HS-SPME/GC/MS Profiles of Convectively and Microwave Roasted Ivory Coast Robusta Coffee Brews

Grażyna BUDRYN[1], Ewa NEBESNY[1], Józef KULA[2], Teresa MAJDA[2] and Wiesława KRYSIAK[1]

[1]Institute of Chemical Technology of Food and [2]Institute of Fundamentals of Food Chemistry, Faculty of Biotechnology and Food Science, Technical University of Lodz, Lodz, Poland

Abstract

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Robusta coffee beans were convectively, microwave, and convectively-microwave heated at 230°C, 700 W, and 230°C/700 W (coupled heating), respectively, over periods of time ensuring the optimum sensory properties of the brews. HS-SPME/GC/MS analysis of the emissions from brews of the roasted coffee beans revealed 119 compounds. The highest total content of volatile substances was found in the brews prepared from convectively-microwave roasted coffee beans but the microwave roasting resulted in the most acceptable sensory properties of the brew aroma, presumably because of the lowest concentrations of the burnt note imparting compounds.

Keywords: coffee brew; HS-SPME/GC/MS; roasting, microwaves; volatile compounds

The characteristic, rich and pleasant aroma of coffee brews is a result of complex processes leading from green coffee beans to the cup of coffee. One of the principal technological processes is roasting that gives rise to the formation of the characteristic flavour and taste of coffee brews (Yeretzian *et al*. 2002). The aroma of roasted coffee depends on the variety of coffee, agricultural factors, post-harvest treatment, and the conditions of storage and roasting (Hashim & Chaveron 1996; Semmelroch & Grosch 1996; Sanz *et al*. 2002; Mondello *et al*. 2005). The flavour of coffee brews is different from the aroma of roasted coffee beans. According to Mayer *et al*. (2000), this difference is the result of different polarities of the volatile compounds. The aroma of brews is more caramel-like, buttery and spicy (Grosch 1998). The polar substances are easily extractable but their concentrations in the headspace can be relatively low due to some chemical reactions.

The analysis of coffee brews aroma is complex and differs from the analysis of coffee beans emissions. The results of the headspace composition analysis depend on the method of the brew preparation, the analytical methods applied, and the conditions comprising among others the temperature and time of equilibration. Some researchers used static methods of headspace analysis (Bicchi *et al*. 1993). The alternative is the solid-phase microextraction (SPME) of the volatile substances using the absorptive material that plays the crucial role in their binding (Sanz *et al*. 2001; Bicchi *et al*. 2002). HS-SPME profiles usually reveal fewer volatile compounds than the profiles obtained by some other methods, e.g. supercritical fluid extraction, but they characterise the aroma of coffee more accurately. Tests on the application of SPME for the analysis of brews were also conducted (Bicchi *et al*. 1997). Semmelroch and Grosch (1996) and Maeztu *et a*l. (2001) found correlations between the intensity of sensory

determinants, overall acceptance of brews, and headspace composition.

More than 1000 volatile compounds have been identified in the headspace of roasted coffee. The qantification and estimation of odour activity values pointed out those with the strongest impact on the typical coffee aroma and, in turn, resulted in the formulation of the model mixture of the compounds imitating the flavour of coffee brews. The template of the latter mixture was the aroma of Arabica coffee, which is more pleasant and acceptable by consumers than Robusta coffee flavour. It is one of the reasons for the higher price of Arabica coffee. Commercial coffee blends contain different proportions of Robusta and Arabica as a compromise between the taste and the price (Sanz *et al*. 2002). An improvement on the sensory properties of Robusta coffee brews, mainly through modifications of roasting and brewing conditions, has recently been the subject of extensive studies. The present study was aimed at the characterisation of the differences in the headspace composition of brews derived from convectively, microwave, and convectively-microwave roasted Robusta coffee samples.

MATERIALS AND METHODS

Material. Green beans of *Coffea canephora* (Robusta), cultivar Kouilou, type Superieur, purchased from Ivory Coast and derived from coffee cherries by a dry method, were delivered by Agros S.A. (Poland). The aroma of Robusta brews was determined for triplicate samples of coffee beans that had been roasted under 3 variants of conditions described in the Methods.

Methods

Roasting. Green coffee beans were roasted in a convective-microwave oven Gourmet 8601 (Bosch GmbH, Stuttgart, Germany), providing convective heating at temperatures of up to 270°C and microwave heating with the power regulation up to 700 W. The convective and microwave heating could be also conducted simultaneously in this roaster. The samples of green coffee beans (100 g) with an initial humidity of 7.5% were either convectively heated at 230°C (CR) or microwaved at 700 W (MR), or roasted using the coupled convective and microwave heating (CMR). Each sample of the beans was spread on a tray to form a monolayer with the initial thickness of 10 mm. Roasting was completed when the roasted coffee beans ensured the optimal sensory attributes of brews. Eight sensory assessors selected from students and laboratory staff were trained to define and recognise the individual taste and aroma determinants of coffee brews according to the known flavour descriptive language. The brews were assessed by QDA (the quantitative descriptive analysis) to determine their overall sensory characteristics based on the International Coffee Organization standards, which included four determinants of taste (sweet, sour, astringent, bitter), five of aroma (described below), and a single one of texture (body). The following substances or products were used as standards of aromas: burnt sugar (burnt), stale black tea (grassy), mixture of almonds, hazelnuts, peanuts, and walnuts 2:2:1:2 (nutty), roasted peanuts (roasted) and roasted Arabica coffee from a local market (the overall aroma). The batches of roasted coffee beans were ground in a laboratory mill WZ-1 (ZBPP, Bydgoszcz, Poland), sieved through 600 and 425 μm mesh, and the isolated middle fraction was extracted according to the standard ISO 6668:2000 – Green coffee. Preparation of samples for use in sensory analysis (7 g of ground coffee was gently mixed for 5 min with 100 ml of boiling water and this extract was cooled to 55°C prior to further analysis). The same brews were subjected to GC analysis. The intensities of taste and aroma sensations were evaluated from 1 (detectable) to 10 (very intensive). A significance index was ascribed to each sensory determinant. The acceptance of the brew was a sum of sensory attribute scores multiplied by their significance indices. The maximum value of acceptance was 25. The temperature of beans was measured on the surface of coffee beans immediately on the completion of roasting (Yoshida & Kajimoto 1994). The colour of roasted coffee beans was determined by CIE $L^*a^*b^*$ method using a spectrophotometer Specord M-40 (Carl Zeiss Jena, Germany).

Headspace aroma isolation. The extraction of volatiles was carried out using SPME apparatus and 2 cm long DVB/Cartoxem/PDMS fibre (Supelco, Bellefonte, USA). The samples of coffee brews (20 ml) were placed in a cylindrical vial (3 × 10 cm) and magnetically stirred at 150 rpm. The fibre exposure was conducted at 60°C for 30 minutes. The temperature of the headspace

formation enabled comparing the results of the headspace analysis and sensory evaluation (Ramos *et al*. 1998; Maeztu *et al*. 2001; Mondello *et a*l. 2005).

GC analysis. GC analysis was carried out using the gas chromatograph HRGC-530 Mega Series (Carlo-Erba Instruments, Milan, Italy), equipped with a flame ionisation detector (FID) and a splitless injector (SSL). The desorption of the compounds from DVB/Cartoxem/PDMS fibres in the injector was conducted for 10 min at 250°C. The compounds were separated on Quandrex (30 m × 0.32 mm) capillary column with FFAP stationary phase (0.5 μm). The column temperature was increased from 35°C to 250°C (at a rate of 4°C/min) with 5 min isotherm at 35°C and 45 min isotherm at 250°C that ensured complete removal of caffeine from the column. The temperatures of the injector and detector were set at 250°C. The flow rate of carrier gas (N_2) was 1 ml/minute. Nitrogen can be used especially in such applications where the peaks of compounds evaporating in the first phase of analysis are apt to incomplete separation because of their quantities (Ferrandino *et al*. 2007). This gas was found to be most appropriate under the separation conditions applied. The surface under each peak and the total surface were computed by using the FID software (Chrom-Card). Figure 1 shows a typical GC chromatogram obtained in our analyses. It was divided into parts A and B which represent the two phases of the sample separation.

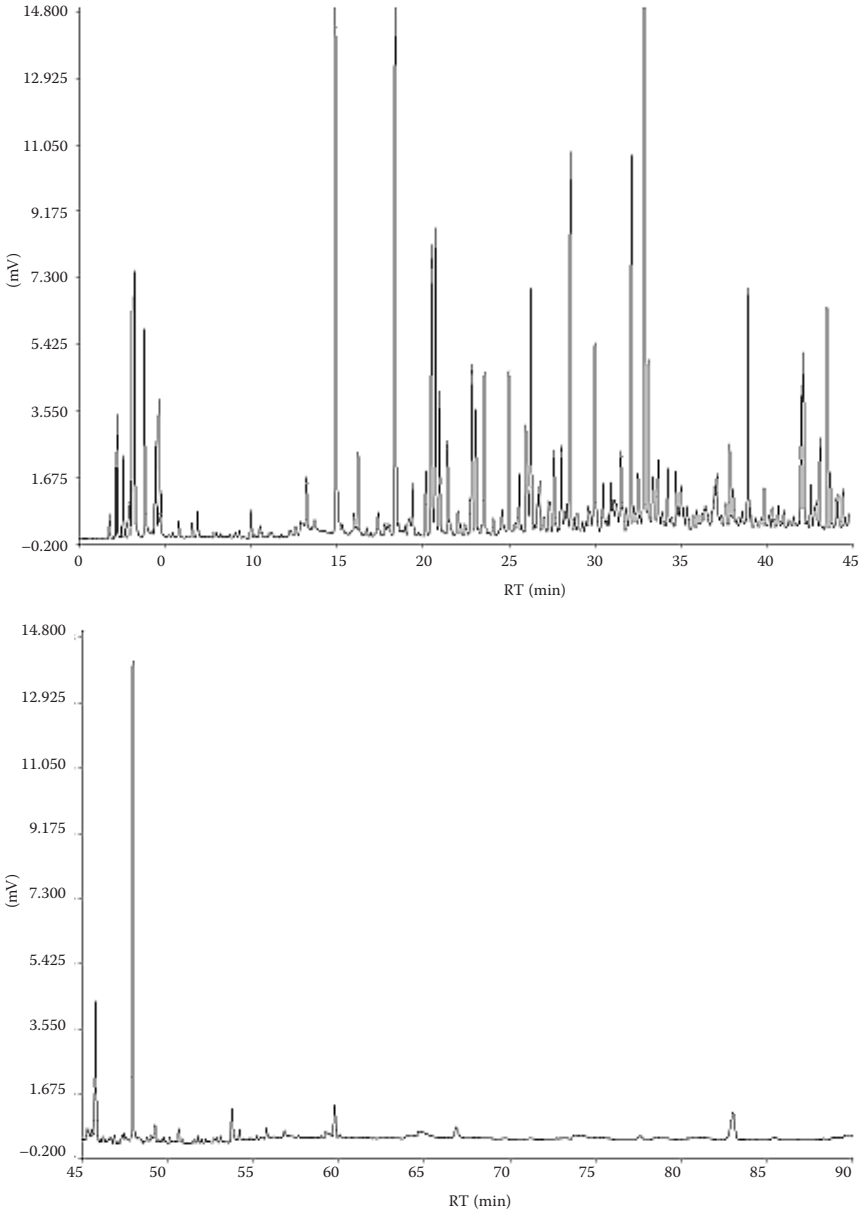


Figure 1. Typical GC chromatogram of HS-SPME of roasted coffee brew's aroma

The volatile compounds were identified on the basis of their spectra determined by gas chromatography/mass spectrometry GC/MS (by using the NIST mass spectral database, only the substances with high spectral match scores were identified by this method), and by comparison of their GC Kovats indeces (KI) and retention times (RT) with previous data. KI of volatiles were determined on the basis of the retention times of *n*-alkanes C_5–$C3_{30}$ (Sigma-Aldrich, St. Louis, USA). These KI values were compared with the indices from the own KI database which contains the results of multiple analyses of various materials that were conducted in the laboratory.

Statistical analysis. The analyses were carried out in triplicates and their results were subjected to statistical analysis. This comprised the determination of standard deviation and one-way ANOVA (analysis of variation) at the significance level $P \leq 0.05$.

RESULTS AND DISCUSSION

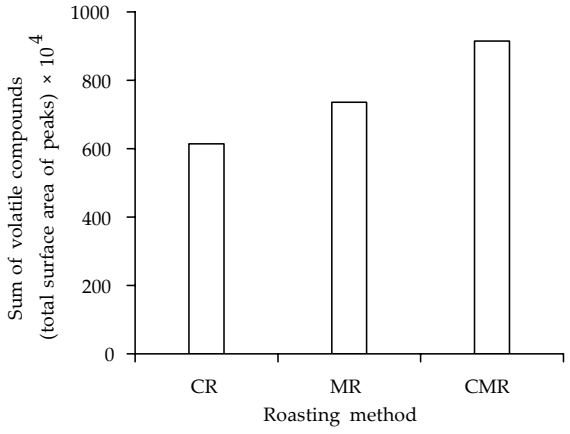
Characteristics of roasted coffee beans

For the three roasting methods, the values of brew acceptance were 9.1, 10.6, and 10.8 for CR, CMR, and MR coffee beans, respectively. For each of the roasting methods applied, the optimum sensory attributes corresponded to the decrease in the solid substance content of approximately 9.5% that was equivalent to the medium roast. Roasting was carried out for 590 s, 670 s, and 370 s, the end-point temperatures (measured by a thermocouple Therm-2285-2B, Lodz. Poland) of roasted coffee beans being 238, 207, and 228°C for CR, MR, and CMR methods, respectively. Water contents in the coffee beans roasted using the three methods were 2.0%, 1.3%, and 2.4%, and the values of L^* were 42.4, 41.0, and 39.0, of a^* 8.4, 9.1, and 10.9, and of b^* 25.8, 26.9, and 29.0 for CR, MR, and CMR method, respectively.

HS-SPME/GC/MS results

HS-SPME/GC/MS profiles of the brews prepared from Robusta coffee beans roasted using the three different methods, i.e. CR, MR, and CMR, were compared in this study. The same compounds were identified in the headspace irrespective of the roasting method but their proportions were different. It is known that both the proportions of the aroma carriers and the absence of any of them affect the flavour of coffee brews (Belitz & Grosch 1999). The effect of the roasting method on the total quantity of odourants (calculated on the basis of the total surface area below all peaks in GC chromatograms) is shown in Figure 2. The greatest accumulation of volatile compounds in the headspace of coffee brews was observed with the samples of coffee beans obtained by CMR. This heating method ensured a very quick increase of the coffee beans temperature, both inside (caused by microwaves) and on their surface (due to the traditional convective heating). Intensive heating generates high quantities of volatile compounds within a relatively short roasting process and the moderate ultimate temperature of roasted coffee beans (207°C) favours the accumulation of these volatiles. The sum of odourants in the headspace of the coffee brews was the lowest for the CR coffee beans, most likely due to their high end-point temperature and relatively long roasting duration that caused volatilisation of odourants. MR, decreased both the time and the end-point temperature of coffee beans when compared to the traditional method. Due to the intensive internal heating, MR resulted in the generation and retention of more volatiles compared to the CR method.

As many as 119 volatile compounds were identified in the headspace of the examined coffee brews. They comprised 25 furans, 25 pyrazines, 19 carbonyl compounds, 9 sulphur compounds,



CR – convectively roasted; MR –microwave roasted; CMR – roasted by the coupled convective-microwave method

Figure 2. The dependence of the overall surface area under the peaks (separated by gas chromatography) of headspace profiles of Robusta coffee brews on roasting method

7 pyrroles, 7 benzene derivatives, 6 alcohols, 6 hydrocarbons, 5 phenols, 4 pyridines, 1 hydrazine, 1 ester, 1 oxazole, 1 each lactone, maltol, and caffeine. Many of these compounds were also identified by other researchers.

HS-SPME/GC/MS revealed that furans were the dominant volatile organic compounds emitted from the examined samples of Robusta coffee brews irrespective of the roasting method. They accounted for approximately 22%, 21%, and 20% of the odourants released from infusions of CR, MR, and CMR coffee samples, respectively. The concentration of 2-furanmethanol, which imparts the burnt aroma, was the highest of all furans and almost the same in the headspace of the brews prepared from the coffee beans roasted by the MR and CMR methods while it was lower in the brews of CR coffee beans (Table 1, No. 81, $P < 0.05$). The concentrations of 2-furanmethyl acetate, 5-methyl-2(5*H*)-furanone, and 5-methyl-2,2'-difurancarboxaldehyd disulfide were also appreciable, their largest contents having been observed in the headspace of brews prepared from CR coffee beans (Table 1, Nos 68, 70, and 82, $P < 0.05$). These furan derivatives are often detected in the coffee headspace aroma (Ramos *et al*. 1998). In the brews of Arabica coffee, their contents were twice as high as in the presented brews of Robusta coffees. Hofmann *et al*. (2001) postulated that another furan derivative – 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone, ranks among the key contributors to the coffee aroma with a very low odour threshold (160 μg/kg water) and a sweet, caramel-like hint. Its concentration was the highest in the headspace of brews prepared from CMR samples of coffee (Table 1, No. 112, $P < 0.05$), and these brews were also scored as the sweetest (Nebesny & Budryn 2006). According to Mayer *et al*. (2000), the extractability of this substance is above 90% and Semmerloch and Grosch (1996) reported that its odour activity value is 250 (this index ranges from less than 1 to almost 4000 for the known compounds).

Pyrazines ranked the second in abundance in the emissions from the examined coffee brews. They accounted for 21%, 19%, and 18% of all volatiles emitted from the brews prepared from CMR, CR, and MR coffee samples, respectively. Pyrazine concentration was the highest compared to its derivatives. Its greatest quantity was detected in the headspace of CR coffee brews (Table 1, No. 32, $P < 0.05$). Despite the occurrence of 2-methylpyrazine (characterised by burnt grass aroma) in the headspace of all the examined brews at a similar and high concentration, it was the least important odourant because of the relatively high odour threshold (60 mg/kg water). More important were 2,5- and 2,6-dimethylpyrazines with nutty and maize-like smells, with odour thresholds of 18 and 15 mg/kg water, respectively. The highest contents of these two substances were detected in the headspace of the brews from CR coffee beans (Table 1, Nos 41 and 42, $P < 0.05$). The reactions of demethylation during roasting yield methylpyrazine. The higher ratio of methyl- to dimethylpyrazines results in more pronounced burnt aroma of coffee. The most advantageous ratio of these substances was observed in the headspace of the brews prepared from CR coffee beans. However, their high concentrations in the latter emissions did not correlate with the scores of nutty and roasted hint of the brews (Nebesny & Budryn 2006). The strongest perception of roasted smell was correlated with the highest content of all pyrazines in the headspace of the brews prepared from CMR coffee beans. Less pleasant aroma is conveyed by other pyrazine derivatives detected in the emissions examined, such as 2-ethyl-5- and 2-ethyl-6-methylpyrazine and 2-methyl-3,5-diethylpyrazine (soil-like aroma). Their contents in the headspace of the compared Robusta brews were at a similar level (Table 1, Nos 50, 51, and 61, $P < 0.05$). Coffee aroma is positively affected by 5-methyl-6,7-dihydro-(5*H*)-cyclopentapyrazine, which has a sweet, caramel-like hint. Its highest concentration was detected in the headspace of CMR coffee brews (Table 1, No. 74, $P < 0.05$), which were scored as the sweetest (Nebesny & Budryn 2006).

Carbonyl components identified by HS-SPME/GC/MS constituted more than 12% of volatiles from MR and CMR coffee brews, and less than 11% of those from CR coffee infusions. 2-Butanone was dominant among carbonyl compounds, particularly those emitted from the infusions of CMR and MR coffee (Table 1, No. 6, $P < 0.05$). The headspace analysis of coffee brews revealed also relatively high concentrations of 2-cyclopenten-1-one, 1-hydroxy-2-butanone, 2-methyl-2-cyclopenten-1-one and 2-hydroxy-3-methyl-2-cyclopenten-1-one. Cyclic ketones have a sweet, caramel-like smell, and the roasting conditions affect their contents in aroma of coffee brews. The highest concentrations of these substances were detected in the headspace of CR coffee infusions (Table 1, Nos 46, 48, 49, and 95, $P < 0.05$). The quantities of 2,3-butanedione, which has a buttery, pleasant

Table 1. HS-SPME/GC profiles of brews prepared from convectively (CR), microwave (MR) and convectively-microwave (CMR) roasted Robusta coffee beans, (tr – traces)

Peak No.	Compound	KI	ID	RT	Surface area of GC peak (%)		
					CR	MR	CMR
1.	1,3-pentadiene	505	A	2.14	0.07	0.22	0.30
2.	methanethiol	511	A	2.24	0.11	0.16[a]	0.19[a]
3.	dimethyl sulphide	562	A	2.60	0.08[a]	0.11[a]	0.17
4.	trimethylhydrazine	684	B	3.09	0.60[a]	1.24	0.70[a]
5.	2-buten-1-ol	805	B	4.38	0.60	0.83[a]	0.85[a]
6.	2-butanone	809	A	4.45	2.76	5.41[a]	5.80[a]
7.	2-methyl-2-buten-1-ol	821	B	4.62	3.07[a]	2.99[a]	1.56
8.	3-methyl-3-buten-2-ol	830	A	4.74	0.49	0.36	0.10
9.	ethanol	883	A	4.42	0.15	0.09	0.01
10.	2,5-dimethylfuran	909	A	5.74	0.05[a]	0.05[a]	0.01
11.	2,4-dimethylfuran	945	B	6,17	0.06[a]	0.04[a,b]	0.02[b]
12.	2,2-dimethylpropanal	974	B	6.52	0.08[a]	0.08[a]	0.04
13.	2,3-butanedione	999	A	6.82	0.06[a]	0.05[a]	0.04[a]
14.	tiophene	1024	A	7.77	0.08[a]	0.06[a]	0.03
15.	2-ethyl-5-methylfuran	1034	B	8.17	0.05[a]	0.02[b]	0.03[a,b]
16.	2-butenal	1056	A	8.99	0.24[a]	0.22[a]	0.16
17.	2,3-pentadiene	1077	B	9.89	0.46[a]	0.37[a]	0.26
18.	dimethyl disulphide	1086	A	10.12	0.18[a]	0.17[a,b]	0.14[b]
19.	phenol	1090	A	10.37	0.10	0.06[a]	0.04[a]
20.	hexanal	1092	A	10,49	0.06[a]	0.04[a]	0.02
21.	2-methyltiophene	1103	A	10.92	tr	0.03	tr
22.	3-methyl-2-butenal	1107	A	11.07	0.09[a]	0.09[a]	0.04
23.	2-butenoic acid methyl ester	1121	A	11.65	0.01[a]	0.03	0.01[a]
24.	3-methyl-3-hexanone	1148	B	12.75	0.90[a]	0.94[a]	0.63
25	1-methylpyrrole	1157	A	13,12	0.29[a]	0.30[a]	0.16
26.	3,4-hexadione	1164	A	13.44	0.07[a]	0.05[a,b]	0.04[b]
27.	3-methylphenol	1168	B	13.59	0.05	0.02[a]	0.03[a]
28.	pyridine	1199	A	14.87	0.23[a]	0.20[a]	0.14
29.	2,4,5-trimethyloxazol	1209	A	15.27	tr	0.02	0.11
30.	2-(2-propenyl)-furan	1226	A	15.95	0.11[a]	0.11[a]	0.08[a]
31.	1,2-dimethylpyrrole	1229	A	16.07	tr	0.19	0.04
32.	pyrazine	1232	A	16.20	5.10[a]	4.73[a,b]	3.77[b]
33.	furfurylmethyl sulphide	1260	A	17.34	0.28[a]	0.65	0.21[a]
34.	tetrahydro-3-methylfuran	1270	B	17.74	0.20[a]	0.19[a]	0.03
35.	pyrazinamid	1275	B	17.87	0.18[a]	0.08	0.14[a]
36.	2-methylpyrazine	1285	A	18.34	1.77[a]	1.74[a]	1.86[a]
37.	2,5-dimethylpyrrole	1292	A	18.54	0.02[a]	0.02[a]	0.01[a]
39.	4-methylthiazole	1297	A	18.82	0.15[a]	0.11[b]	0.12[a,b]
39	2-hydroxy-2-butanone	1299	A	18.92	tr	0.08	0.14
40.	1,2-ethanediol	1310	B	19.35	2.46[a,b]	1.93[a]	2.68[b]
41.	2,5-dimethylpyrazine	1330	A	20.12	0.17[a]	0.16[a]	0.10
42.	2,6-dimethylpyrazine	1339	A	20.47	0.18	0.10	0.03
43.	2-ethylpyrazine	1345	A	20.70	0.29	0.17	0.09
44.	2-hydroxy-3-pentanone	1351	A	20.94	0.10[a]	0.10[a]	0.05
45.	2,3-dimethylpyrazine	1363	A	21.40	0.20	tr	0.12
46.	2-cyclopenten-1-one	1372	A	21.60	1.22[a]	0.65	0.95[a]
47.	2-methyl-3-hexanone	1380	B	22.00	0.83[a]	0.44	0.80[a]
48.	2-methyl-2-cyclopenten-1-one	1381	A	22.14	0.43	0.33	0.56

Table 1 to be continued

Peak No.	Compound	KI	ID	RT	Surface area of GC peak (%)		
					CR	MR	CMR
49.	1-hydroxy-2-butanone	1388	A	22.40	0.76[a]	0.70[a]	0.78[a]
50.	2-ethyl-6-methylpyrazine	1398	A	22.80	1.86[a]	1.31	1.93[a]
51.	2-ethyl-5-methylpyrazine	1405	A	23.04	0.36[a]	0.32[a]	0.36[a]
52.	2-amino-4-methylthiazole	1414	B	23.39	tr	tr	0.20
53.	2-ethyl-3-methylpyrazine	1418	A	23.52	0.82[a]	0.78[a]	1.31
54.	5-methyl-2(*5H*)-furanone	14332	A	24.05	0.01	tr	0.06
55.	vinylpyrazine	1447	A	24.55	1.03[a]	0.87[a]	1.47
56.	2-methyl-5-propylpyrazine	1458	B	24.97	1.95[a]	1.65[a]	2.51
57.	2,6-diethylpyrazine	1475	A	25.57	0.90[a]	0.82[a]	1.12
58.	2-furfural	1483	A	25.85	0.37[a]	0.29[a]	0.29[a]
59.	2-(1-propenylthio)-propane	1494	B	26.25	0.21[a]	0.27[a]	0.13
60.	2-furfuryl methyl sulphide	1506	A	26.67	0.22[a]	0.26[a]	0.24[a]
61.	2-methyl-3,5-diethylpyrazine	1509	A	26.77	0.25[a]	0.23[a]	0.23[a]
62.	2-methyl-5-vinylpyrazine	1516	A	27.00	0.24[a]	0.31[a]	0.28[a]
63.	furfuryl formate	1524	A	27.30	0.76[a]	0.69[a]	0.72[a]
64.	*1H*-pyrrole	1534	A	27.64	0.37[a]	0.42[a]	0.59
65.	benzaldehyde	1564	A	28.04	0.24	0.75[a]	0.62[a]
66.	2,3-dimethyl-2-cyclopenten-1-one	1550	A	28.20	0.40[a]	0.14	0.31[a]
67.	1-acetyloxy-2-butanone	1553	A	28.27	0.17[a]	0.12[b]	0.16[a,b]
68.	2-furanmethanol acetate	1557	A	28.40	5.66	3.91[a]	4.38[a]
69.	2-acetyl-1-methylpyrrole	1574	A	28.99	tr	0.05[a]	0.05[a]
70.	5-methyl-2-furfural	1605	A	30.04	3.53	1.49	1.15
71.	isopropenylpyrazine	1620	B	30.52	1.03[a,b]	0.98[a]	1.30[b]
72.	2-amino-5-methylphenol	1634	B	30.95	1.74	1.29	2.29
73.	2,2´-methylenedifuran	1637	B	31.07	0.44	0.83	1.20
74.	5-methyl-6,7-dihydro-(*5H*)-cyklopentapyrazine	1643	A	31.24	0.17	0.48	1.16
75.	2-isoamyl-6-methylpyrazine	1648	B	31.39	tr	0.29[a]	0.27[a]
76.	2-acetyl-5-methylfuran	1653	A	31.55	0.44	0.61	1.40
77.	2-acetylpyrazine	1662	A	31.87	0.15	0.24	0.52
78.	γ-butyrolactone	1671	A	32.15	1.32[a]	1.12[a]	1.83
79.	1,2,4-triazolo[1,5-a]pyrazine	1675	B	32.29	tr	0.51	0.30
80.	2,3-dimethyl-6-isobutylpyrazine	1683	B	32.54	0.73[a]	0.87[a]	0.92[a]
81.	2-furanmethanol	1694	A	32.89	3.80	6.01[a]	6.80[a]
82.	5-methyl-2,2´-difurfuryl disulphide	1700	B	33.07	2.76	1.47	0.77
83.	2,6-dimethyl-*p*-benzoquinone	1711	B	33.39	1.15[a]	1.66	1.19[a]
84.	2-acetyl-3-methylpyrazine	1721	B	33.69	0.61	0.84[a]	0.79[a]
85.	5,6-epoxy-*p*-ment-8-en-3-one	1728	B	33.89	0.06	0.55[a]	0.52[a]
86.	2-allyl-3-methylpyrazine	1739	B	34.24	0.42	tr	0.26
87.	4-(5-methyl-2-furanyl)-2-butanone	1745	B	34.40	0.13	0.42	0.27
88.	3-methyl-2(*5H*)-furanone	1750	B	34.54	0.66[a]	0.73[a]	1.02
89.	pyrazine carboxamide	1755	B	34.69	0.45[a]	0.82	0.51[a]
90.	3,4-dimethyl-2,5-furandione	1764	B	34.95	0.69[a]	1.12	0.69[a]
91.	3-octen-2-ol	1769	B	35.12	tr	0.09	0.14
92.	3-ethyl-4-methyl-2,5-furandione	1777	B	35.34	0.09	0.21	0.09
93.	methyl salicylate	1801	B	35.89	0.15	0.05	0.45
94.	2-pyridinecarboxylic acid 6-methyl ester	1804	B	36.15	0.30[a]	0.20	0.28[a]
95.	2-hydroxy-3-methyl-2-cyclopenten-1-one	1829	B	36.92	1.16[a]	1.34[a]	0.72
96.	ethyl salicylate	1832	B	37.00	0.59[a]	0.57[a]	0.67[a]
97.	3-octen-2-one	1851	B	37.57	0.56[a,b]	0.68[a]	0.53[b]

Table 1 to be continued

Peak No.	Compound	KI	ID	RT	Surface area of GC peak (%)		
					CR	MR	CMR
98.	1-(2-furanylmethyl)-*1H*-pyrrole	1858	B	37.79	2.39[a]	2.62[a]	2.44[a]
99.	3-phenylfuran	1880	B	38.49	0.59[a]	0.53[a]	0.87
100.	2-metoxyphenol	1892	B	38.85	2.63[a]	3.01[a]	1.93
101.	3-acetoxy-4-methylpyridine	1897	B	39.00	0.45	0.71	0.22
102.	α-ethylbenzenon	1908	B	39.30	0.09	tr	0.34
103.	1-(2-phenyl)-1-propanol	1920	B	39.64	0.10	0.01	0.14
104.	2-hydroxy-2,3-dimethyl-2-cyclopenten-1-one	1926	B	39.82	0.76[a]	0.74[a]	0.68[a]
105.	furfurylmethyl disulphide	1938	B	40.14	0.14	0.09[a]	0.08[a]
106.	trans-bicyclodecane	1963	B	40.84	0.13	0.09	0.21
107.	maltol	2006	B	42.02	1.58[a]	2.08	1.51[a]
108.	3-formyl-1-methylpyrrole	2012	B	42.19	0.46[a]	0.56[a]	0.53[a]
109.	2,2'-(oxydimethylene)-difuran	2028	B	42.60	0.44	tr	0.19
110.	*p*-hydroxybenzen sulphonic acid	2048	B	43.12	1.52[a]	1.86[a]	1.03
111.	*p*-ethyl-2-metoxyphenol	2065	B	43.55	4.49[a]	9.49	3.95[a]
112.	2,5-dimethyl-4-hydroxy-3(*2H*)-furanone	2071	B	43.74	0.40	0.07	0.63
113.	2-methyl-4-quinazolinone	2085	B	44.09	0.74	0.22[a]	0.23[a]
114.	4-methyl-2(*1H*)-quinolinone	2114	B	44.85	0.15	0.21	0.08
115.	3,6-dimethyl-*4H*-pyrido[1,2-a]pyrimidin-4-one	2144	B	45.62	0.13	0.05	0.36
116.	4-methylpyrrolo[1,2-a]pyrazine	2167	B	46.22	0.08[a]	0.14	0.09[a]
117.	4-acetoxy-3-metoxystyrene	2235	B	47.97	5.41[a]	6.73[a]	8.55
118.	indole	2476	B	53.77	tr	0.01	0.06
119.	caffeine	3163	B	82.94	0.01[a]	tr	0.01[a]

KI – Kovats index

ID – identification method

A – mass spectrum consistent with the NIST mass spectra database

B – mass spectrum and Kovats index consistent with literature data

Values in each line bearing the same letters are not significantly different ($P > 0.05$) from one another

smell and contributes significantly to the aroma of coffee brews, were rather small and almost the same (Table 1, No. 13, $P < 0.05$). 2,3-butanedione present in roasted and ground coffee beans, with its odour activity of 160, is extractable with water to 80% (Semmelroch & Grosch 1996; Mayer *et al*. 2000).

Benzene derivatives were also important odourants of the coffee brews accounting for 13, 12, and 9% of the headspace for CMR, MR, and CR coffee beans, respectively. They were most abundant in the headspace of CMR coffee brews, which received high scores for bitter and astringent taste (Nebesny & Budryn 2006). Their concentrations decreased in the order: 4-acetoxy-3-methoxystyrene, *p*-hydroxybenzene sulfonic acid and 2,5-dimethyl-*p*-benzoquinone (Table 1, Nos 83, 110 and 117, $P < 0.05$).

HS-SPME/GC/MS revealed a relative abundance of phenols, which constituted almost 14%, 8%, and 9% of the aroma of MR, CMR, and CR coffee brews. The most abundant, in particular in MR coffee brews, were *p*-ethyl-2-methoxyphenol (*p*-ethylguaiacol), with a spicy and sharp note, and 2-metoxyphenol (guaiacol), which has a more smoky hint (Table 1, Nos 100, and 111, $P < 0.05$). Both of them are unique and significant contributors to the aroma of a cup of coffee (Clarke 1990; Hofmann *et al*. 2001). According to Mayer *et al*. (2000) the extractability of guaiacol and ethylguaiacol is 65% and 50% and their odour activities are 490 and 13, respectively. The headspace analysis revealed also a relatively high content of 2-amino-5-methylphenol, particularly in CMR coffee brews (Table 1, No. 72, $P < 0.05$).

Alcohols accounted for 7%, 6%, and 5% of volatiles emitted from the brews of MR, CR, and CMR coffee beans. Out of the 6 detected alcohols, the most abundant were 2-methyl-2-buten-1-ol (particularly in the brews of CR and MR coffees,

Table 1, No. 7, $P < 0.05$), and 1,2-ethanediol (in the brews of CMR and CR coffees, Table 1, No. 40, $P < 0.05$).

The emissions from the brews contained approximately 4% of pyrroles that adversely affect coffee aroma because of smoky and mushroom notes. The most abundant was furan derivative, i.e. 1-(2-furanylmethyl)-1*H*-pyrrole (similar concentrations in all analysed samples, Table 1, No. 98, $P < 0.05$).

Sulphur compounds are also of importance for the aroma of a cup of coffee. Their content was only slightly above 1% in the examined brews while in the aroma of coffee beans their concentration reached 2–3% (Ramos *et al*. 1998). Despite the low concentrations, sulphur compounds rank among significant headspace contributors because of low boiling temperatures and odour thresholds. This group comprises methanethiol, which has a putrid smell. Its lowest concentration was found in CR coffee brews (Table 1, No. 2, $P < 0.05$). Methanethiol ranks among the key contributors to the aroma of coffee brews because of its good extractability (above 70%), high odour activity (3000), and a very low odour threshold (0.02 μg/kg water). One of the characteristic headspace components is dimethyl sulfide (sulphur- and garlic-like note). Its highest concentration was detected in the emissions from the brews of CMR coffee (Table 1, No. 3, $P < 0.05$), which received high scores for the roast aroma (Nebesny & Budryn 2006). Some thiazole derivatives, like 2-amino-4-methylthiazole, negatively affect coffee aroma since they impart the note of burnt rubber. The highest content of this compound was noted in the brews of CMR coffee (Table 1, No. 52, $P < 0.05$).This compound received also high scores for the burnt smell (Nebesny & Budryn 2006).

HS-SPME/GC/MS revealed low, approximately 1% concentrations of pyridines in the brews aroma. Because of a sharp and bitter note, they rank among the undesirable aroma contributors. The abundance of 3-acetoxy-4-methylpyridine was higher than that of other pyridines, its content being the highest in the aroma of MR coffee brews (Table 1, No. 101, $P < 0.05$).

One of the desirable aroma components is maltol, which has a sweet and burnt smell. Its largest quantity was found in the aroma of MR coffee brews (Table 1, No. 107, $P < 0.07$).

To find the correlation between the concentrations of volatiles in the headspace of coffee brews and their sensory attributes seems a difficult task, as our and other authors reports indicate. The infusions from MR coffee beans were scored as the most acceptable although the brews prepared from CMR coffee beans were characterised by a higher total content of odour compounds. However, the first brews contained fewer compounds that impart the burnt aroma. Although MR requires a longer time compared to CMR processing, the end-point temperature of coffee beans is lower. This explains the lower quantity of substances, which act as markers of over-roasting. Besides, the aroma of MR coffee brews contained relatively high contents of guaiacol derivatives with the smoky aroma. CR gave rise to relatively high concentrations of such compounds that positively affect the aroma of coffee brews (certain furans and pyrazines). However, the sum of volatile compounds emitted from these coffee brews was the lowest and coincided with the lower scores for the total aroma relative to the infusions of the MR coffee beans. Thus, MR of the Ivory Coast coffee beans analysed was found to improve the aroma of their brews due to the lower end-point temperature compared to CR.

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Corresponding author:

Dr. Grażyna Budryn, Technical University of Lodz, Faculty of Biotechnology and Food Science, Institute of Chemical Technology of Food, Stefanowskiego 4/10, Lodz, Poland
tel.: + 48 426 313 460, e-mail: grazyna.budryn@p.lodz.pl