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Changes in Headspace Volatile Concentrations of Coffee Brews Caused by the Roasting Process and the Brewing Procedure

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Headspace-solid-phase microextraction technique (HS-SPME) coupled with gas chromatography−mass spectrometry (GC-MS) and gas chromatography−olfactometry (GC-O) were used to characterize the aroma compounds of coffee brews from commercial conventional and torrefacto roasted coffee prepared by filter coffeemaker and espresso machine. A total of 47 volatile compounds were identified and quantified. Principal component analysis (PCA) was applied to differentiate coffee brew samples by volatile compounds. Conventional and torrefacto roasted coffee brews were separated successfully by principal component 1 (68.5% of variance), and filter and espresso ones were separated by principal component 2 (19.5% of variance). By GC olfactometry, a total of 34 aroma compounds have been perceived at least in half of the coffee extracts and among them 28 were identified, among which octanal was identified for the first time as a contributor to coffee brew aroma.

KEYWORDS: Coffee; HS-SPME; GC-MS; GC-O; torrefacto, espresso coffee; filter coffee

INTRODUCTION

One of the most contributory factors for the high acceptability of coffee by population is aroma that involves more than 800 volatile compounds. Its complex composition depends on the botanical variety of coffee, processing, grinding, and packaging and especially the roasting process and extraction method. Torrefacto is a roasting process in which sugar is added to robusta coffee. This roasting technique is used in several countries of southern Europe (in Spain it represents 83% of the consumption of coffee in hotel trade) and South America where some segments of the population prefer coffees with a dark brown, intense aroma and a strong taste with a tendency to bitterness. The influence of torrefacto roast in ground coffee aroma (*1*), in some coffee brew volatiles (*2*−*4*), and in the antioxidant activity of coffee (*5*, *6*) has been previously reported. The addition of sugar at the end of the torrefacto roasting process might intensify the development of Maillard reactions and, consequently, volatile formation. However, no research related to the aroma profile of coffee brews from commercial conventional and torrefacto roasted coffees has been completed so far.

Coffee aroma compounds have been widely studied (*7*, *8*). However, the influence of the extraction methods in coffee brew aroma has been focused on some volatile compounds in filter coffee (*8*−*10*) or in espresso coffee (*3*, *11*, *12*). No studies about espresso and filter coffee aroma from torrefacto and conventional commercial coffee samples have been reported so far. Espresso coffee was selected because it is the most common pressure method, and filter coffee was selected because it is the infusion method generally used in northern Europe and in the United States. Espresso coffee aroma has been widely studied (*11*, *12*).

Solid-phase microextraction (SPME) has been extensively applied to the study of coffee brew aroma as a simple, rapid, solvent-free, and inexpensive method (*4*, *13*−*15*). However, investigations on coffee brew aroma using SPME method have mainly dealt with selection of fibers or optimization of both extraction and desorption parameters. Roberts et al. (*15*) found that polydimethylsiloxane (PDMS)/divinylbenzene (DVB) coating had the highest overall sampling sensitivity, whereas carboxen (CAR)/PDMS was the most effective for small molecules and acids. Bicchi et al. (*14*) compared the method using different fiber coatings including DVB/CAR/PDMS. On the basis of the previous studies in coffee and other beverages, DVB/CAR/PDMS fiber was chosen because its three-component composition gives high recoveries for analytes with different structures and polarities (*14*, *15*). On the other hand, only one study in torrefacto blend coffee brew aroma using SPME had been reported (*4*).

Moreover, not all the volatiles in coffee are odorant, and their contribution to flavor is not usually directly related to their abundance (*8*, *9*, *16*). For the determination of those components that have a real contribution to the aroma, gas chromatography−olfactometry (GC-O) analysis has proved to be a powerful way of determining key aroma compounds in wine (*17*), fruit juices

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(*18*, *19*), and coffee (*9*, *20*). In this technique, the separated compounds at the effluent from a GC column are evaluated qualitatively one by one, by human assessors. From our point of view, an integrated approach involving the joint determination of the volatile compounds by gas chromatography−mass spectrometry (GC-MS) and GC-O will provide useful information about the most important active contributors to the aroma of different coffee brews.

Two aims were established for the present work. The first one was the characterization of the aromatic profile of coffee brew as affected by different roasting processes (torrefacto vs conventional) and by two extraction methods (filter coffeemaker vs espresso machine) by the combination of SPME coupled with GC-MS and principal component analysis (PCA) to determine the most important factors contributing to the aroma of coffee brew. The second aim was to identify the aroma impact compounds in the different coffee brews.

MATERIALS AND METHODS

Coffee Samples. Two commercial roasted coffee samples from the same brand were purchased in a local market: a conventional roasted coffee blend arabica/robusta (namely, as C) and a 100% torrefacto roasted coffee robusta variety (T) as whole beans that was ground, for 40 s, using a home grinder (model Moulinex 980 26-F). Espresso coffee brew was prepared from 7 g of ground roasted coffee for a volume of 40 mL using an espresso coffee machine (model Saeco Aroma, Italy). Filter coffee brew was prepared from 24 g of ground-roasted coffee for a volume of 400 mL using a filter coffeemaker (model KF 147 Aroma Select, Braun).

Reference Odorants. The following reference compounds were from the suppliers given in parentheses: 2,3-pentanedione, hexanal, pyridine, pyrazine, 2-methylpyrazine, 2,5-dimethylpyrazine, 2-furfuryl methylsulfide, 5-methylfurfural, and 2-acetylpyrrole (Aldrich, Saint Quentin Fallavier, France), 2-ethyl-3,5(6)-dimethylpyrazine (Acros organic, Noisy le Grand, France), and guaiacol (International Flavor and Fragance, Longvic, France).

Headspace Solid-Phase Microextraction (HS-SPME) Sampling. The manual holder and the SPME fiber Sableflex 2 cm-50/30 μm DVB/CAR/PDMS were purchased from Supelco Co. (Bellefonte, PA). The fiber was conditioned at 250 °C for 4 h in the GC injector. Before sampling, the fiber was reconditioned for 30 min in the GC injection port at 240 °C. Six milliliters of coffee brew, prepared immediately before, were introduced into a 10-mL vial, which was immediately sealed with a silicone rubber Teflon cap. An optimization of the experimental conditions was previously realized. Different equilibrium times (15, 20, and 30 min) and trapping times of volatile compounds (5, 10, 15, and 20 min) were tested. Thus, each vial was equilibrated for 20 min in a thermostatic bath at 60 °C (usual coffee brew consumption temperature). The SPME fiber was exposed to the brew headspace for 15 min.

Gas Chromatography Mass Spectrometry. The SPME coating containing the headspace volatile compounds was immediately inserted into the GC injection port equipped with a 0.75-mm i.d. liner (Supelco Co., Bellefonte, PA) and was thermally desorbed for 10 min at 250 °C in a gas chromatograph model 6890 (Hewlett-Packard, Palo Alto, CA). The fused silica capillary column DB-Wax (J&W Scientific, i.d. 0.32 mm, 30 m, film thickness = 0.5 μm) was used. Operating conditions were as follows: injection system, splitless time, 3 min; injection temperature, 240 °C; temperature program from 40 °C to 240 °C at 5 °C min^{-1} and then held constant for 10 min. Helium was used as carrier gas in constant flow mode (1.5 mL min^{-1}) with a linear velocity of 44 cm s^{-1}. Mass spectrometry was performed on a mass selective detector model 5973 (Agilent Technologies, Palo Alto, CA) operated in the electron impact mode (70 eV). The mass spectrometer scanned mass from *m*/*z* 29 to 350. Ion source temperature was set at 230 °C.

Identification of the Volatile Compounds. The identification of the volatile compounds was carried out by comparison of their mass spectra with those of the pure reference compounds and Wiley library and also by comparing their retention indexes with those of standard compounds and data from the literature **(Table 2)**. Linear retention indexes (RI) of the compounds were calculated using a series of alkanes (C10−C30) injected in the same chromatographic conditions.

Quantitative Measurements. The content of coffee aroma compounds identified was quantified by GC-MS. Areas of peaks were measured by calculation of the total ionic current (TIC). The relative percentage of each individual compound (x) was calculated from the total content of volatiles identified ($TIC_x/TIC_{sum} \times 100$).

Gas Chromatography−Olfactometry. The odor active compounds of coffee brews from different coffee samples and extracted by different extraction methods were analyzed by GC-O on a 6890 HP equipped with a flame ionization detector (FID, 250 °C) and a sniffing port. After sampling, described above, the SPME fiber was placed into the injection port of the GC equipped with a 0.75-mm i.d. liner (Supelco) for 10 min at 240 °C. Operating conditions were as follows: DB-Wax (J&W Scientific, i.d. 0.32 mm, 30 m, film thickness = 0.5 μm) from 40 °C to 200 °C at 5 °C min^{-1} and from 200 °C to 240 °C at 8 °C min^{-1} and then held constant for 5 min. Helium was used as carrier gas with a linear velocity of 44 cm s^{-1}. The GC effluent was split 1:1 between the FID and the sniffing port (240 °C). Humidified air was added in the sniffing port at 100 mL min^{-1}.

Odor Detection Frequency. GC-O frequency analysis was performed following the methodology described by Charles et al. (*21*) with some modifications. A panel of eight trained judges, seven women and one man, carried out the sniffing of the extracts in duplicate. Assessors were asked to smell the effluent of the column (35 min), and each judge carried out one session per day. For each odor stimulus, panelists recorded the detection time and gave a verbal description of each perceived odor. The detection frequency of odor having the same retention time and a similar description were calculated (sum of odor detections at this retention time: maximum = 16). Homemade software COCONUT (*22*) was used for data acquisition. Linear retention indexes (RI) of the compounds were calculated using a series of alkanes (C10−C30) injected in the same chromatographic conditions and were compared with available literature data.

Statistical Analysis. Each coffee brew sample was analyzed in triplicate. All results are shown as mean and standard deviation. The global effect of coffee roasting process and extraction method on the release of coffee volatile compounds was analyzed by a two-way analysis of variance (ANOVA). As interactions occur between the two effects, a Student's test was used to determine whether there were differences in the values of each compound between samples obtained with the same extraction method. Principal component analysis (PCA) was applied to the analytical data expressed in relative percentages (on the basis of the Pearson correlation matrix) to observe differences among coffee brew samples. All statistical analyses were performed using the SPSS v.14.0 software package. The analyses of GC-O data were performed using an integrated and computerized method based in Matlab V.7.2.0.232 (The Mathwork Inc.) and developed by Cabus et al. (*23*). This program has been previously successfully employed by Ballester (*24*).

RESULTS AND DISCUSSION

Volatile Compounds in Coffee Brews. In the HS-SPME analysis of volatile components present in espresso and filter coffees, a total of 47 compounds were identified and quantified including 3 aldehydes, 3 ketones, 13 furans, 8 pyrroles, 13 pyrazines, 1 pyridine, 5 phenolic compounds, and 1 indole (**Figure 1**). All samples studied presented similar profiles with the same volatile compounds. However, differences in total areas between coffee samples and between extraction methods were shown (**Figure 2**). In relation to coffee sample for both filter and espresso coffees, the conventional roasted coffee (C) gave higher total areas than the torrefacto one (47% higher in filter coffee and 44% higher in espresso coffee). In both coffee samples, chromatographic areas obtained for espresso coffee volatiles were higher than those obtained for filter coffee volatiles, 44% higher in conventional coffee samples and 40% higher in torrefacto coffee samples. The increase in total

Table 1. Two-Way ANOVA Results of Percentage of Coffee Volatile Compounds

	coffee roasting process effect		coffee extraction method effect		interaction effect	
	F	*p*	*F*	*p*	*F*	*p*
acetaldehyde	23.583	0.001	54.209	<0.001	0.393	0.548
2-methylfuran	20.942	0.002	75.133	<0.001	60.942	<0.001
2-methylbutanal	48.402	<0.001	962.939	<0.001	58.061	<0.001
2,5-dimethylfuran	0.181	0.682	26.050	0.001	20.583	0.002
2,3-pentanedione	28.009	0.001	140.083	<0.001	5.787	0.043
2-vinylfuran	65.951	<0.001	11.805	<0.001	56.195	<0.001
hexanal	340.485	<0.001	0.485	0.506	0.485	0.506
2,3-hexanedione	37.333	<0.001	1.714	0.227	12.190	0.008
0.081-methyl-1H-pyrrole	551.087	<0.001	73.058	<0.001	226.449	<0.001
pyridine	186.613	<0.001	20.17	0.193	39.792	<0.001
pyrazine	13.333	0.006	34.133	<0.001	10.800	0.011
furfurylmethylether	22.562	0.001	18.062	0.003	138.062	<0.001
2-methylpyrazine	970.252	<0.001	23.716	0.001	175.881	<0.001
2,5-dimethylpyrazine	740.985	<0.001	9.729	0.14	18.090	<0.001
2,6-dimethylpyrazine	739.203	<0.001	6.959	0.30	48.235	<0.001
2-ethylpyrazine	726.599	<0.001	24.605	0.001	78.790	<0.001
2,3-dimethylpyrazine	298.227	<0.001	10.227	0.013	24.045	0.001
2-ethyl-6-methylpyrazine	2094.754	<0.001	78.969	<0.001	88.754	<0.001
2-ethyl-5-methylpyrazine	1278.112	<0.001	40.668	<0.001	2.195	0.177
2-ethyl-3-methylpyrazine	228.844	<0.001	23.154	0.001	0.618	0.454
propylpyrazine	78.125	<0.001	45.125	<0.001	10.125	0.013
2,6-diethylpyrazine	239.521	<0.001	24.527	0.001	3.449	0.100
2-ethyl-3,5-dimethylpyrazine	953.473	<0.001	78.581	<0.001	8.300	0.020
furfural	5745.661	<0.001	0.441	0.525	161.439	<0.001
2-furfurylmethylsulfide	409.074	<0.001	66.852	<0.001	58.674	<0.001
2-methyl-3,5-diethylpyrazine	652.687	<0.001	0.521	0.491	20.021	0.002
2-acetylfuran	163.532	<0.001	33.884	<0.001	18.170	0.003
1*H*-pyrrole	274.578	<0.001	46.248	<0.001	16.963	0.003
furfuryl acetate	5912.592	<0.001	114.594	<0.001	20.630	0.002
5-methylfurfural	453.282	<0.001	44.156	<0.001	84.043	<0.001
2-furfuryl-propanoate	428.451	<0.001	32.856	<0.001	0.913	0.367
2-furfurylfuran	1210.182	<0.001	100.699	<0.001	26.881	0.001
2-formyl-1-methylpyrrole	511.011	<0.001	8.430	0.020	9.677	0.014
furanmethanol	539.089	<0.001	30.880	0.001	15.831	0.004
2-methyl-1*H*-pyrrole	338.000	<0.001	8.000	0.22	112.500	<0.001
B-damascenone	1624.500	<0.001	24.500	0.001	40.500	<0.001
N-furfurylpyrrole	144.643	<0.001	0.071	0.796	1.446	0.263
2-methoxyphenol	146.350	<0.001	5.054	0.55	0.413	0.539
2-acetylpyrrole	373.364	<0.001	20.485	0.002	23.758	0.001
difurfuryl ether	1780.840	<0.001	1.000	0.347	0.040	0.846
1*H*-pyrrole-2-carboxaldehyde	25.773	0.001	9.278	0.016	1.485	0.258
4-ethyl-2-methoxyphenol	1428.376	<0.001	287.109	<0.001	253.176	<0.001
4-methylphenol	87.111	<0.001	16.000	0.004	11.111	0.010
4-ethylphenol	108.000	<0.001	225.333	<0.001	33.333	<0.001
2-methoxy-4-vinylphenol	19.049	0.002	150.867	<0.001	102.745	<0.001
1-furfuryl-2-formylpyrrole	22.000	0.002	52.545	<0.001	22.000	0.002
indole	14.286	0.005	57.143	<0.001	28.000	0.001
total aldehydes	50.795	<0.001	637.471	<0.001	18.374	0.003
total ketones	41.546	<0.001	100.998	<0.001	13.419	0.006
total furans	3015.786	<0.001	431.988	<0.001	1.381	0.274
total pyrroles	0.619	0.454	1.027	0.340	23.137	0.001
total pyrazines	4396.661	<0.001	167.843	<0.001	42.040	<0.001
total pyridines	187.709	<0.001	1.956	0.200	40.128	<0.001
total phenolic compounds	543.597	<0.001	259.574	<0.001	169.005	<0.001
total indoles	18.289	0.003	67.191	<0.001	31.772	<0.001

chromatographic areas obtained for espresso coffee brew volatiles could be explained by the pressure of the espresso coffee machine; filter coffee is an infusion method, and the espresso machine works at a pressure of 15 bar. With respect to the coffee roasting process and according to Rocha et al. (*4*), it is possible to infer that conventional roasted coffees (C) have a more intense aroma than torrefacto ones (T) but a similar relative composition. The decrease in volatile compounds of the torrefacto coffee brews could be partly explained by the substitution of part of the coffee by sugar (15%) in the torrefacto roasting process. Furthermore, it is well-known that a lower roasting degree in torrefacto coffee is applied by some companies to avoid an excess of burnt caramel which could explain that less volatile compounds are formed.

A two-way analysis of variance was performed to establish the impact of the coffee roasting process and the extraction method on the volatile coffee compounds (**Table 1**). In most cases, significant interaction between the coffee roasting process and the coffee extraction method has been observed. Those volatile compounds that have no significant interaction effect were significantly affected by both factors, except in hexanal, *N*-furfurylpyrrole, 2-methoxyphenol, and difurfurylether cases which were not significantly affected by the coffee extraction method. Moreover, *F* values corresponding to the coffee roasting process were higher than the *F* values of the coffee extraction method showing greater importance of the effect of the coffee roasting process than that of the coffee extraction method. Thus, the effect of the roasting process was deeper studied. **Table 2**

Table 2. Relative Percentage of Filter and Espresso Coffee Volatile Compounds[a]

				filter			espresso		
peak[b]	retention index[c]	identification[d]	compound name	C	LS[e]	T	C	LS[e]	T
1	645[f]	B	acetaldehyde	0.55 ± 0.05	*	0.67 ± 0.02	0.72 ± 0.02	*	0.81 ± 0.05
2	832[f]	B	2-methylfuran	1.15 ± 0.05	ns	1.25 ± 0.06	1.66 ± 0.05	**	1.28 ± 0.04
3	880[f]	B	2-methylbutanal	1.33 ± 0.03	**	1.11 ± 0.02	1.69 ± 0.02	ns	1.70 ± 0.03
4	930[f]	B	2,5-dimethylfuran	0.59 ± 0.03	*	0.49 ± 0.05	0.59 ± 0.05	*	0.71 ± 0.02
5	1058[f]	A	2,3-pentanedione	0.70 ± 0.04	**	0.83 ± 0.03	0.54 ± 0.02	ns	0.59 ± 0.04
6	1075[f]	B	2-vinylfuran	0.32 ± 0.02	ns	0.31 ± 0.02	0.44 ± 0.01	**	0.27 ± 0.03
7	1084[f]	A	hexanal	0.15 ± 0.01	**	0.32 ± 0.02	0.14 ± 0.01	**	0.32 ± 0.02
8	1138	B	2,3-hexanedione	0.21 ± 0.01	ns	0.19 ± 0.02	0.23 ± 0.02	**	0.16 ± 0.02
9	1149	B	1-methyl-1*H*-pyrrole	0.39 ± 0.00	**	0.92 ± 0.02	0.71 ± 0.02	**	0.83 ± 0.04
10	1196	A	pyridine	3.24 ± 0.07	**	4.84 ± 0.26	3.85 ± 0.08	**	4.44 ± 0.01
11	1223	A	pyrazine	0.28 ± 0.01	**	0.34 ± 0.02	0.25 ± 0.01	ns	0.26 ± 0.02
12	1247	B	furfurylmethylether	0.30 ± 0.02	*	0.34 ± 0.02	0.40 ± 0.01	**	0.29 ± 0.01
13	1276	A	2-methylpyrazine	3.52 ± 0.11	**	5.94 ± 0.09	3.98 ± 0.10	**	4.96 ± 0.08
14	1333	A	2,5-dimethylpyrazine	2.04 ± 0.02	**	2.78 ± 0.03	2.06 ± 0.05	**	2.60 ± 0.06
15	1339	B	2,6-dimethylpyrazine	1.98 ± 0.03	**	3.03 ± 0.07	2.10 ± 0.08	**	2.74 ± 0.02
16	1344	B	2-ethylpyrazine	1.85 ± 0.08	**	3.68 ± 0.09	2.04 ± 0.13	**	2.97 ± 0.04
17	1357	B	2,3-dimethylpyrazine	0.39 ± 0.01	**	0.57 ± 0.02	0.41 ± 0.01	**	0.51 ± 0.01
18	1395	B	2-ethyl-6-methy lpyrazine	2.84 ± 0.03	**	3.75 ± 0.03	2.38 ± 0.05	**	3.76 ± 0.06
19	1402	B	2-ethyl-5-methylpyrazine	2.02 ± 0.04	**	2.90 ± 0.05	1.81 ± 0.06	**	2.78 ± 0.03
20	1414	B	2-ethyl-3-methylpyrazine	1.87 ± 0.04	**	2.62 ± 0.15	1.57 ± 0.01	**	2.41 ± 0.10
21	1428	B	propylpyrazine	0.20 ± 0.00	**	0.25 ± 0.01	0.18 ± 0.01	*	0.21 ± 0.01
22	1444	B	2,6-diethylpyrazine	0.95 ± 0.04	**	1.24 ± 0.04	0.80 ± 0.03	**	1.18 ± 0.04
23	1455	A	2-ethyl-3,5-dimethylpyrazine	2.79 ± 0.07	**	4.05 ± 0.11	2.26 ± 0.04	**	3.79 ± 0.08
24	1469	B	furfural	11.14 ± 0.19	**	15.73 ± 0.13	10.15 ± 0.09	**	16.60 ± 0.07
25	1493	A	2-furfurylmethylsulfide	0.71 ± 0.02	**	0.47 ± 0.02	1.01 ± 0.05	**	0.48 ± 0.04
26	1503	B	2-methyl-3,5-diethylpyrazine	1.36 ± 0.01	**	1.84 ± 0.03	1.24 ± 0.06	**	1.93 ± 0.04
27	1510	B	2-acetylfuran	2.38 ± 0.06	**	2.07 ± 0.04	2.74 ± 0.10	**	2.13 ± 0.04
28	1521	B	1*H*-pyrrole	0.40 ± 0.04	**	0.76 ± 0.04	0.35 ± 0.01	**	0.57 ± 0.02
29	1542	B	furfuryl acetate	11.58 ± 0.22	**	4.81 ± 0.05	12.99 ± 0.21	**	5.39 ± 0.10
30	1578	A	5-methylfurfural	11.38 ± 0.18	**	8.68 ± 0.06	11.14 ± 0.13	**	10.09 ± 0.20
31	1602	B	2-furfuryl-propanoate	1.39 ± 0.08	**	0.77 ± 0.03	1.60 ± 0.09	**	0.92 ± 0.01
32	1615	B	2-furfurylfuran	1.37 ± 0.03	**	0.78 ± 0.01	1.67 ± 0.06	**	0.87 ± 0.02
33	1626	B	2-formyl-1-methylpyrrole	1.66 ± 0.02	**	2.07 ± 0.04	1.66 ± 0.03	**	1.97 ± 0.03
34	1667	B	furanmethanol	11.02 ± 0.10	**	9.11 ± 0.10	11.95 ± 0.28	**	9.27 ± 0.13
35	1796	B	2-methyl-1*H*-pyrrole	0.28 ± 0.01	**	0.14 ± 0.01	0.24 ± 0.01	**	0.20 ± 0.01
36	1828	B	B-damascenone	0.09 ± 0.01	**	0.19 ± 0.01	0.09 ± 0.00	**	0.17 ± 0.00
37	1833	B	N-furfurylpyrrole	2.54 ± 0.09	**	1.89 ± 0.03	2.50 ± 0.15	**	1.96 ± 0.04
38	1864	A	2-methoxyphenol	1.92 ± 0.04	**	1.57 ± 0.09	1.87 ± 0.05	**	1.47 ± 0.03
39	1975	A	2-acetylpyrrole	0.89 ± 0.04	**	0.61 ± 0.02	1.07 ± 0.04	**	0.61 ± 0.03
40	1986	B	difurfuryl ether	0.50 ± 0.02	**	0.16 ± 0.01	0.49 ± 0.01	**	0.14 ± 0.01
41	2028	B	1*H*-pyrrole-2-carboxaldehyde	0.76 ± 0.02	ns	0.83 ± 0.04	0.79 ± 0.03	**	0.90 ± 0.02
42	2032	B	4-ethyl-2-methoxyphenol	4.05 ± 0.16	**	1.27 ± 0.00	2.34 ± 0.06	**	1.22 ± 0.01
43	2090	B	4-methylphenol	0.19 ± 0.01	**	0.13 ± 0.01	0.16 ± 0.01	*	0.13 ± 0.01
44	2174	B	4-ethylphenol	0.13 ± 0.01	*	0.12 ± 0.01	0.10 ± 0.00	**	0.05 ± 0.01
45	2199	B	2-methoxy-4-vinylphenol	4.05 ± 0.17	**	3.03 ± 0.08	2.48 ± 0.10	**	2.88 ± 0.10
46	2254	B	1-furfuryl-2-formylpyrrole	0.39 ± 0.02	ns	0.39 ± 0.01	0.30 ± 0.03	**	0.37 ± 0.01
47	2499	B	indole	0.19 ± 0.01	**	0.15 ± 0.00	0.13 ± 0.01	ns	0.14 ± 0.01
			total aldehydes	2.03 ± 0.02	ns	2.10 ± 0.02	2.54 ± 0.01	**	2.83 ± 0.03
			total ketones	1.00 ± 0.02	**	1.22 ± 0.02	0.86 ± 0.01	*	0.92 ± 0.02
			total furans	53.82 ± 0.08	**	44.96 ± 0.05	56.97 ± 0.09	**	48.43 ± 0.06
			total pyrroles	7.30 ± 0.03	*	7.62 ± 0.03	7.62 ± 0.04	ns	7.41 ± 0.03
			total pyrazines	22.08 ± 0.09	**	33.00 ± 0.06	21.08 ± 0.0	**	30.08 ± 0.05
			total pyridines	3.24 ± 0.07	**	4.84 ± 0.26	3.85 ± 0.08	**	4.44 ± 0.01
			total phenolic compounds	10.34 ± 0.08	**	6.11 ± 0.04	6.94 ± 0.04	**	5.75 ± 0.03
			total indoles	0.19 ± 0.01	**	0.15 ± 0.00	0.13 ± 0.01	ns	0.14 ± 0.01

[a] All values are shown as means ± standard deviations ($n = 3$). [b] Compounds corresponding to chromatographic peaks in **Figure 1**. [c] Retention index determined on DB-Wax column. [d] Identification proposal is indicated by the following: A, mass spectrum agreed with standards injected in the same conditions; B, tentative identification by comparing mass spectrum with Wiley mass spectral database and retention indexes with literature data. [e] Level of significance for the differences between different coffee samples in each extraction method; ns, not significant ($p > 0.05$); * $p \leq 0.05$; ** $p \leq 0.01$. [f] From literature.

shows the relative percentage of 47 compounds identified in the four coffee brews. The comparative study between the aromatic profile in the conventional and the torrefacto coffee showed differences among the relative percentages for the chemical class. Relative percentages of aldehydes, ketones, pyrazines, and pyridines were higher in both torrefacto coffee brews than in conventional ones. These results are in agreement with Sanz et al. (*1*) who reported higher quantities of aldehydes and ketones identified in a torrefacto coffee sample than in a conventional one. Higher pyrazine and pyridine content was observed in torrefacto coffee brews than in conventional ones. In the roasting process, Maillard reactions are produced between reducing carbohydrates and proteins, are naturally present in green coffee, and are responsible for the development of many heterocyclic compounds including pyrazines, pyridines, and pyrroles. As suggested by López-Galilea et al. (*6*) and in agreement with other authors (*25*, *26*), addition of sugar in the roasting process might have a great effect on the rate of Maillard reactions and, consequently, in the formation of Maillard reaction products (MRPs). Among the pyrazines, 2-ethylpyrazine

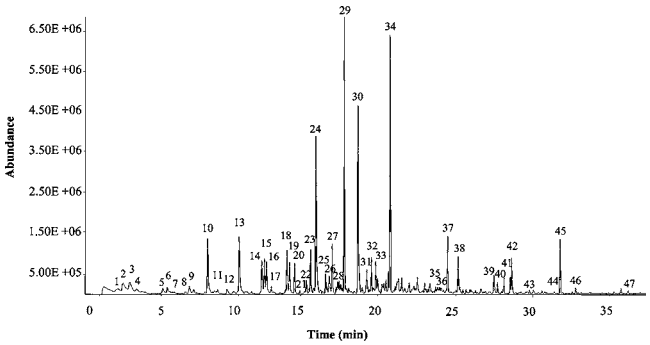

Figure 1. HS-SPME-GC-MS chromatogram of a coffee brew. For peak identification, see **Table 2**.

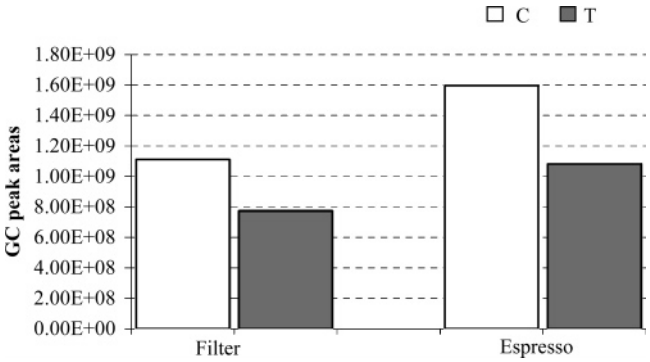

Figure 2. Gas chromatographic peak total areas of volatile compounds of coffee brews.

(**16**, identification corresponding to **Table 2**), 2-ethyl-6-methylpyrazine (**18**), and 2-ethyl-3,5-dimethylpyrazine (**23**), which have been considered as key odorants in coffee, are strongly incremented by the torrefacto roasting process. The relative percentages of furans and phenolic compounds for both filter and espresso coffees were significantly higher in conventional coffee brews than in torrefacto ones. Shibamoto (*27*) stated that the development of sugar caramelization and carbohydrate degradation is enhanced by sugar addition in the torrefacto roasting process, and thus a higher relative percentage of furans in torrefacto coffee brews would be expected. Furfural (**24**), furfuryl acetate (**29**), 5-methylfurfural (**30**), and furanmethanol (**34**) showed generally relative percentages higher than 10% being the most presented compounds in coffee brews. As was observed by other authors (*1*, *4*), while furfuryl acetate (**29**) and 5-methylfurfural (**30**) percentages were higher in conventional coffee brews than in torrefacto ones, furfural (**24**) presented superior values in torrefacto coffee brews than in conventional ones. However and contrarily with these previous works, furanmethanol (**34**) values were significantly higher in conventional coffee brews than in torrefacto ones.

Principal components analysis (PCA) was used to study the main sources of variability between the different coffee brews. **Figure 3** shows bidimensional representation of PC1 and PC2 scores for all the variables and coffee brews. The first two principal components (PCs) explained 68.5 and 19.5% of the total variance, respectively. As can be seen, torrefacto coffee brews are placed on the positive values of PC1, while the conventional coffee brews are found on the negative half graphic. The aroma compounds that determine the scores on PC1 are mainly compounds that are highly produced in Maillard reactions and for the positive area include pyrazines, pyridines, and some pyrroles such as 1H-pyrrole (**28**), 2-formyl-1-methylpyrrole (**33**), and 1H-pyrrole-2-carboxaldehyde (**41**) and for the negative area include furans, phenolic compounds, and pyrroles such as

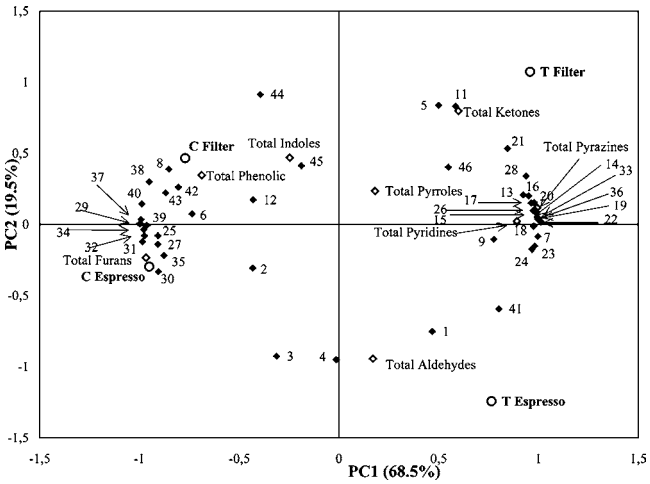

Figure 3. Principal component analysis of coffee brews. For compound identification, see **Table 2**.

2-methyl-1H-pyrrole (**35**), *N*-furfurylpyrrole (**37**), and 2-acetylpyrrole (**39**). Meanwhile, PC1 helps in separating torrefacto from conventional coffee brews, and PC2 discriminates coffee samples according to the extraction method used. Coffee brews from filter coffeemaker are placed on the top of the graphic whereas espresso coffee ones are placed on the bottom. PC2 is characterized by ketones and aldehydes in positive and negative side, respectively. Differences between extraction methods are more important in torrefacto coffee brews than in conventional ones because of the highest differences existing among aldehyde and ketone content. PCA results showed that HS-SPME-GC-MS volatile profile analysis of coffee brews prepared from commercial conventional and torrefacto roasted coffee and extracted by filter coffeemaker and by espresso machine was principally determined by the coffee roasting process.

GC-O. Among the 100 odors detected by the panelists, 34 odors have a frequency of detection of at least 8 in one of the coffee extracts. These 34 odorants, their descriptors associated, and the frequency of detection are shown in **Table 3**. The odor descriptions varied from pleasant notes such as flowery, fruity, chocolate-like, and caramel-like to unpleasant notes such as cheesy, sweaty, roasty, or musty. Olfactometric analyses (**Table 3**) allow the detection of components that were not detected by GC-MS (**Table 2**). Some of the intense olfactory responses were found in regions with low FID signals. So, tentative identification by using the results of mass spectrometry, the retention index, as well as the aroma description has been carried out. On the other hand, some compounds present in a high amount such as furfural (**24**), furfuryl acetate (**29**), 5-methylfurfural (**30**), or furanmethanol (**34**) are not selected after GC-O; they do not have a high odorant impact. Four classes of compounds seem to have a high impact for aroma coffee brew: pyrazines, furans, aldehydes, and ketones. Eight pyrazines are mainly responsible for roasty, earthy, musty, and woody notes with the exception of 2-ethyl-6-methylpyrazine that was associated to flowery and fruity notes as already mentioned by other authors (*28*). Among them, 2-ethyl-3,5-dimethylpyrazine (**23**), which was smelled in more than 90% of the coffee extracts, has already been identified as a key odorant in coffee brew (*16*). 2,6-Diethylpyrazine (**22**) with pyrazine-like and potato-like notes also has a high frequency of detection but has never been described as a coffee odorant compound. In **Table 2**, significant differences have been observed on the relative percentages of both compounds between torrefacto and conventional coffee brews. As these two pyrazines are smelled by all the panelists, it is not possible to see

Table 3. Descriptor of the Volatile Components Detected by GC-O and Identified by GC-MS in Filter and Espresso Coffee Brews

					frequency of detection			
					filter		espresso	
peak[a]	retention index[b]	identification[c]	compound name	odor quality[d]	C	T	C	T
NQ[e]	839[f]	B	butanal	chocolate, caramel	4	7	8	9
3	880[f]	B	2-methylbutanal	chocolate-like, fruity	12	12	12	8
NQ[e]	1020[f]	B	2,3-butanedione	buttery, fruity, caramel-like	14	13	12	11
5	1058[f]	A	2,3-pentanedione	buttery, caramel-like	12	10	12	5
12	1247	B	furfurylmethylether	herbal, potato-like	9	4	10	7
NQ[e]	1256		NPI[g]	herbal, musty	5	9	1	8
NQ[e]	1269	B	3(2H)-furanone, dihydro-2-methyl	dusty, musty	8	3	3	8
NQ[e]	1293	B	octanal	orangelike	14	10	14	5
NQ[e]	1303	B	1-octen-3-one	mushroomlike	16	16	14	15
NQ[e]	1310		NPI[g]	earthy, woody	9	9	3	6
NQ[e]	1390	B	dimethyltrisulfide	putrid, unpleasant	9	10	16	9
18	1395	B	2-ethyl-6-methylpyrazine	flowery, fruity	11	8	10	10
NQ[e]	1410	B	5-ethyl-2-methylthiazole	rubberlike	10	7	8	6
20	1414	B	2-ethyl-3-methylpyrazine	roasty, peanutlike	13	8	12	10
21	1428	B	propylpyrazine	herbal	8	0	0	0
22	1444	B	2,6-diethylpyrazine	pyrazine, potato-like	14	16	14	14
23	1455	A	2-ethyl-3,5-dimethyl pyrazine	potato-like, earthy,	15	15	14	15
NQ[e]	1471	B	pyrazine?	pyrazine, unpleasant	9	5	6	5
25	1493	A	2-furfurylmethylsulfide	leatherlike	7	7	8	11
NQ[e]	1496		NPI[g]	acrid, rubberlike	9	4	4	0
26	1503	B	2-methyl-3,5-diethylpyrazine	roasty	2	5	9	0
27	1510	B	2-acetylfuran	roasty, tobacco-like	3	1	9	7
NQ[e]	1536	B	pyrazine?	green-pea-like, herbal	16	12	15	10
NQ[e]	1547	B	2,3-diethyl-5,6-dimethylpyrazine	roasty, cardboardlike	7	7	8	6
31	1602	B	2-furfuryl propanoate	flowery, fruity	7	6	6	11
NQ[e]	1636	B	2-methyl-3-trans-propenylpyrazine	roasty	15	9	13	12
NQ[e]	1660	B	1-(1H-pyrrol-2-yl)1-ethanone	roselike	14	11	13	8
NQ[e]	1679	B	2-methoxyformanilide	sweaty, cheeselike	8	11	6	12
NQ[e]	1687	B	2-/3-methylbutanoic acid	sweaty, acidlike	10	10	11	11
NQ[e]	1732	B	2-/4-methylanisole	aniselike	9	6	6	7
36	1828	B	*B*-damascenone	fruity	7	8	3	7
38	1864	A	2-methoxyphenol	phenolic, burnt	2	4	8	5
NQ[e]	1876		NPI[g]	coffee, pharmaceutical	9	2	5	5
NQ[e]	1885	B	1-(5-methylfurfuryl)-pyrrole	pharmaceutical, roasty	6	6	3	8

[a] Compounds corresponding to chromatographic peaks in **Figure 1**. [b] Retention index determined on DB-Wax column. [c] Identification proposal is indicated by the following: A, mass spectrum agreed with standards; B, tentative identification by comparing mass spectrum with Wiley mass spectral database and retention indexes with literature data or according to aroma description. [d] More cited odor quality in GC-O analysis. [e] NQ, not quantified in GC-MS. [f] From literature. [g] NPI, not positively identified.

differences by the frequency of detection (*29*). Odors detected at RI 1471_{DBWAX} and RI 1536_{DBWAX} were, respectively, pyrazine-like and green pealike. It was not possible to precisely identify the corresponding compound because of their low amount; however, mass fragment allowed us to suppose that they could belong to the pyrazine class. The four furans smelled (**12**, **25**, **27**, **31**) as herbal-like, leatherlike, or fruity and have been identified and quantified by GC-MS. These compounds are generally detected with a higher frequency in espresso coffee brews than in filter ones which is in agreement with their relative percentages **(Table 2)**. Nevertheless, no clear differences between roasting processes have been detected by GC-olfactometry.

Ketones are described with buttery, caramel-like, musty, mushroomlike, or fruity notes. 2,3-Butanedione and 2,3-pentanedione (**5**) are slightly more perceived in conventional coffee brews than in torrefacto ones. The mushroom aroma description at RI 1303_{DBWAX} was attributed to the presence of 1-octen-3-one only after looking for specific MS ions (*m*/*z*: 55, 70, 27, 43) because this compound was present in a very low amount. Because of its low olfactory detection threshold, 0.005 ppb in water (*30*), it is recognized by all the panelists. Moreover, this compound was previously found in coffee brews (*9*, *16*). Two aldehydes are responsible for the chocolate-like note, butanal and the Strecker aldehyde 2-methylbutanal. At RI 1293_{DBWAX}, a strong orangelike odor was detected, but the compound eluted was 4-methyl thiazole which is not an orangelike odorant. As the odor description and RI were similar to that of octanal (*18*), a search by specific ions (*m*/*z*: 41, 43, 57) allowed us to find octanal coeluted with 4-methyl thiazole which has a low odor threshold of 0.7 ppb in water (*30*). Among the other odors detected, dimethyltrisulfide, coeluted with 3-ethylpyridine, has been tentatively identified by specific ions (*m*/*z*: 126, 45, 79). The two compounds have similar odor descriptors (unpleasant and putrid notes) but have different perception thresholds in water, 2000 ppb for the ethylpyridine and 0.005 ppb (*30*) for the dimethyltrisulfide; thus, this difference could point out dimethyltrisulfide as responsible for the odor. 5-Ethyl-2-methylthiazole with a rubberlike note is present in a very low amount. The rose odor at RI 1660_{DBWAX} was associated with 1-(1H-pyrrol-2-yl)1-ethanone, but this compound has never been associated with this odor in coffee brews. Sweaty, cheeselike, and acidlike notes were associated with 2-methoxyformanilide and 2-/3-methylbutanoic acid which is in agreement with other works (*16*). 2-Methoxyphenol (guaiacol) (**38**) has been largely considered as a key odorant in coffee (*9*, *16*). However, in the present study, its frequency of detection is lower in filter coffee brews than in espresso ones, and it was smelled by at least half of the panelists only in conventional espresso coffee brew. One undefined compound that appears as a well-determined peak (RI 1876_{DBWAX}) with the following mass fragmentation (*m*/*z*) 109, 152, 53, 43, and 95 was described as coffeelike. Three other compounds with RI 1256_{DBWAX} and herbal-like, musty notes; RI 1310_{DBWAX} with earthy, woody notes; and RI 1496_{DBWAX} with acrid, rubberlike notes remain unidentified.

In conclusion, using HS-SPME-GC-MS with a DVB/CAR/PDMS fiber, we were able to quantify 47 compounds in coffee brews belonging to different chemical classes. Among these compounds, pyrazines, pyridines, and pyrroles are present in a higher amount in torrefacto coffee brews than in conventional ones. Significant differences were also observed by changing the extraction method. These differences are higher for torrefacto coffee brew where ketones (with buttery and fruity notes) are present in higher amounts using filter coffeemaker, whereas aldehydes (with chocolate-like odor) are present in higher amount using espresso coffee machine. These differences in the composition may induce differences in aroma perception. Using GC-olfactometry, we were able to identify 34 compounds of high odor impact. Using frequency of detection method, it was not possible to show significant differences among the coffee extracts. However, this method allowed us to identify new odorant compounds in brew coffee, for example, the octanal responsible for the orange note is more intense in conventional coffee brews.

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