

Optimizing Headspace Temperature and Time Sampling for Identification of Volatile Compounds in Ground Roasted Arabica Coffee

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Equilibration time and temperature were the factors studied to choose the best conditions for analyzing volatiles in roasted ground Arabica coffee by a static headspace sampling extraction method. Three temperatures of equilibration were studied: 60, 80, and 90 °C. A larger quantity of volatile compounds was extracted at 90 °C than at 80 or 60 °C, although the same qualitative profile was found for each. The extraction of the volatile compounds was studied at seven different equilibration times: 30, 45, 60, 80, 100, 120, and 150 min. The best time of equilibration for headspace analysis of roasted ground Arabica coffee should be selected depending on the chemical class or compound studied. One hundred and twenty-two volatile compounds were identified, including 26 furans, 20 ketones, 20 pyrazines, 9 alcohols, 9 aldehydes, 8 esters, 6 pyrroles, 6 thiophenes, 4 sulfur compounds, 3 benzenic compounds, 2 phenolic compounds, 2 pyridines, 2 thiazoles, 1 oxazole, 1 lactone, 1 alkane, 1 alkene, and 1 acid.

Keywords: *Static headspace; roasted coffee; volatile compounds*

INTRODUCTION

Due to its unique aroma and flavor, considerable research has been carried out in the analysis of flavor-related compounds in coffee. Researchers on volatile flavor compounds have used several different techniques (1), all mainly based in the isolation and further identification of the peaks obtained by GC-MS. Other papers include data of sniffing profiles, establishing a relationship between the presence of certain peaks and their sensorial profiles (2) so that it can be shown that the odor threshold of components was a very important factor from a sensorial point of view.

Headspace sampling is one of the most popular methods for flavor isolation (3) because it is the most suitable for the study of very volatile compounds (4–8) and because its composition better represents the smell that is perceived by the consumer (9).

The direct and accurate analysis of volatiles in ground roasted coffee by static headspace (SH-GC) requires careful standardization of instrumental parameters such as sample size, equilibration time and temperature, and instrumental conditions required for the separation of volatile compounds (10).

Static headspace has been used by different authors when researching volatile flavor compounds; Kallio et al. (11) studied different ratios of several pairs of compounds in the headspace of roasted coffee as an indicator of the storage time of the coffee. Shimoda and Shibamoto (12) used GC-MS with headspace analysis and identified 62 volatile compounds in roasted brewed coffee. Leino et al. (13) characterized the changes in roasted ground Arabica and Robusta coffees stored during 18 months by headspace and identified 38

volatile compounds. Holscher and Steinhart (14) investigated the volatiles forming the pleasant odor arising from freshly roasted coffee beans by a headspace technique. Bicchi et al. (15) characterized roasted coffee using a static headspace, and Mayer et al. (16) quantified 28 potent odorants extracted with a static headspace from ground coffee samples and brews. A syringe was used to inject the headspace into the chromatograph for analysis in each case. As the injection procedure can be automated using a headspace sampler (17) eliminating the errors associated with manual handling, an HP 7694 static headspace sampler was used for the analysis of the volatile compounds in this work.

There are virtually no reports on the study of the headspace sampling temperature and time for the analysis of volatile compounds in ground roasted coffee.

The main objective of our research was to optimize a method based on static headspace gas chromatography (SH-GC) applied to the extraction of volatile compounds from roasted ground Arabica coffee. In addition, a more specific objective was to identify the headspace volatiles obtained by the method and present in every chromatogram. The 122 volatiles identified were grouped by chemical class and semiquantified to find the best equilibration time and temperature for the extraction of the largest quantity of volatile compounds from roasted ground Arabica coffee.

EXPERIMENTAL PROCEDURES

Materials. A commercial sample (100% Arabica coffee, roasted) was obtained from a local manufacturer, and just before each analysis, the coffee was ground with a Retsch mill to a particle size of 0.75 mm.

Pure reference standards of 2-methylpropanal, 2-methyl-1-propanol, 2-butanone, 3-methylbutanal, 2,3-butanedione, 2,3-pentanedione, and 2-butenal were purchased from Acros; 2-propen-1-ol, 3-penten-2-one, 2-pentanol, 2-methylfuran,

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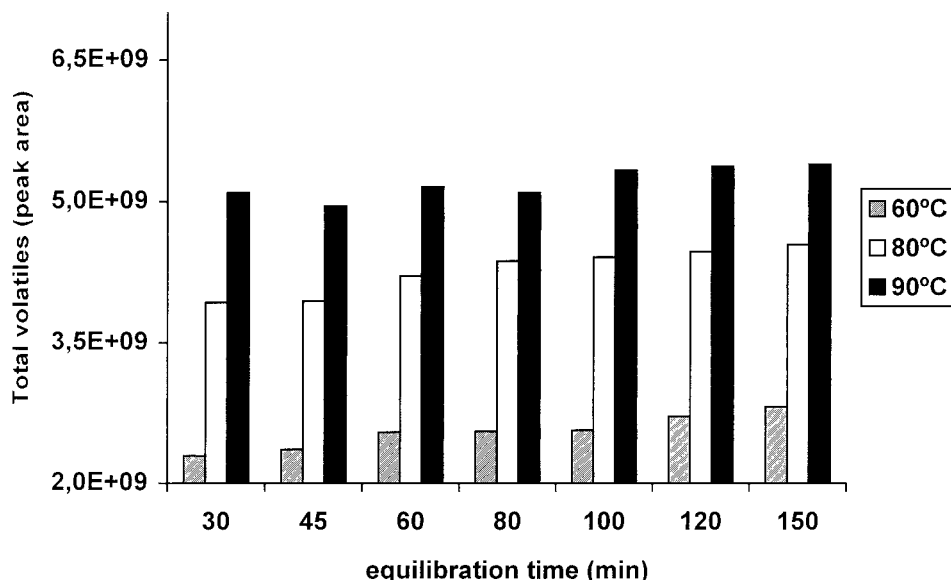


Figure 1. Effect of equilibration temperature on total volatile.

thiophene, propionaldehyde, and dimethyl sulfide were obtained from Aldrich (Steinheim, Germany), and hexanal was obtained from Sigma (Steinheim, Germany).

Static Headspace Gas Chromatography–Mass Spectrometry (SH-GC-MS). SH-GC analysis was performed with an HP 6890 gas chromatograph (Hewlett-Packard) equipped with a static headspace sampler Hewlett-Packard model 7694.

Ten milliliter vials containing 2 g of roasted ground coffee were immediately sealed with silicone rubber Teflon caps.

Temperature of Equilibration. To choose the optimal temperature of analysis, three different temperatures at seven different equilibration times were tested. Vials were equilibrated at 30, 45, 60, 80, 100, 120, and 150 min using temperatures of 60, 80, and 90 °C.

Time of Equilibration. To select an optimal equilibration time for the extraction of each type of compound, vials were equilibrated at 30, 45, 60, 80, 100, 120, and 150 min using a temperature of 90 °C. Analysis was performed in triplicate.

After the vials had been pressurized with carrier gas for 12 s, 3 mL of the coffee headspace sample was injected into a capillary column HP-Wax (60 m × 0.25 mm × 0.5 μm film thickness; Hewlett-Packard).

The injector temperature was set at 180 °C, and helium (10 mL/min linear speed) was the carrier gas. The oven temperature was maintained at 40 °C for 6 min and programmed to 190 °C at 3 °C/min.

Mass spectrometry analysis was carried out using a Hewlett-Packard mass selective detector model 5973 coupled to the gas chromatograph. The mass spectrometer operated in the electron impact ionization mode (70 eV), with a scan range of 33 to 300 amu. The ion source temperature was set at 230 °C.

Identification of the Volatile Compounds. Volatile compounds were identified by comparing their spectra to those of the Wiley library and also by comparison of their GC Kovats index and retention time to those of standard compounds and data from literature.

Quantitative Measurements. The total content of the volatile of each headspace analysis was defined by integrating the peak areas of the 122 compounds identified. The relative percentages of individual compounds were calculated from the total contents of volatile on the chromatograms.

Statistical Analysis. The data were subjected to one-way analysis of variance (ANOVA) and a Tukeys posteriori test using SPSS 9.0 for Windows. A significance level of $p \leq 0.05$ was used for all mean evaluations.

RESULTS AND DISCUSSION

The time and temperature of equilibration are known to be important factors affecting volatile analysis of

coffee using SH-GC (10). Volatile analysis by SH-GC was standardized by subjecting 2 g samples of roasted ground coffee to different equilibration temperatures and time periods.

Effect of Temperature of Equilibration. One way of improving the sensitivity of the headspace technique is by raising the temperature of the sample (17–19) so that more volatile compounds are released from the solid matrix.

The total area of chromatograms obtained at three different equilibration temperatures using seven equilibration times was calculated (Figure 1).

A temperature of 90 °C permitted the extraction of a larger quantity of volatile compounds than did 80 or 60 °C at each of the seven times of equilibration studied (Figure 1). Figure 2 shows the chromatograms obtained at 60 °C/30 min and at 90 °C/150 min, and a clear difference in the total area can be observed. However, no differences were found in the qualitative profiles. A temperature of 90 °C was selected to be used in order to study the influence of the equilibration times on the extraction of the individual volatile compounds in roasted ground coffee.

Effect of Equilibration Time. The factors controlling equilibrium in food systems are very complex, which indicate that long equilibration times are needed to reach equilibrium (17). Initially, the total chromatographic area follows a linear relationship with incubation time, after which it reaches a plateau indicating that equilibrium has been established between the matrix and the headspace.

Table 1 shows the percentage of the extraction of each chemical class at 90 °C at the seven equilibration times studied. As can be observed in this table, each chemical class had its maximum extraction rate in one of the seven different equilibration times studied: Aldehydes, alcohols, pyrroles, thiophenes, esters, oxazoles, and benzenic compounds are highly extracted at 45 min of equilibration; ketones, furans, and phenolic compounds at 60 min; lactones at 80 min; and pyridines at 100 min. The quantity of sulfur-containing extracted compounds decreased when the equilibration time was increased, and this was probably due to their sensitivity to O₂. The proportion of extracted thiazoles and alkanes did not depend on the time of equilibration programmed, and

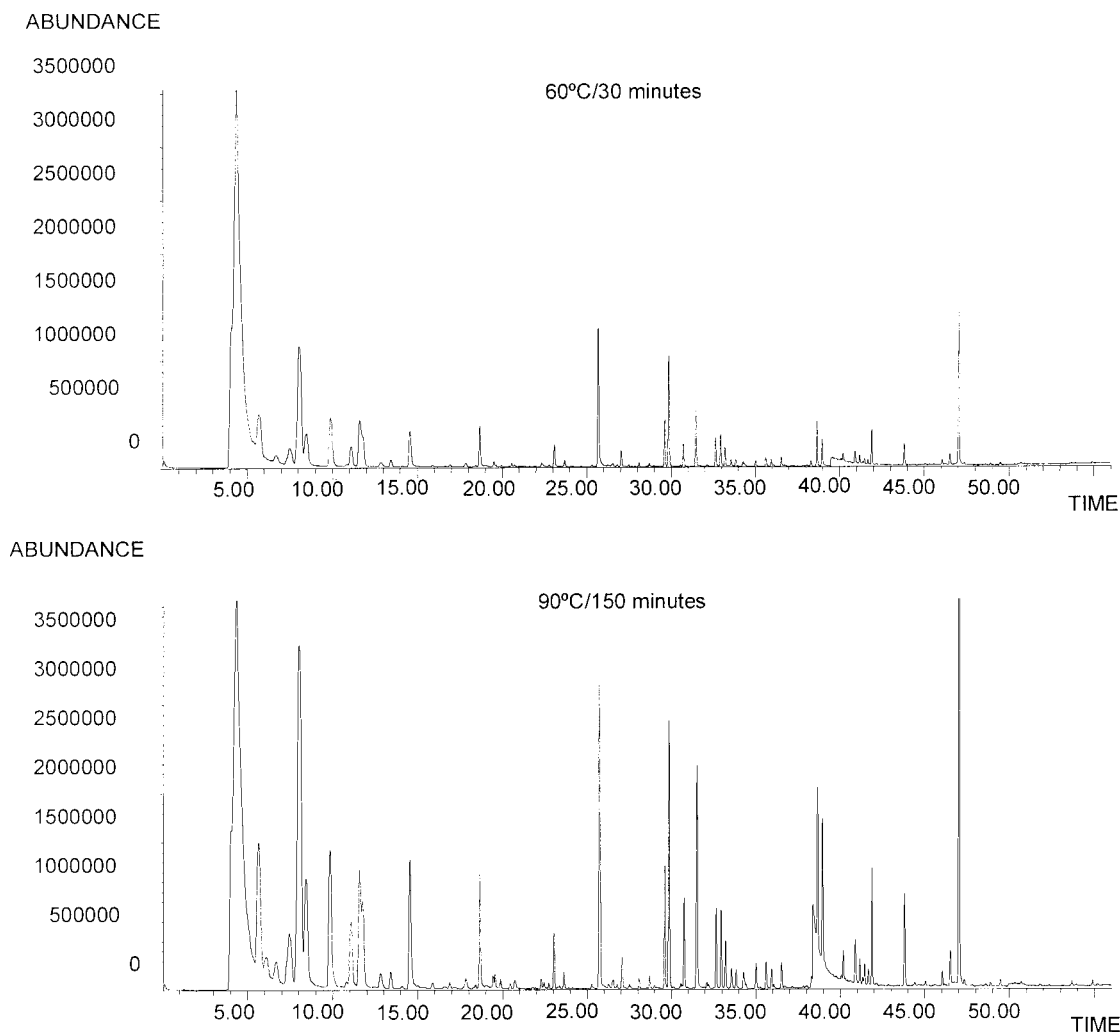


Figure 2. Chromatograms obtained at 60 °C/30 min and at 90 °C/150 min.

Table 1. Percentages of Extraction of Each Chemical Class with Regard to the Total Area at 90 °C

compound	30 min	45 min	60 min	80 min	100 min	120 min	150 min
aldehydes	12.56 (2.14) ^a	13.74 (2.48)	13.40 (2.84)	12.61 (2.16)	12.81 (2.23)	13.02 (1.69)	12.69 (1.40)
ketones	28.40 (3.12)	28.45 (2.01)	29.24 (2.85)	28.04 (2.84)	27.50 (2.60)	27.40 (2.47)	26.79 (2.29)
alcohols	0.94 (0.26)	1.02 (0.26)	1.01 (0.29)	0.94 (0.22)	0.95 (0.24)	0.95 (0.26)	0.97 (0.27)
pyrroles	1.47 (0.30)	1.52 (0.21)	1.42 (0.27)	1.23 (0.37)	1.30 (0.27)	1.25 (0.17)	1.25 (0.14)
pyrazines	7.35 (0.49)	6.05 (1.39)	6.15 (1.46)	7.05 (1.42)	7.15 (0.06)	6.71 (0.62)	6.85 (0.84)
furans	21.31 (3.00)	21.37 (1.39)	21.58 (2.48)	20.52 (3.23)	21.06 (1.76)	20.77 (1.57)	19.97 (1.72)
thiazoles	0.03 (0.01)	0.03 (0.01)	0.03 (0.01)	0.03 (0.01)	0.03 (0.00)	0.03 (0.01)	0.03 (0.00)
thiophenes	0.20 (0.05)	0.23 (0.06)	0.20 (0.06)	0.18 (0.06)	0.19 (0.05)	0.19 (0.04)	0.19 (0.03)
esters	3.76 (0.42)	4.26 (0.04)	4.22 (0.16)	4.10 (0.14)	4.04 (0.12)	4.03 (0.04)	3.99 (0.07)
oxazoles	0.03 (0.01)	0.04 (0.01)	0.03 (0.01)	0.03 (0.01)	0.03 (0.00)	0.03 (0.00)	0.03 (0.00)
lactones	0.63 (0.09)	0.44 (0.26)	0.59 (0.14)	0.66 (0.02)	0.61 (0.05)	0.61 (0.02)	0.52 (0.07)
sulfur compounds	0.52 (0.13)	0.46 (0.11)	0.39 (0.07)	0.35 (0.09)	0.32 (0.07)	0.30 (0.04)	0.29 (0.05)
pyridines	4.06 (1.30)	3.04 (1.95)	3.06 (2.25)	3.91 (0.23)	4.14 (1.11)	3.60 (0.47)	4.01 (0.32)
alkanes	0.10 (0.01)	0.10 (0.01)	0.10 (0.01)	0.08 (0.02)	0.09 (0.02)	0.08 (0.01)	0.08 (0.01)
alkenes	0.43 (0.03)	0.44 (0.06)	0.45 (0.03)	0.45 (0.04)	0.45 (0.02)	0.45 (0.00)	0.44 (0.02)
phenolic compounds	0.07 (0.01)	0.06 (0.01)	0.06 (0.01)	0.06 (0.01)	0.06 (0.01)	0.05 (0.01)	0.06 (0.01)
acids	7.31 (2.00)	7.56 (3.55)	7.55 (2.51)	8.59 (1.07)	7.88 (1.58)	8.75 (1.51)	8.80 (1.39)
benzenic compounds	0.05 (0.01)	0.06 (0.01)	0.05 (0.01)	0.05 (0.02)	0.05 (0.01)	0.05 (0.01)	0.05 (0.01)
unidentified compounds	17.16	18.29	17.28	18.78	18.44	19.57	21.00

^a Numbers in parentheses are standard deviations.

pyrazines showed an irregular extraction when these times were varied.

No significant differences relating to the total quantity of the volatile compounds extracted were found among the different equilibration times studied.

Volatile Compounds Identified. One hundred and twenty-two volatile compounds were identified by head-

space analysis in roasted ground coffee (Table 2): 26 furans, 20 ketones, 20 pyrazines, 9 alcohols, 9 aldehydes, 8 esters, 6 pyrroles, 6 thiophenes, 4 sulfur compounds, 3 benzenic compounds, 2 phenolic compounds, 2 pyridines, 2 thiazoles, 1 oxazole, 1 lactone, 1 alkane, 1 alkene, and 1 acid. Ninety-nine of them have been previously identified in coffee (11, 13–15, 20–25).

Table 2. Volatile Compounds Identified in Headspace Gas of Roasted Ground Coffee

KI ^a	ID ^b	compound ^c	KI ^a	ID ^b	compound ^c	KI ^a	ID ^b	compound ^c
		aldehydes		C	<i>N</i> -furfurylpyrrole	1650	C	2-acetyl-5-methylfuran*
645	C	acetaldehyde			pyrazines	1686	C	furfuryl alcohol
712	A	propanal	1231	B	pyrazine	1706	C	5-methyl-2-furfurylfuran*
747	A	2-methylpropanal	1288	B	2-methylpyrazine			thiazoles
839	C	butanal	1347	B	2,5-dimethylpyrazine	1260	C	2-methylthiazole
880	C	2-methylbutanal	1353	B	2,6-dimethylpyrazine	1270	C	1,3-thiazole
884	A	3-methylbutanal	1359	B	2-ethylpyrazine			thiophenes
1042	A	2-butenal	1372	C	2,3-dimethylpyrazine	1021	A	thiophene
1084	A	hexanal	1411	C	2-ethyl-6-methylpyrazine	1097	B	2-methylthiophene
1102	C	2-methyl-2-butenal	1419	C	2-ethyl-5-methylpyrazine	1127	C	3-methylthiophene
		ketones	1432	C	2-ethyl-3-methylpyrazine	1185	C	2-ethylthiophene*
753	C	2-propanone*	1433	C	2,3,5-trimethylpyrazine	1565	C	2-methyltetrahydrothiophen-3-one*
866	A	2-butanone	1447	C	<i>N</i> -propylpyrazine*	1734	C	2-thiophenecarboxaldehyde
962	A	2,3-butanedione	1463	C	2,6-diethylpyrazine			esters
1053	C	3-hexanone	1467	C	2-vinylpyrazine*	782	C	acetic acid, methyl ester
1058	A	2,3-pentanedione	1474	C	3-ethyl-2,5-dimethylpyrazine*	850	B	acetic acid, ethyl ester
1138	A	3-penten-2-one	1493	C	2,3-dimethyl-5-ethylpyrazine	872	C	propanoic acid, methyl ester
1143	C	3,4-hexanedione	1521	C	2-methyl-6-vinylpyrazine*	1015	C	isovaleric acid, methyl ester
1307	C	3-hydroxy-2-butanone	1524	C	2-methyl-3,5-diethylpyrazine	1050	C	methyl thiol acetate*
1323	C	1-hydroxy-2-propanone	1529	C	2-methyl-5-vinylpyrazine	1266	C	3-methyl-2-buten-1-ol, acetate*
1366	C	2-hydroxy-3-pentanone	1665	C	2-acetylpyrazine	1335	C	lactic acid, methyl ester*
1385	C	2-cyclopenten-1-one	1667	C	5-methyl-6,7-dihydro-(5 <i>H</i>)-cyclopentapyrazine	1403	C	glycolic acid, methyl ester*
1397	C	2-methyl-2-cyclopenten-1-one			furans			oxazoles
1351	C	1-hydroxy-2-butanone			furan	1214	C	trimethylloxazole
1483	C	1-acetyloxy-2-propanone	716	C	furan			lactones
1546	C	1-(2-furyl)-2-propanone*	832	C	3-methylfuran	1673	C	γ -butyrolactone*
1549	C	3,3-dimethyl-2-butanone	858	A	2-methylfuran			sulfur compounds
1554	C	1-acetyloxy-2-butanone	930	B	2,5-dimethylfuran	635	C	methanethiol
1562	C	3-methyl-2-cyclopenten-1-one	975	B	2-ethylfuran	660	C	carbon disulfide
1582	C	2,3-dimethylcyclopent-2-en-1-one	1056	B	2,3,5-trimethylfuran	671	A	dimethyl sulfide
1723	C	1-(5-methyl-2-pyrazinyl)-1-ethanone*	1160	B	2-vinyl-5-methylfuran	1077	B	dimethyl disulfide
		alcohols	1181	C	2-(2-propenyl)-furan*			pyridines
913	C	ethanol	1220	C	2-propenylfuran	1203	B	pyridine
1026	C	2-butanol*	1241	C	2-pentylfuran	1239	C	2-methylpyridine
1103	A	2-methyl-1-propanol	1251	B	2-(methoxymethyl)furan			alkanes
1124	A	2-propenol*	1283	B	2-methyltetrahydrofuran-3-one	915	C	2,2,4,6,6-pentamethylheptane*
1130	A	2-pentanol*	1304	C	<i>trans</i> -2-methyl-5- <i>n</i> -propenylfuran*			alkenes
1220	C	3-methylbutan-1-ol	1462	C	5-methyl-3-tetrahydrofuran-2-one	624	C	1,3-pentadiene
1264	C	3-methyl-3-buten-1-ol	1490	C	2-furancarboxaldehyde			phenolic compounds
1332	C	2-heptanol	1516	C	2-furfuryl methyl sulfide	1075	C	phenol
1337	C	3-methyl-2-buten-1-ol	1536	C	2-acetylfuran			2-methoxyphenol
		pyrroles	1519	C	furfuryl formate			benzenic compounds
1149	B	1-methylpyrrole	1559	C	furfuryl acetate	1040	B	toluene
1194	C	1-ethyl-1 <i>H</i> -pyrrole	1605	C	5-methylfurfural	1273	C	ethenylbenzene
1542	C	1 <i>H</i> -pyrrole	1620	C	furfuryl propionate	1248	C	<i>p</i> -methylanisole*
1661	C	2-formyl-1-methylpyrrole	1626	C	2,2'-bis(furan)			acids
1647	C	2-acetyl-1-methylpyrrole	1636	C	2-furfurylfuran	1480	B	acetic acid

^a KI, Kovats index calculated for the HP-Wax capillary column. ^b The reliability of the identification proposal is indicated by the following: A, mass spectrum, retention time, and Kovats index agreed with standards; B, mass spectrum and Kovats index agreed with literature data; C, mass spectrum, compared with Wiley mass spectral databases. ^c Asterisks denote compounds not previously identified in other papers. Note: Work conditions: 90 °C and all equilibrium times tested.

However, the smell of coffee is not necessarily connected with the number of peaks in the chromatogram. The odor threshold is much more important than any detector response, and it should be studied with other techniques such as sniffing.

Large amounts of ketones, furans, and aldehydes were detected in roasted ground coffee. Among the ketones, 2-propanone, 2,3-butanedione, and 1-hydroxy-2-propanone were particularly high. Of all the compounds extracted, at 90 °C, 2-propanone represented between 15.50% at 45 min and 14.50% at 150 min. 2,3-Butanedione, responsible for the buttery note in roasted ground coffee (14, 25–27), constituted between 3.09% at 60 min and 2.48% at 100 min and 1-hydroxy-2-propanone between 1.92% at 30 min and 1.29% at 45 min (Table 3). These low molecular weight ketones are quite abundant in coffee and readily lost during storage (28).

The furans are particularly important in quantity and quality of coffee flavor (29) with 99 members identified. Holscher and Steinhart (14) identified 23 furans that were the major constituents of the headspace sample

(13.8%). Twenty-six furans were identified in this work representing, at 90 °C, between 21.58% of all the compounds extracted at 60 min and 19.97% at 150 min (Table 1).

Numerous furan compounds in coffee are often responsible for the burnt sugar, burnt, and caramel aromas (1, 13). Furfuryl alcohol, which appears to be the compound with the lowest vapor pressure in a headspace over brewed coffee (12), has been associated with bitter and burnt aromas (13, 28). However, Ho et al. (29) related that alkyl- and alkenyl-substituted furans, such as 3-methylfuran, do not present any sensory interest. Furfuryl alcohol and 3-methylfuran were the most abundant furans identified in our work representing, at 90 °C, between 7.89% of all the volatiles extracted at 30 min and 6.86% at 150 min for furfuryl alcohol and between 6.29% at 45 min and 5.47% at 80 min for 3-methylfuran (Table 3).

Among the aldehydes, which are considered to be some of the most volatile components in coffee (28), acetaldehyde, propanal, and 2-methylpropanal were predominantly present and were related by Semmelroch

Table 3. Percentages of Extraction of Some Volatile Compounds with Regard to the Total Area at 90 °C

compound	30 min	45 min	60 min	80 min	100 min	120 min	150 min
2-propanone	14.74 (1.53)	15.50(1.56)	15.43(1.57)	15.37(1.41)	14.80 (1.23)	14.70 (1.48)	14.50 (1.00)
2,3-butanedione	2.92 (0.30)	2.86 (0.33)	3.09 (0.39)	2.77 (0.10)	2.48 (0.27)	2.66 (0.08)	2.55 (0.31)
1-hydroxy-2-propanone	1.92 (0.32)	1.29 (0.56)	1.80 (0.08)	1.78 (0.34)	1.81 (0.26)	1.75 (0.24)	1.59 (0.34)
furfuryl alcohol	7.89 (2.02)	7.05 (0.78)	7.71 (0.87)	7.87 (1.42)	7.84 (0.65)	7.54 (0.65)	6.86 (1.05)
3-methylfuran	5.61 (0.76)	6.29 (1.00)	5.90 (1.23)	5.47 (1.01)	5.69 (0.98)	5.90 (0.36)	5.46 (0.46)
acetaldehyde	2.04 (0.31)	2.13 (0.32)	2.15 (0.26)	2.11 (0.34)	2.04 (0.29)	2.00 (0.31)	1.95 (0.24)
2-methylpropanal	4.03 (0.69)	4.36 (0.86)	4.32 (0.91)	4.18 (0.64)	4.20 (0.65)	4.25 (0.63)	4.13 (0.49)
propanal	2.30 (0.26)	2.40 (0.26)	2.49 (0.25)	2.44 (0.29)	2.40 (0.29)	2.35 (0.28)	2.31 (0.19)
ethanol	0.64 (0.26)	0.61 (0.18)	0.71 (0.29)	0.66 (0.25)	0.66 (0.26)	0.65 (0.26)	0.67 (0.28)
1-methylpyrrole	0.73 (0.21)	0.78 (0.17)	0.73 (0.22)	0.63 (0.24)	0.67 (0.22)	0.67 (0.12)	0.66 (0.12)
2-methylpyrazine	3.63 (0.30)	3.74 (0.55)	2.98 (0.66)	3.61 (0.84)	3.58 (0.13)	3.46 (0.46)	3.46 (0.58)
2-methoxyphenol	0.07 (0.01)	0.06 (0.01)	0.06 (0.01)	0.05 (0.01)	0.06 (0.01)	0.05 (0.01)	0.05 (0.01)

^a Numbers in parentheses are standard deviations.

and Grosch (25, 27) to be potent odorants of coffee powders and brews. Acetaldehyde constituted between 2.15% of all the extracted compounds at 60 min and 1.95% at 150 min, 2-methylpropanal between 4.36% at 45 min and 4.03% at 30 min, and propanal between 2.49% at 60 min and 2.30% at 30 min (Table 3).

Alcohols were present at relatively high concentrations in freshly roasted coffee, although they are readily lost by volatilization and oxidation. Ethanol was the most abundant alcohol detected in the ground roasted coffee studied, but it represented only between 0.71% at 60 min at 90 °C and 0.64% at 30 min (Table 3).

Four sulfur-containing compounds such as methanethiol, dimethyl sulfide, dimethyl disulfide, and carbon disulfide were detected in roasted ground coffee using headspace gas analysis. Sulfur compounds, which are known to be very O₂ sensitive (14), have very low threshold values and play an important role in the aroma (26). The most important one is methanethiol, which mainly corresponds to the decrease of aroma freshness (14). Due to the O₂ sensitivity of the sulfur-containing compounds, the quantity of this chemical class extracted decreased when the time of equilibration increased, from 0.52% at 30 min to 0.29% at 150 min (Table 1). All four of the sulfur-containing compounds were highly extracted when using 30 min as the equilibration time.

Leino et al. (13) reported that 1-methylpyrrole was the only volatile alkylpyrrole detected with the headspace technique. In this work, five other pyrroles were identified: 1-ethyl-1*H*-pyrrole, 1*H*-pyrrole, 2-formyl-1-methylpyrrole, 2-acetyl-1-methylpyrrole, and *N*-furfurylpyrrole. 1-Methylpyrrole was the most abundant pyrrole, representing between 0.78% at 45 min and 0.63% at 80 min (Table 3).

Flament (30) found 79 pyrazines in coffee, and Clarke (28) reported that 81 compounds containing a pyrazine ring have been detected. Twenty pyrazines have been detected by headspace gas analysis in this work. 2-Methylpyrazine was the most abundant one detected in our coffee, representing, at 90 °C, between 2.98% at 60 min and 3.74% at 45 min of all the compounds extracted (Table 3).

Pyrazines are abundant in coffee (13) and are usually associated with the generation of roasted and burnt flavor notes (29), although it may alter depending on the concentration and by synergistic/antagonistic effects among the compounds present (13). Many pyrazines are recognized as the volatiles contributing to roasted aromas of cooked foods (12, 21).

Two pyridines have been detected in roasted ground coffee: pyridine and 2-methylpyridine. Pyridine has

bitter and roasty notes, and 2-methylpyridine is astringent (26, 28). Pyridines have been found in only a relatively small number of foods that have been subjected to some heat treatment (31). The presence of pyridines is often associated with off-flavors. Pyridines are described as having green, bitter, astringent, and/or roasty notes.

One phenolic compound was detected in roasted ground coffee. This type of compound, usually present in coffee in low concentrations, has been related to burnt aroma and other aromas such as smoky, spicy, or clove-like and also imparts astringency (26, 28). 2-Methoxyphenol is the unique phenolic compound detected in our work between 0.05% at 80, 120, and 150 min and 0.07% at 30 min (Table 3).

Trace amounts of thiazoles, thiophenes, esters, oxazoles, lactones, alkanes, alkenes, benzenic compounds, and acids were also detected in roasted ground coffee.

In summary, at higher temperature of equilibration, greater extraction of the volatile compounds was obtained and no differences in the qualitative profiles were observed. When the time of equilibration was increased, the quantity of the volatile compounds extracted also increased, but in an irregular way depending on the chemical family considered. The time of equilibration for headspace analysis of roasted ground Arabica coffee should be selected depending on the chemical class or the compound that is being studied: short equilibration times for the analysis of sulfur compounds, aldehydes, alcohols, pyrroles, pyrazines, thiophenes, esters, and phenolic compounds and longer times for pyridines, ketones, acids, and furans.

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