracted. Extraction method can be carried out with solvent, such as Ultrasonic Assisted Extraction, and solvent-free, such as Headspace-solid phase microextraction (HS-SPME). UAE is a type of extraction that use ultrasound wave. The advantage of

using UAE are fast and medium temperature (can be used for heat sensitive compound) [8]. SPME is a type of a headspace sampling, which studies the volatile compounds in the space above a sample in a sealed container [9]. SPME is a fast, solvent-free alternative to conventional sample extraction techniques. SPME uses a fiber coated with a liquid (polymer), a solid (sorbent), or a combination of both. The fiber coating extracts the compounds from sample by absorption in the case of solid coatings [9]. The objectives of this study were to use GC-MS paired with UAE and HS-SPME to identify volatile compounds in roasted coffee from Malang.

2. Materials and Methods

2.1. Materials

Coffee beans (1 kg) used in this research were medium roasted Java Arabica and Java Robusta coffee from Arjuno Mountain, UB Forest Malang, East Java. Both coffee beans were processed following full-wash method. Chemicals used include ethyl acetate, hexane, and dichloromethane pa. (Merck).

2.2. Methods

Two factors being studied were two different coffee species (Arabica and Robusta) and aroma extractions methods, with and without solvents. The solvents used were ethyl acetate, hexane, and dichloromethane. The solvent-free method employed Headspace Solid Phase Microextraction (HS-SPME) coupled with Gas Chromatography-Mass Scpectrometry (GC-MS).

2.2.1. Ultrasonic assisted extraction

The method used was modified from Kuś et al. [10]. As many as 1.5 g of coffees were extracted with 30 ml solvent (ethyl acetate; hexana; dicloromethane). The extraction was supported by ultrasound. Indirect sonication mode of ultrasonic bath (Elmasonic Type S 40 H) at 25 ± 5^{o}C was applied. The extracts were sentrifuge at 5000 rpm for 10 min. 1µl was used for GC-MS analyses.

2.2.2. Headspace solid-phase microextraction (HS-SPME)/ GC-MS condition

The headspace microextraction was performed with divinylbezene -Carboxen- polydimethylsiloxane (DVB-Carboxen-PDMS) fibre. After extraction, the SPME fiber was moved to the splitless injection port of GC for manual injection. An Varian CP-3800 gas chromatograph coupled with an MS Saturn 2200 mass spectrometer, equipped with VF-5ms column (30 length x 0.25 mm internal diameter). Inlet temperature of GC was set at 300^{o}C with constant column flow 0.7 ml/min. The transfer line temperature was set at 250^{o}C. The oven parameters used were 40^{o}C with holding for 2 min, rising to 240^{o}C at a rate of 15.0^{o}C/min, holding for 14.0 min.

Aroma compounds were identified based on NIST MS library database. Qualitative and quantitative data were tabulated in MS Excel 2013. Statistical analysis was performed using Minitab 17.0 Statistical Software (Minitab Inc., State College, Pennsylvania, USA).

3. Results and Discussion

3.1. Chemical properties

Chemical properties of coffee such as starch, protein, lipid, ash, and caffeine may be important to coffee flavour. These components contribute to volatile appearance while roasting. Table 1 shows chemical properties in Arabica and Robusta.

Arabica and Robusta were compared to see their differences. It can be seen from Table 1 that those two species had different chemical properties. Arabica was found to have less starch, protein, ash and caffeine than the Robusta counterpart. However, Arabica contains more lipid than Robusta. Those chemical differences were thought to have an influence on the characteristics of the brewed coffee.

Table 1. Chemical Properties in Arabica and Robusta.

Component (%)	Arabica	Robusta
Starch	0.82 ± 0.03	1.16 ± 0.09
Protein	12.48 ± 0.59	13.13 ± 0.12
Lipid	12.79 ± 1.04	11.26 ± 0.20
Water	3.18 ± 0.03	2.60 ± 0.16
Ash	3.91 ± 0.14	4.07 ± 0.32
Caffeine	1.01 ± 0.04	1.53 ± 0.01

3.2. Aroma compounds

3.2.1. Ultrasonic assisted extraction

There are three groups of aroma compounds were identified. They were 3 acids, 2 esters, and 1 alcohol. Aroma compound from alcohol and ester groups were found in arabica's extract with ethyl acetate solvent. It were furfuryl alcohol (0.64%) and propanoic acid, ethyl ester (3.80%). Ester group was also found in robusta's extract with hexana solvent. It was 2,3-dihydroxypropyl ester (0.15%). Meanwhile, aroma compound from acid group was found in all the extract. It were hexadenoic acid, acetic acid, octadecanoic acid.

3.2.2. HS-SPME

In Arabica, among 65 peaks observed in a chromatogram, 47 volatile compounds were identified. They were nine aldehydes, eleven pyrazines, seven ketones, four phenols, three esters, three pyrroles, 3 acids, 2 furanones, 3 alcohols, 1 sulfur-containing compound, and 1 pyridine. The major constituents in Arabica were 5-methyl-furfural (14.01%), 2-furancarboxyaldehyde (11.83%), and 2-furanmethanol acetate (11.74%). Meanwhile, in Robusta, among 80 peaks observed in a chromatogram, 57 volatile compounds were identified. They were eleven aldehydes, thirteen pyrazines, eleven ketones, five phenols, three esters, three pyrroles, two acids, three furanones, one alcohols, three hydrocarbons, and one pyridine. The major constituents in Robusta were 2-methoxy-4-vinylphenol (12.24%), 2-furanmethanol acetate (9.27%), and 5-methylfurfural (8.46%). Table 2 shows volatile compounds identified from Arabica dan Robusta.

Table 2. Volatile compounds identified from Arabica and Robusta.

No	Volatile Compound	RT	% Area	Flavour description [literature]
		Arabica		
Aldehyde				
1	*Isobutyraldehyde*	2.270	0.70	Burnt, Caramel, Cocoa, Malt [11]
2	*Butanal,3-methyl-*	3.213	0.95	Malty [3]
3	*Butanal,2-methyl-*	3.348	1.66	Almond, cocoa, fermented, malt [3]
4	*Hexanal*	6,933	0.43	Green [12]
5	*2.4-pentadienal*		-	Fruity [12]
6	*2-Furancarboxaldehyde*	8.079	11.83	Almond like, caramel, spice [12]
7	*5-methyl-furfural*	13.339	14.01	Caramel [12]
8	*1H-pyrrole-2-carboxaldehyde, 1-methyl*	15.113	1.58	Roasted nut [12]
9	*Benzeneacetaldehyde*	16.764	0.55	Green, sweet, floral [11]
Pyrazine				
10	*Pyrazine,methyl-*	7.837	1.45	Nutty [11]

No	Volatile Compound	RT	% Area	Flavour description [literature]
11	*Pyrazine,2,5-dimethyl-*	11.329	2.43	Roasted nut [11]
12	*Pyrazine,2,6-dimethyl-*		-	Roasted nut [11]
13	*Pyrazine,ethyl-*	11.490	0.50	Nutty [11]
14	*Pyrazine,2-ethyl-6-methyl-*	14.856	2.13	Potato-like, nutty [11]
15	*Pyrazine,2-ethyl-3-methyl-*	15.024	2.74	Nutty [11]
16	*Pyrazine,2-ethyl-3,5-dimethyl-*	18.006	2.42	Earthy, roast [11]
17	*Pyrazine,3-ethyl-2,5-dimethyl-*	18.266	0.33	Chocolate, musty [11]
18	*2-Acetyl-3-methylpyrazine*	19.757	0.10	Nutty [11]
19	*Pyrazine,2,3-diethyl-5-methyl-*	20.878	0.21	Musty [11]
20	*Pyrazine,3,5-diethyl-2-methyl-*	21.007	0.61	Nutty [11]
Ketone				
21	*Trans.beta-Ionon-5,6-epoxide*	1.655	0.69	Woody, berry, floral, and fruity [12]
22	*Ethanone,1-(2-furanyl)-*	11.176	2.12	Balsamic-sweet, Nutty [12]
23	*1-(2-furyl)-2-propanone*	12.978	0.39	Herbal, green [12]
24	*Bicyclo[4.1.0]heptan-2-one,6-methyl-*	14.489	0.18	Mint [12]
25	*1-Propane,1-(2-furanyl)-*	15.237	0.53	Herbal, green [12]
26	*Ethanone,1-(1-methyl-1H-pyrrol-2-yl)*	17.934	0.50	Earthy, Nutty [12]
27	*beta.Damascenone*	28.944	0.15	Honey-like, fruity [6]
Phenol				
28	*Phenol*	4.504	0.48	Sweet [12]
29	*Phenol,3,5-dimethyl-*	13.230	0.21	Smoky, sweet [12]
30	*Phenol,4-ethyl-2-methoxy-*	25.369	0.30	Spicy, woody [12]
31	*2-Methoxy-4-vinylphenol*	26.662	2.54	Woody, smoky [12]
Acid				
32	*Propanoic acid,2-oxo*	1.979	1.33	Sour-acetic odor, Caramellic sweetness
33	*Acetic acid*	2.410	1.09	Pungent, vinegar [12]
34	*Acetic acid,anhydride*	2,457	0.77	Strong acetic [11]
Furanone				
35	*Furan,2-methyl-*	2.566	1.40	Cocoa [12]
36	*2-furfuryl furan*	18.184	0.88	Roasted [12]
Ester				
37	*Acetic acid, methyl ester*	2.116	0.68	Roasted nut [11]
38	*Furfurylformate*	11.023	1.00	Floral [12]
39	*2-Furanmethanol.acetate*	14.647	11.74	Fruity [12]
Alcohol				
40	2-Furanmethanol	8.934	7.16	Burnt, caramel [12]
41	Linalool oxide	17.790	0.49	Floral [12]
42	Linalool L	18.917	1.00	Floral [12]
Pyrrole				
43	*1H-Pyrrole,1-methyl-*	4.907	0.53	Herbal
44	*1H-Pyrrole,1-(2-furanylmethyl)-*	21.943	1.98	Earthy-green [12]
45	*N-furfuryl pyrrole*		-	Vegetable [12]
Sulfur-containing Compound				
46	*3-Acetyl-2,5-dimethylthiophene*	25.581	0.14	Burnt, nutty
Pyridine				
47	*Pyridine*	5.379	0.95	Sour, smoky, warm [11]

Robusta

No	Volatile Compound	RT	% Area	Flavour description [literature]
Aldehyde				
1	*Isobutyraldehyde*	2.270	0.12	Burnt, Caramel, Cocoa, Malt
2	*Butanal,3-methyl-*	3.213	0.31	Fruity, peach-like [3]
3	*Butanal,2-methyl-*	3.348	0.46	Almond, cocoa, fermented, malt [3]
4	*2,4-pentadienal*	6.927	0.09	Fruity [12]
5	*2-Furancarboxaldehyde*	8.095	3.82	Almond like, caramel, spice [12]
6	*5-methyl-furfural*	13.352	8.46	Caramel [12]
7	*1H-pyrrole-2-carboxaldehyde, 1-methyl*	15.121	1.39	Roasted nut [12]
8	*2-Formyl pyrrole*	15.458	0.20	Musty [12]
9	*Benzeneacetaldehyde*	16.776	0.49	Green, sweet, floral [13]
10	*Tea pyrrole*	16.933	0.25	Burnt, roasted, smoky [12]
11	*Nonanal*	19.141	0.92	Floral, green, lemon [12]
Pyrazine				
12	*Pyrazine,methyl-*	7.837	1.99	Nutty [11]
13	*Pyrazine,2,6-dimethyl-*	11.333	2.11	Roasted nut [11]
14	*Pyrazine,ethyl-*	11.494	0.78	Nutty [11]
15	*Pyrazine,2-ethyl-6-methyl-*	14.867	1.48	Potato-like, nutty [11]
16	*Pyrazine,2-ethyl-3-methyl-*	15.020	2.03	Nutty [11]
17	*Pyrazine,2-ethyl-5-methyl-*		-	Fruity [11]
18	*Pyrazine,2-ethyl-3,5-dimethyl-*	18.016	2.09	Earthy, roast [11]
19	*Pyrazine,3-ethyl-2,5-dimethyl-*		-	Chocolate, musty [11]
20	*Pyrazine,2-ethyl-3,5-dimethyl-*	18.272	0.33	Earthy, roast [11]
21	*Pyrazine,3-ethyl-2,5-dimethyl-*		-	Chocolate, musty [11]
22	*2-acetyl-3-methylpyrazine*	19.764	0.41	Nutty [11]
23	*Pyrazine,2,3-diethyl-5-methyl-*	20.891	0.33	Musty [11]
24	*Pyrazine,3,5-diethyl-2-methyl-*	21.015	0.77	Nutty [11]
Ketone				
25	*Trans.beta.-Ionon-5,6-epoxide*	1.658	0.15	Woody, berry, floral, and fruity [12]
26	*Ethanone,1-(2-furanyl)-*	11.188	1.15	Balsamic-sweet, Nutty [12]
27	*1-(2-furyl)-2-propanone*	12.985	0.25	Herbal, green [12]
28	*1-Propanone,1-(2-furanyl)-*	15.246	0.33	Herbal, green [12]
29	*Ethanone,1-(1H-pyrrol-2-yl)-*	17.510	0.73	Earthy, Nutty [12]
30	*alpha.alpha-dihydroxyacetophenone*	17.647	0.21	Green [12]
31	*Ethanone,2,2-dihydroxy-1-phenyl-*		-	Spice [12]
32	*1-(2-furyl)-butan-3-one*	17.843	0.55	Spice [12]
33	*Ethanone,1-(1-methyl-1H-pyrrol-2-yl)*	17.949	0.83	Savory [12]
34	*cis- dihydrocarvone*	21.647	0.71	Herb-like,spearmint-like [11]
35	*beta.Damascenone*	28.954	0.40	Floral, woody [6]
Phenol				
36	*Phenol,2,3-dimethyl-*	13.244	0.11	Phenolic [12]
37	*Phenol,3-methyl-*	17.101	0.31	Medical-leathery
38	*Phenol,2-methoxy-*	18.396	3.85	Burnt, woody [12]
39	*Phenol,4-ethyl-2-methoxy-*	25.383	4.30	Spicy, woody [12]
40	*2-Methoxy-4-vinylphenol*	26.672	12.24	Woody, smoky [12]
Acid				
41	*Acetic acid*	2.434	0.10	Pungent, vinegar [12]
42	*Acetic acid,anhydride*	2.467	0.12	Strong acetic [11]

No	Volatile Compound	RT	% Area	Flavour description [literature]
Furanone				
43	*Furan,2-methyl-*	2.566	0.63	Cocoa [12]
44	*Furan, 2,5-dimethyl*	4.077	0.07	Meaty [12]
45	*2-furfuryl furan*	18.196	1.44	Roasted [12]
46	*Difurfuryl ether*	26.212	1.94	Coffee, earth [12]
Ester				
47	*Furfurylformate*	11.037	0.29	Floral [12]
48	*2-Furanmethanol,acetate*	14.658	9.27	Fruity [12]
49	*Furfurylpentanoate*	23.445	0.56	Sweet, fruity, pineapple-like [12]
Alcohol				
50	2-Furanmethanol	8.950	6.91	Burnt, caramel [12]
Hydrocarbon				
51	1H-Indole	26.095	0.35	Burnt, floral [12]
52	1H-Indole, 3-methyl	29.226	0.15	Animal [12]
53	3,4-dimethoxystyrene	28.479	0.54	Floral, green [12]
Pyrrole				
54	*1H-Pyrrole,1-methyl-*	4.907	0.08	Herbal
55	*N-furfuryl pyrrole*	21.954	3.59	Vegetable [12]
56	*1H-pyrrole,1-(2-furanylmethyl)-*		-	Earthy-green [12]
Pyridine				
57	*Pyridine*	5.223	1.44	Sour, smoky, warm [11]

Based on Table 2, aroma compounds of aldehyde group (38%) dominated in arabica, while phenol group (25%) dominated in Robusta. Several key flavour compound were identified by GC-MS. They were 2-methylbutanal (1.66% in Arabica; 0.46% in Robusta), 3-methylbutanal (0.95% in Arabica; 0.31% in Robusta), 2,5-dimethylpyrazine (2.43% in Arabica), 2-ethyl-3,5-dimethylpyrazine (2.42% in Arabica; 2.09% in Robusta), β-damascenone (0.15% in Arabica; 0.40% in Robusta), Linalool (1.00% in Arabica), and 1-methyl pyrrole (0.53% in Arabica; 0.08% in Robusta).

4. Conclusion

In conclusion, aroma extracts produced through UAE method consist of aroma compounds that majorly belong to 3 groups, i.e. acid, ester, and alcohol, where acid group dominated in all treatments. Meanwhile, the HS-SPME GC-MS analysis or the extraction from the headspace of samples could identify 12 groups of aroma compound, such as aldehyde, pyrazine, pyrrole, pyrimidine, ketones, phenol, ester, acid, furan, alcohol, hydrocarbon, and sulfur compound. Aroma compounds of Java Arabica coffee was dominated by aldehydes, while phenols were found to be the major compounds identified in Robusta.

Acknowledgments

We acknowledge the Faculty of Agricultural Technology, Universitas Brawijaya, Malang, Indonesia and UB Forest for their ongoing support on this research.

References

[1] International Coffee Organization 2018 Total production by all exporting countries, retrieved from www.ico.org on 27/07/2018.

[2] Direktorat Jenderal Perkebunan 2016 Statistik Perkebunan Indonesia (Indonesian Plantation Statistics) Sekretariat Direktorat Jenderal Perkebunan Kementrian Pertanian Jakarta Indonesia. [In Indonesian]
[3] Sunarharum W 2016 The compositional basis of coffee flavour Thesis the University of Queensland Brisbane Australia.
[4] Lee K G, Shibamoto T 2002 Analysis of volatile components isolated from Hawaiian green coffee beans (*Coffea arabica* L.) *Flavour Frag. J.* **17** 349-351.
[5] Fisk I, Alec K, Sonja H, Amarjeet V, Javier S 2012 Discrimination of roast and ground coffee aroma *Flavour* **1** 1-9
[6] Sunarharum, W B, Williams D J, Smyth H E 2014 Complexity of coffee flavour: a compositional and sensory prespective *Food Res. Int.* **62** 315-325.
[7] Yang N, Chujiao L, Xingkun L, Tina K, Morten M, Ian F 2016 Determination of volatile marker compounds of common coffee roast defects *Food Chem.* **211** 206-214.
[8] Luque-García J L, Luque de Castro M D 2004 Ultrasound-assisted soxhlet extraction: an expeditive approach for solid sample treatment. Application to the extraction of total fat from oleaginous seeds *J. Chromatogr. A.* **1034** 237-242.
[9] Pawliszyn J 2001 Solid phase microextraction *Adv. Exp. Med. Biol.* **488** 73-87
[10] Kuś PM, Marijanović Z, Jerković I 2015 Evaluation of HS-SPME and ultrasonic solvent extraction for monitoring of plant flavours added by the bees to herb honeys: traceability biomarkers *Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess.* **32** 1761-1771.
[11] Burdock G 2010 Fenaroli's Handbook of Flavour Ingredients 6th Ed. CRC Press Florida USA.
[12] Anonymous 2015 Flavour demo formulas retrieved from http://www.thegoodscentscompany.com/ on 7th April 2018.