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Analytical Methods

Volatile compounds as potential defective coffee beans' markers

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Abstract

Although Brazil is the largest raw coffee producer and exporter in the world, a large amount of its Arabica coffee production is considered inappropriate for exportation. This by-product of coffee industry is called PVA due to the presence of black (P), green (V) and sour (A) defective beans, which are known to contribute considerably for cup quality decrease. Data on the volatile composition of Brazilian defective coffee beans are scarce. In this study, we evaluated the volatile composition of defective coffee beans (two lots) compared to good quality beans from the respective lots. Potential defective beans' markers were identified. In the raw samples, 2-methylpyrazine and 2-furylmethanol acetate were identified only in black-immature beans and butyrolactone only in sour beans, while benzaldehyde and 2,3,5,6-tetramethylpyrazine showed to be potential markers of defective beans in general. In the roasted PVA beans, pyrazine, 2,3-butanediol *meso*, 2-methyl-5-(1-propenyl)pyrazine, hexanoic acid, 4-ethyl-guayacol and *iso*propyl *p*-cresol sulfide also showed to be potential defective coffee beans' markers.

Keywords: Defective coffee beans; PVA; Coffee quality; Coffee flavor; Volatile; Mass spectrometry

1. Introduction

Brazil is the world's largest coffee producer and exporter and, recently, it has become the second largest consuming country of this beverage (ABIC, 2007). In order to harvest large amounts of coffee fruits in a short period of time, the most preferred harvesting practices in Brazil are stripping and mechanical, in which all fruits and leaves are collected from the branches. Because usually coffee fruits do not reach ripeness at the same time, these ways of harvesting may render fruits in different maturation points. In addition to fruits on the branches, fruits that oxidize or ferment after falling on the ground are frequently collected at the end of harvesting season. For all these reasons, about 20% of the Brazilian coffee production contain defective beans and are considered to be inappropriate for exportation.

The defective coffee beans may be classified by the Brazilian Association of Coffee Industry (ABIC) as extrinsic and intrinsic (Toledo, & Barbosa, 1998). Extrinsic defective beans are stones, sticks, husks, twigs, etc., which may be incorporated to the fruits during harvesting. Intrinsic defective beans – considered to be the most relevant for cup quality – are immature, black, sour, black-immature, bored or insect damaged and broken beans, among others. Immature beans originate mainly from immature fruits and are known to increase beverage astringency (Bee et al., 2005; Pimenta, 2003; Smith, 1985). Sour beans can be generated by water paucity during fruits development or by abnormal fermentation of immature or mature beans (Bee et al., 2005; Pimenta, 2003). According to Pimenta (2003), sour beans may precede the formation of black beans. Nevertheless, black beans most commonly originate from over-ripened cherries, which may fall naturally on the ground by the action of rain, or during harvest, remaining in contact with the soil and favoring microbial fermentation (Clarke, 1987;

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Sampaio, 1967). According to Bee et al. (2005), black beans may also originate from carbohydrate deficiency caused by poor agricultural practices or by microbial fermentation during post-harvesting processing. In the black–green or black-immature bean the silverskin is dark or black–green due to the action of high temperatures on the immature bean (Bee et al., 2005). Alternatively, according to Teixeira et al. (Teixeira, Hashizume, Nobre, Cortez, & Fazuoli, 1982), black-immature beans may derive from inadequate drying process of immature beans. These black-immature beans can be differentiated from ground-fermented black beans by the shining and adherent silver skin on the beans' surface. Black-immature and immature beans are considered to be serious defects because they dramatically affect the cup quality (Clarke, 1987; Teixeira, Gomes, Pereira, Moraes, & Castilho, 1970). Shell or ear and shell-core beans are splitting of the elephant bean (growth defect) generally through handling (dehulling or dehusking), producing the separation of the inner and outer parts (Bee et al., 2005). The withered beans derive from underdeveloped fruits due to genetic and physiological problems, nutritional deficiency, drought or heavily stressed trees (Bee et al., 2005; Toledo, & Barbosa, 1998). Dried cherries are generated by incorrect dehusking, allowing whole dried cherries to pass through (Bee et al., 2005).

The mixture of coffee beans that after electronic sorting are inappropriate for exportation is called PVA and is usually incorporated by the internal market. Because defective beans may dramatically decrease cup quality and have health implications, there is a general concern about the amount of defective beans which are incorporated to good quality beans in the Brazilian industry. Recently, there has been a growing effort aiming to characterize the chemical composition of such defective beans to identify large amounts of them in the coffee blends. However, very little is known about their chemical composition, which is variable. Particularly, the volatile composition is an aspect which may vary considerably according to genetics, soil, climate, and agricultural practices. 2-methyl-isobutanol, 2,4,6-trichloroanisole, geosmin, 2-methoxy-3-isopropylpyrazine and 2-methoxy-3-isobutylpyrazine have been identified as responsible for negative notes in coffee (Bortoli & Fabian, 2001; Cantergiani et al., 1999; Spadone, Takeoka, & Liardon, 1990), but none of them was characterized as being derived from defective beans typical of Brazil. Also, ethyl isobutanoate, isoamyl acetate, isobuthyl acetate, ethyl butanoate, 2-methyl-ethyl butanoate, *n*-hexyl acetate, 2-acethylpyrazine and β-linalool have been exclusively observed in stinker coffee beans when compared to healthy beans (Guyot et al., 1982).

The aim of this study was to investigate the volatile composition of the most common Brazilian defective coffee beans in comparison with good quality beans from the respective lots, to possibly identify potential marker compounds characteristic of specific defects.

2. Materials and methods

2.1. Coffee samples

Two lots of good cup quality beans and defective beans were used in this study. The first group (group 1) was from Pirajú (São Paulo, Brazil) and contained raw healthy and good cup quality beans (control 1) classified as "soft" (Farah, Monteiro, Calado, Franca, & Trugo, 2006); the respective rejected mixture of defective beans (PVA 1) composed of 7.1% of black beans, 22% of immature beans, 9.9% of sour beans, 5.1% of black-immature beans, 40.8% of healthy beans and 15.1% of other defects; the respective sorted defects; and PVA 1 sample roasted to moderately light or light medium roasting degree (# 75), as classified by the Roast Color Classification System (SCAA, USA) in a bed fluid roaster (210 °C, 6 min; I-Roast, Gurnee, IL, USA). The second group of coffee beans (group 2) was from Viçosa (Minas Gerais, Brazil) and contained raw healthy and good cup quality beans (control 2) classified as "strictly soft" (Farah et al., 2006); the respective rejected mixture of defective beans (PVA 2) composed of 6.5% of black beans, 29.7% of immature beans, 2.3% of sour beans, 16.7% of black-immature beans, 4.2% of shell or ear, 0.5% of shell-core beans, 1.4% of withered beans, 1% of dried cherry or pod, 2.2% of husk fragments, 5.3% of insect damaged beans, 20% of healthy beans and 10.2% of other defects; the respective sorted defects; the good cup quality sample and PVA 2 roasted to moderately light roasting degree (# 75). All samples were ground to pass a 500 μm sieve immediately before they were transferred to the extraction vials.

2.2. Sample equilibration and extraction

A SPME triple phase 50/30 μm fiber, (divinylbenzene/carboxen/polydimethylsiloxane) purchased from Supelco Co. (Bellefonte, PA, USA), was used for the extraction of volatiles from the coffee samples' headspace. When using SPME, the sample equilibration time, the extraction temperature and the ratio volume of samples' bottle to that of the solid sample are critical factors that may influence accuracy and precision of the measured results (Avila, Breiter, & Mott, 2007; Wang, O'Reilly, Chen, & Pawliszyn, 2005). Therefore, the fiber was reconditioned for 2 h in the injection part at 250 °C before being used for analyses. Prior to each sample analysis, 0.5 g of each coffee sample was placed in a sealed 4 ml vial, and stored at 5 °C for 12 h. Raw samples were sonicated (Sonorex TK 52, Berlin, Germany) for 30 min. After the insertion of the fiber in the vial, the fiber was exposed to the headspace above the coffee sample for 30 min at 60 °C in a silicone bath and then immediately inserted into the GC injector. For roasted coffee samples, each vial was placed in a silicone bath at 90 °C for 30 min. After the insertion of the fiber in the vial, the fiber was exposed to the headspace above the coffee sample for 30 min at 90 °C and then immediately inserted into the

GC injector. After sampling, the fiber was thermally desorved in the GC injection port for 5 min at 250 °C, followed by further 7 min in a separate GC injection port to prevent analyte carry over (Sanz, Ansorena, Bello, & Cid, 2001, adapted). Verification of the coffee beans' volatile profile was achieved through triplicate sample analysis.

2.3. GC/MS analysis

Analyses were performed using Shimadzu QP5050 GC/MS (Kyoto, Japan). A Omegawax™ 250 (30 m × 0.25 mm × 0.25 μm film thickness) column purchased from Supelco Co. (Bellefonte, PA, USA) was used. Chromatographic conditions were as follows: injection system – splitless; time – 5 min; injection temperature – 250 °C; temperature program – from 40 °C (5 min) to 150 °C (15 min) at 3 °C/min to 250 °C at 5 °C/min (4 min); detector – quadrupole; temperature – 250 °C; carrier gas – helium; flow rate – 1.5 ml/min (Bicchi, Panero, Pellegrino, & Vanni, 1997, adapted). The MS detector voltage was 1.2 kV. The mass spectral data acquisition scan interval was 1.0 s and data were collected over a mass range of 40–400 u.

2.4. Data elaboration

Total ion chromatograms (TIC) were processed using the automated data processing software GCMS-Solutions Shimadzu (LabSolutions, Version 2.0, Kyoto, Japan). For peak identification the mainlib NIST-2004 spectral library, Kovats Indexes and standards of 3-methylbutanal, pentanal, hexanal, heptanal, 1-penten-3-ol, pyridine, pyrazine, 3-methylbutanol, 2-methylpyrazine, 1-hexanol, benzaldehyde, 2,3-butanediol, 1H-pyrrole, benzenemethanol and butyrolactone (Sigma–Aldrich, Steinheim, Germany) were used.

3. Results and discussion

3.1. Raw samples

A total of 53 different volatile compounds were identified in the investigated raw coffee samples, with very low intensity peaks compared to those of roasted beans.

Control samples – the volatile compounds identified in the control samples characterized the coffee that originated the defective beans, being present in almost all the defective beans of the same group. Therefore, in the present work, such compounds will be called as reference compounds. Nine compounds were identified in the control sample of group 1 (Table 1), being six alcohols, two acids and one hydrocarbon. The control sample of group 2 presented 14 compounds, being eight alcohols, two acids, two furans, one ether and one unidentified compound. It may be noted that both groups of raw samples were rich in alcohols (Table 2), being in accordance with the literature (Clifford, 1985; Flament, 2002). The compounds 1-hexanol, acetic acid, 2-ethyl-1-hexanol, 2,3-butanediol isomers, 3-methylbutanoic acid and 2-phenyl-1-ethanol were present in the control samples of both groups.

Immature beans – in addition to the reference compounds, four volatile compounds were identified in the immature defects of group 1 (Table 1). In group 2, eight compounds were identified (Table 2). 2-methylpyrazine and 2-furylmethanol acetate were present in the immature defects of both groups. Therefore, these compounds are potential immature defective beans' markers. 2-ethyl-1-hexanol, a reference compound, was not identified in the immature beans of both groups.

Sour beans – in addition to the reference compounds, 14 volatile compounds were observed in the raw sour beans of group 1 (Table 1), while in group 2 only six volatile compounds were identified (Table 2). Butyrolactone and benzaldehyde were identified in both groups. The presence of butyrolactone in the sour defective bean may be related to fermentative processes originated by microbial activity (Toledo & Barbosa, 1998). While butyrolactone could be a potential marker for the sour defective beans, benzaldehyde was also identified in black and black-immature defective beans of group 1. Therefore, it cannot be considered as a specific marker for sour beans, but a potential marker for defective coffee beans in general. 2-phenyl-1-ethanol, a reference compound, was not detected in the sour beans of both groups. Moreover, in sour beans of group 1 3-methyl-1-butanol, a reference compound, seems to have been converted into 3-methylbutanal, which may be a negative-impact compound for coffee aroma depending on its concentration (Flament, 2002; Semmelroch, & Grosch, 1996). The formation of volatile aldehydes has been previously attributed to self-oxidation of alcohols (Guyot et al., 1982; Dart, & Nurten, 1985).

Black beans – in addition to the reference compounds, 14 and 3 volatile compounds were identified in groups 1 and 2, respectively (Tables 1 and 2). No compound was common to both investigated groups of samples. However, it may be noted that both groups of black defective beans were rich in aldehydes, which were not observed in any other major defective bean. The presence of benzaldehyde in these beans indicates the occurrence of fermentative process.

Black-immature beans – in addition to the reference compounds, 15 volatile compounds were identified in the raw sour beans of group 1 (Table 1), while in group 2, only three volatile compounds were identified (Table 2). From these compounds, 2,3,5,6-tetramethylpyrazine and benzaldehyde were identified in both groups. While in group 2, 2,3,5,6-tetramethylpyrazine was only detected in black-immature beans, in group 1 it was also detected in sour and black defective beans, indicating association with fermentative process as occurred with butyrolactone. Benzaldehyde was also identified in the sour beans of both groups, as reported above. While 2,3,5,6-tetramethylpyrazine or benzaldehyde alone may only be considered as a general defective beans' marker, the simultaneous presence

Table 1
Relative concentration (%) of volatile compounds identified in SPME-headspace gas of raw samples of group 1

No.	Compound	ID[a]	Ik[b]	Control	Sour	Immature	Black	Black-immature	PVA
1	Hexane	C	798	45.5	t	18.1	nd	nd	nd
2	3-Methyl-1-butanol	A	1243	24.3	4.2	12.4	nd	nd	3.3
3	1-Hexanol	A	1370	27.5	2.5	11.4	2.2	t	2.3
4	Acetic acid	B	1464	9.2	8.4	6.6	1.3	11.7	1.4
5	2-Ethyl-1-hexanol	C	1496	5.4	nd	nd	0.9	nd	0.7
6	2,3-Butanediol (*levo*[c])	A	1546	7.9	5.8	10.4	nd	6.2	7.4
7	2,3-Butanediol (*meso*[c])	A	1580	8.8	6.4	9.3	nd	8.0	8.0
8	3-Methylbutanoic acid	C	1674	12.8	6.5	4.6	nd	9.2	3.6
9	2-Phenyl-1-ethanol (phenylethyl alcohol)	C	1910	4.3	nd	3.8	nd	2.3	nd
10	3-Methylbutanal	A	1006	nd	11.0	nd	nd	15.1	nd
11	Hexanal	A	1144	nd	19.2	nd	49.1	8.1	22.2
12	2-Ethyl-1-butanol	C	1175	nd	t	nd	nd	nd	nd
13	2-Penthylfuran	C	1262	nd	2.6	nd	13.9	2.4	18.6
14	1-Pentanol	C	1278	nd	2.3	nd	3.8	nd	3.6
15	Butyl propanoate	C	1304	nd	t	nd	nd	3.7	nd
16	5-Methyl-2-hexanol	C	1341	nd	7.1	9.0	2.2	7.0	2.4
17	2,3,5-Trimethylpyrazine	C	1409	nd	3.8	nd	3.2	6.9	nd
18	2-Methyl-2-ethenyl-5-(2-hydroxy-2-methyl)ethano-2-yl-tetrahydrofuran	C	1447	nd	1.3	nd	nd	2.8	nd
19	1-Octen-3-ol	A	1460	nd	4.4	3.4	9.0	3.9	6.6
20	2,3,5,6-Tetramethylpyrazine	C	1475	nd	2.2	nd	2.0	4.5	1.6
21	Benzaldehyde	A	1525	nd	3.9	nd	2.3	4.4	2.0
22	2-Methoxy-3-methylpyrazine	C	1527	nd	1.5	nd	nd	1.5	1.4
23	Butyrolactona	A	1625	nd	1.7	nd	nd	3.4	nd
24	2-Methylpyrazine	A	1302	nd	nd	7.3	nd	nd	nd
25	2-Furylmethanol acetate	C	1555	nd	nd	3.9	nd	nd	nd
26	Nonanal	C	1403	nd	nd	nd	t	nd	1.0
27	2-Octen-2-ona	C	1416	nd	nd	nd	3.2	nd	1.8
28	3-Ethyl-2-methyl-1,3-hexadiene	C	1420	nd	nd	nd	1.1	nd	0.9
29	(2*E*)2-Octenal	C	1435	nd	nd	nd	2.4	nd	2.7
30	2-Butyl-2-octenal	C	1667	nd	nd	nd	1.7	nd	1.6
31	Hexanoic acid	C	1848	nd	nd	nd	1.7	1.2	3.1
32	3,7-Dimethyl-1,6-octadien-3-ol (β-linalool)	C	1555	nd	nd	nd	nd	9.3	1.1
33	2-Hydroxy-2-methyl benzoate (methyl salicilate)	C	1774	nd	nd	nd	nd	3.6	nd

[a] 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 agreed with Nist and Kovats Index agreed with literature data; C – mass spectrum agreed with first three indications in Nist virtual library (Kovats index not available in the searched literature).
[b] KI, Kovats index value calculated for the SUPELCO-Omegawax column. t – trace; nd – not detected.
[c] Isomers according to Peinado, Moreno, Maestre, and Mauricio (2007).

of both compounds in one sample may be considered as a potential black-immature defect marker.

When comparing the volatile profile of black-immature beans with those of black, sour and immature beans (Tables 1 and 2), it may be noted that black-immature beans have more similarities with immature and sour beans than with black beans. This indicates that black-immature beans are derived from immature sour beans that have been exposed to high temperatures, which is in total agreement with the definition of Bee et al. (2005) for black-immature beans.

Shell-core beans – in addition to the reference compounds, 2 volatile compounds were identified in shell-core beans: 2,3,5-trimethylpyrazine, not observed in any other defect, and pyridine, also present in immature beans (Table 2).

Shell beans – in addition to the reference compounds, only one unidentified compound, with Kovats Index 1325, was observed in the shell beans (Table 2). Moreover, its amount was very low, close to the method detection limit. Given the presence of practically only reference compounds in shell beans, we may consider that the presence of these defective beans might not contribute negatively to the final cup quality of the beverage.

Husk fragments – in addition to the reference compounds, eight volatile compounds were observed in the husk fragments of group 2 (Table 2), including nonanal. Although, nonanal was not identified in any other defect of group 2, it was also identified in the black beans of group 1 (Table 1). Therefore, nonanal should be investigated more thoroughly as a potential marker compound for defects. An unidentified compound with Kovats index 1530 was also observed in the husk fragments.

Dried cherry beans – in addition to the reference compounds, six volatile compounds were observed in the dried cherry beans of group 2, being three of them aldehydes (Table 2). The same unidentified compound present in husk fragments (Kovats index 1530) was also observed here.

Table 2
Relative concentration (%) of the volatile compounds identified in SPME-headspace gas of raw samples of group 2

No.	Compound	ID[a]	Ik[b]	Control	Sour	Immature	Black	Black-immature	Shell core	Shell	Husk fragment	Dried cherry	Withered bean	Insect damaged	PVA
1	Unknown	–	1312	7.3	nd	nd	nd	nd	9.9	nd	nd	nd	nd	nd	nd
2	5-Methyl-2-hexanol	A	1348	8.9	13.8	11.3	8.8	8.4	t	t	4,8	3.9	nd	nd	9.0
3	1-Hexanol	A	1378	6.8	t	5.6	nd	nd	9.4	9.5	2,6	6.2	21.4	8.5	8.1
4	2-Methyl-2-ethenyl-5-(2-hydroxy-2-methyl)ethano-2-yl-tetrahydrofuran	C	1460	6.4	nd	nd	nd	3.7	nd	nd	2.9	5.1	nd	nd	5.0
5	1-Octen-3-ol	B	1473	3.9	t	2.8	8.2	5.8	nd	t	3.8	4.5	nd	nd	5.0
6	Acetic acid	B	1553	4.9	3.6	nd	7.4	12.0	10.1	7.5	9.0	5.9	nd	6.8	5.0
7	2-Ethyl-1-hexanol	C	1475	7.5	21.9	nd	8.1	4.3	8.7	14.2	10.0	19.5	42.5	10.0	nd
8	2,3-Butanediol (*levo*[c])	A	1555	14.5	11,2	nd	t	8.8	8.9	19.4	6.1	5.7	15.3	14.6	2.3
9	3,7-Dimethyl-1,6-octadien-3-ol (β-linalool)	C	1566	7.2	8.2	5.5	19.7	12.7	6.2	10.1	4.2	6.3	nd	nd	8.6
10	2,3-Butanediol (*meso*[c])	A	1594	11.0	18.0	nd	6.4	10.0	9.9	22.6	7.3	6.5	20.8	19.6	10.7
11	2-Furylmethanol	B	1679	7.6	nd	12.4	3.4	3.3	6.9	nd	nd	3.5	nd	nd	nd
12	3-Methylbutanoic acid	C	1689	4.2	8.7	nd	7.0	4.0	4.2	t	7.9	nd	nd	5.0	9.8
13	2-Hydroxy-2-methyl benzoate (methyl salicilate)	C	1787	3.5	4.2	3.0	14.5	5.7	4.0	7.5	6.8	nd	nd	nd	2.0
14	2-Phenyl-1-ethanol (phenylethyl alcohol)	B	1922	6.3	nd	2.5	5.0	5.0	4.3	9.2	3.2	2.3	nd	nd	1.8
15	Unknown	–	1325	nd	t	nd	nd	nd	nd	t	nd	nd	nd	nd	nd
16	Unknown	–	1424	nd	t	nd	nd	nd	nd	nd	8.1	nd	nd	nd	nd
17	Benzaldehyde	A	1539	nd	t	nd	nd	3.4	nd	nd	4.0	5.3	nd	nd	3.2
18	2,2-Dimethyl-1-propanol benzoate	C	1541	nd	t	nd	nd	3.3	nd	nd	nd	nd	nd	nd	nd
19	Unknown	–	1550	nd	t	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
20	Butyrolactone	A	1601	nd	4.7	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
21	Pyridine	A	1224	nd	nd	18.3	nd	nd	12.3	nd	nd	nd	nd	nd	nd
22	3-Methyl-1-butanol	A	1252	nd	nd	5.5	nd	4.4	nd	nd	nd	nd	nd	nd	8.9
23	2-Methylpyrazine	A	1295	nd	nd	8.0	nd	nd	nd	nd	nd	nd	nd	nd	nd
24	2,5-Dimethylpyrazine	C	1343	nd	nd	2.8	nd	nd	nd	nd	nd	nd	nd	nd	nd
25	2,5-Dimethyl-3-ethylpyrazine	B	1460	nd	nd	3.4	nd	nd	nd	nd	nd	nd	nd	nd	nd
26	2-Furancarbaldehyde (furfural)	C	1483	nd	nd	3.6	nd	nd	nd	nd	nd	nd	nd	nd	nd
27	2-Furylmethanol acetate	B	1557	nd	nd	10.7	nd	nd	nd	nd	nd	nd	nd	nd	nd
28	5-Methyl-2-furancarbaldehyde	C	1566	nd	nd	4.5	nd	nd	nd	nd	nd	nd	nd	nd	nd
29	3-Methylbutanal	A	1014	nd	nd	nd	t	nd	nd	nd	t	nd	nd	nd	nd
30	Pentanal	A	1034	nd	nd	nd	t	nd	nd	nd	nd	nd	nd	nd	nd
31	Hexanal	A	1153	nd	nd	nd	t	nd	nd	nd	nd	7.3	nd	25.8	t
32	2,3,5,6-Tetramethylpyrazine	C	1489	nd	nd	nd	nd	2.8	nd	nd	nd	nd	nd	nd	nd
33	2,3,5-Trimethylpyrazine	C	1424	nd	nd	nd	nd	nd	5.2	nd	nd	nd	nd	nd	8.1
34	Nonanal	B	1403	nd	nd	nd	nd	nd	nd	nd	4.6	nd	nd	nd	nd
35	Unknown	–	1521	nd	nd	nd	nd	nd	nd	nd	4.6	nd	nd	nd	nd
36	Unknown	–	1530	nd	nd	nd	nd	nd	nd	nd	5.0	5.9	nd	nd	3.2
37	Unknown	–	1869	nd	nd	nd	nd	nd	nd	nd	2.2	nd	nd	nd	nd
38	Unknown	–	1895	nd	nd	nd	nd	nd	nd	nd	2.8	nd	nd	nd	nd
39	Heptanal	A	1155	nd	nd	nd	nd	nd	nd	nd	nd	6.3	nd	nd	t
40	1,3-Dioxolona	C	1874	nd	nd	nd	nd	nd	nd	nd	nd	3.3	nd	nd	nd
41	Benzenemethanol (benzyl alcohol)	A	1897	nd	nd	nd	nd	nd	nd	nd	nd	2.6	nd	nd	4.4
42	1-(2-Methyl-phenyl)-ethanone	C	1290	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	8.5	nd

t – trace; nd – not detected.

[a] 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 agreed with Nist and Kovats Index agreed with literature data; C – mass spectrum agreed with first three indications in Nist virtual library of mass spectral (Kovats index not available in the searched literature).

[b] KI, Kovats index value calculated for the SUPELCO-Omegawax column.

[c] Isomers according to Peinado et al. (2007).

Therefore, this compound may be derived from coffee husk.

Withered beans – only four reference compounds were identified in the withered beans (Table 2). These beans showed the poorest volatile profile of all investigated types of coffee beans.

Insect damaged beans – in addition to the reference compounds, 2 volatile compounds were observed in the insect damaged beans – hexanal and 1-(2-methyl-phenyl)-ethanone (Table 2), the former being identified only in defective beans and the latter only in this specific defect. It is possible that this compound originates from decomposition of non-volatile compounds by a digestive enzyme of the insect coffee berry borer (*Hypothenemus haempei*). According to Toledo and Barbosa (1998) and Bee et al. (2005), only slight changes in sensorial aspects of the beverage such as acidity and bitterness take place, but the sensorial impact of the presence of 1-(2-methyl-phenyl)-ethanone in green beans should be thoroughly investigated after the roasting of the beans.

PVA – PVA 1 contained compounds identified in either sour, black, or black-immature beans. Although immature beans were the major defective beans in both PVA mixtures, typical compounds of immature beans were not observed. However, PVA 2 contained compounds characteristic of all defective beans, except for shell and withered, which presented the poorest volatile profile of all defects.

The compounds 2-methyl-isobutanol, 2,4,6-trichloroanisole, geosmin, 2-methoxy-3-isopropylpyrazine and 2-methoxy-3-isobutylpyrazine, which have been identified as responsible for coffee off-flavors (Bortoli & Fabian, 2001; Cantergiani et al., 1999; Spadone et al., 1990) were not detected in the investigated sets of samples. From the eight volatile compounds observed in raw defective coffee beans by Guyot et al. (1982), only β-linalool was detected in the present study. However, this volatile compound cannot be only associated with defective beans, because although it was detected in the black-immature beans of group 1, it was also detected in the healthy beans of group 2.

3.2. Roasted samples

PVA sample of group 1, and PVA and control samples of group 2 were roasted in the same conditions to moderately light or light medium degree. A total of 86 volatile compounds were observed in the roasted samples from groups 1 and 2 (Table 3), pyrazines and furans being major classes of compounds, with 20 and 14 compounds, respectively.

Eight compounds were identified in the control sample of group 2 (Table 3), that were not in PVA 2. However, these compounds were present in PVA 1 (Table 3), which could be explained by the presence of 41% of healthy beans in the mixture. Other compounds characteristic of good cup quality beans were also identified in PVA 1. An example is 2,3-pentanedione, that has an oily-butter odor (Czerny, Mayer, & Grosch, 1999; Semmelroch, & Grosch, 1996).

Eight compounds were exclusive of both roasted PVA samples: pyrazine, 2,3-butanediol *meso,* 2-methyl-5-(1-propenyl)pyrazine, hexanoic acid, 2-methoxy-4-ethyl-phenol, 1-methyl-4-[(methylethyl)thio]benzene (apparently identified for the first time in coffee), and two unidentified compounds. Although it was not possible to find the respective aromatic notes for all these compounds in the searched literature, most of them appear to confer negative notes to coffee aroma. Pyrazine has a characteristic pungent, sweet and slightly ammoniacal odor; 2,3-butanediol has been identified in stinker coffee beans – a kind of bean with a normal appearance, but with a very unpleasant flavour (Bee et al., 2005) – and its formation could be due to undesired fermentation (Vincent, Barel, & Challot, 1976); hexanoic acid has been associated with a heavy, acrid-acid, fatty rancid odor often described as sweat-like (Arctander, 1967, cited by Flament, 2002, p. 154) and 2-methoxy-4-ethyl-phenol (4-ethyl-guayacol) has been associated with roasted or burnt flavor, as well as with typical soy sauce flavor (Maga, 1978).

2-Phenyl-1-ethanol (PVA 2) and 2-methoxy-4-ethyl-phenol (4-ethyl-guayacol) (PVA 1 and 2) – were exclusively identified in defective beans, the latter being considered as an impact compound (Czerny, & Grosch, 2000). The presence of these two phenolic compounds in defective beans is in accordance with Farah et al. (2006), who observed a strong correlation between the contents of non-volatile phenolic compounds in coffee – caffeoylquinic and feruloylquinic acids – and low cup quality. The authors suggested that products from oxidation of phenolic compounds or from other chemical reactions involving phenolic compounds could be associated with low quality and perhaps with a specific off-flavor named Rio.

Pyridine, 2-penthylfuran, 2-ethenylpyrazine, furfuryl formate, 2-(2-furanylmethyl)-5-methylfuran, 2-phenyl-1-ethanol, and six unidentified compounds were found in PVA 1 or 2 but not in both investigated groups. This fact is coherent with the fact that both PVA samples were from different origins, and presented different percentual compositions of defective beans and therefore may generate different types and amounts of compounds during roasting. Pyridine is characterized by a pungent, penetrating and diffusive odor, generally described as nauseating, but in extreme dilution it becomes warm, burnt and smokey (Flament, 2002). 2-penthylfuran is perceived as earthy, moudly, oily anisic (Chemisis, 1994). In spite of 2-phenyl-1-ethanol's pleasant floral-woody, honey-like character, its presence at an excessive concentration may be undesirable (Arctander, 1967). Some of these compounds may confer pleasant or unpleasant notes depending on their concentrations. 2-ethenylpyrazine added a green and burnt note to a sugar syrup at a concentration of 40 ppm (Winter et al., 1975). 2-(2-furanylmethyl)-5-methylfuran, according to Winter et al (Winter et al., 1976), at a concentration of 10 ppm in a sugar syrup has a green-cooked taste, and in

Table 3
Relative concentration (%) of the volatile compounds identified in SPME-headspace gas of the roasted coffee beans

No.	Compound	ID[a]	IK[b]	Control group 2	PVA group 2	PVA group 1	No.	Compound	ID[a]	IK[b]	Control group 2	PVA group 2	PVA group 1
1	Pyridine	A	1118	nd	4,05	nd	46	2-Acethyl-3-methylpyrazine	C	1690	0.96	1.40	0.70
2	2,3-Pentanedione	B	1133	0.64	nd	t	47	Unknown	–	1695	nd	0.59	0.30
3	Pyrazine	A	1144	nd	1.06	0.68	48	Unknown	–	1700	nd	nd	0.10
4	2-Penthylfuran	B	1162	nd	nd	1.27	49	2-Methyl-5-(1-propenyl)pyrazine	C	1706	nd	0.58	t
5	2-Methylpyrazine	A	1187	3.78	7.23	4.02	50	Pyrazinamide	C	1724	0.44	0.62	0.70
6	1-Hydroxy-2-propanone	B	1318	1.04	0.76	1.24	51	Unknown	–	1728	nd	0.44	t
7	2,5-Dimethylpyrazine	B	1335	1.75	3.61	1.63	52	3-Methoxy-2-methyl-2-cyclopentenone	C	1735	0.77	0.52	0.60
8	2,6-Dimethylpyrazine	B	1341	1.85	3.49	1.88	53	4-Penten-1-ol	C	1741	0.28	0.30	0.40
9	2-Ethylpyrazine	B	1346	1.13	1.90	1.13	54	Unknown	–	1775	nd	0.49	nd
10	2,3-Dimethylpyrazine	B	1356	0.37	0.94	0.37	55	Unknown	–	1793	0.57	0.83	0.80
11	2-Ethyl-6-methylpyrazine	B	1392	1.41	2.25	1.10	56	1-Penthylpyrrole	C	1800	0.77	0.54	0.60
12	2-Ethyl-5-methylpyrazine	B	1398	1.00	1.84	0.87	57	1-(2,6,6-Trimethyl-1,3-cyclohexadien-yl)-(*E*)-2-Buten-1-one	C	1818	t	t	0.20
13	2,3,5-Trimethylpyrazine	B	1411	2.77	4.99	1.69							
14	2,6-Diethylpyrazine	B	1439	0.26	0.44	nd	58	3-Methyl-1,2-cyclopentadione	C	1828	0.78	t	0.30
15	2-Etenhylpyrazine	B	1443	nd	0.38	nd	59	1-(2-Furanylmethyl)-1H-pyrrole	C	1832	1.09	0.82	1.10
16	2,5-Dimethyl-3-ethylpyrazine	B	1448	1.73	1.85	1.25	60	Hexanoic acid	C	1849	nd	t	1.00
17	Unknown	–	1461	nd	nd	0.30	61	2-Metoxy-phenol (o-guayacol)	B	1861	0.07	0.82	0.50
18	Acetic acid	B	1464	4.60	1.93	4.73	62	6-Hydroxypyrazolo[3,4-d]pyrimidin-4-one	C	1867	0.79	0.61	0.70
19	2-Furancarbaldehyde (furfural)	B	1474	8.14	1.63	6.47	63	Unknown	–	1893	t	nd	0.20
20	1-Acethyloxy-2-propanone	B	1478	1.66	1.54	2.39	64	Unknown	–	1905	nd	nd	0.40
21	2-Etenhyl-6-methylpyrazine	B	1492	0.29	0.37	t	65	2-Phenyl-1-ethanol (phenylethyl alcohol)	B	1911	nd	0.44	nd
22	2-Methyl-3,5-diethylpyrazine	B	1494	1.19	1.53	0.90	66	1-Methyl-4-[(1-methylethyl)thio]benzene (isopropyl *p*-cresyl sulfide)	C	1922	nd	0.58	0.60
23	Unknown	–	1505	0.61	0.52	0.50							
24	Furfuryl formate	B	1508	nd	nd	0.40	67	2-Methyl-3-hydroxy-4H-piran-4-ona (maltol)	B	1956	3.04	0.92	1.20
25	1-(2-Furanyl)-ethanona	C	1510	2.10	1.30	0.80	68	1-(1H-pyrrol-2-yl)-ethanone	B	1968	0.97	1.12	1.10
26	1H-pyrrole	B	1524	0.49	1.24	1.00	69	Unknown	–	1986	1.26	0.77	1.40
27	Unknown	–	1528	0.53	0.32	0.60	70	Unknown	–	2008	nd	0.45	nd
28	2-Methyl-3-pentanone	C	1539	0.84	0.63	1.00	71	1-Pyrrole-2-carbaldehyde	B	2020	1.16	1.37	1.40
29	1-Acethyloxy-2-butanone	B	1543	0.41	t	0.60	72	2-Methoxy -4-ethylphenol (4-ethylguayacol)	B	2026	nd	0.70	0.50
30	2-Furylmethanol acetate	C	1546	4.66	4.33	4.60	73	2,5-Dimethyl-4-hydroxy-3-(2H)furanone	B	2030	1.94	0.52	0.90
31	Unknown	–	1571	nd	nd	0.30	74	Unknown	–	2039	0.55	0.29	0.70
32	5-Methyl-2-furancarbaldehyde	B	1577	11.81	6.07	8.00	75	Unknown	–	2076	t	nd	t
33	2,3-Butanediol (*meso*[c])	A	1582	nd	t	1.00	76	3-Pyridinemethanol (nicotinyl alcohol)	C	2100	t	0.55	0.60
34	1-(Methylethenyl)pyrazine	C	1594	t	0.61	0.50	77	2-Methoxy-4-vinylphenol (4-vinylguayacol)	B	2194	7.14	4.18	7.10
35	Furfuryl propanoate	B	1604	t	t	0.40	78	5-Methoxy-2,3-dimethylphenol	C	2208	0.95	t	0.50
36	2,2-Methylenebis-furan	B	1615	0.53	0.57	0.50	79	Unknown	–	2211	0.51	nd	0.50
37	1-Methyl-1H-pyrrole-2-carbaldehyde	C	1620	0.86	0.94	0.80	80	2-Furfurylden- 2 -furylmethylamine	C	2223	0.92	t	0.70
38	Butyrolactone	A	1627	1.07	2.42	1.80	81	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	C	2238	1.22	t	0.51
39	1-Acethyl-3-methylpyrazine	B	1637	t	0.61	0.40							
40	Unknown	–	1649	0.48	0.41	0.50	82	2,3-Dihydro-benzofuran	C	2302	t	nd	0.33
41	1-(1-Methyl-1H-pyrrol-2-yl)ethanone	C	1656	0.49	0.98	0.50	83	2-Hydroxypyridine	C	2310	t	nd	0.49
42	2-Furylmethanol	B	1667	12.12	15.30	14.30	84	2,3-Benzopyrrole (indole)	B	2320	t	nd	0.28
43	3-Methylbutanoic acid	C	1675	1.15	1.08	1.10	85	5-(hydroxymethyl)-2-furancarbaldehyde	C	2343	0.87	nd	0.31

(*continued on next page*)

Table 3 (*continued*)

No.	Compound	ID[a]	IK[b]	Control group 2	PVA group 2	PVA group 1	No.	Compound	ID[a]	IK[b]	Control group 2	PVA group 2	PVA group 1
44	Unknown	–	1682	0.72	0.66	0.50	86	Unknown	–	2360	nd	nd	t
45	2-(2-Furanylmethyl)-5-methylfuran	C	1685	nd	nd	0.20							

t – trace; nd – not detected.

[a] 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 agreed with Nist and Kovats Index agreed with literature data; C – mass spectrum agreed with first three indications in Nist virtual library of mass spectral (Kovats index not available in the searched literature).

[b] KI, Kovats index value calculated for the SUPELCO-Omegawax column.

[c] Isomers according to Peinado, Moreno, Maestre, and Mauricio (2007).

a concentration of 1 ppm, it imparts a liquorice-like note to a neutral soluble coffee beverage.

The compounds 1H-pyrrole, 2-ethylpyrazine, 2-acethyl-3-methylpyrazine, 1-(1H-pyrrole-2-yl)ethanone, 2-ethyl-5-methylpyrazine, 1-(2-furanylmethyl)-1H-pyrrole, and 1-pyrrole-2-carbaldehyde, that have been described by Agresti et al. (Agresti, Franca, Oliveira, & Augusti, 2007) as characteristic of defective beans, were detected in all roasted samples, including the control sample of group 2. This is in accordance with other previous studies which have also identified these compounds in roasted coffees of different cup qualities (Flament, 2002; López-Galilea, Fournier, Cid, & Guichard, 2006; Ryan et al., 2004; Sanz et al., 2001).

4. Conclusions

In the present work, a total of 124 different volatile compounds were observed in raw and roasted coffee samples, 97 being identified. From these compounds, 1-methyl-4-[(1-methylethyl)thio]benzene (isopropyl *p*-cresyl sulfide) seem to have been identified in coffee for the first time.

The present results indicate that it is possible by SPME-GC-MS to identify defective coffee beans' marker compounds for both raw and roasted coffees. 2-Methylpyrazine and 2-furylmethanol acetate showed to be potential markers of raw immature defective beans while butyrolactone showed to be a potential marker for raw sour defective beans. The detection of benzaldehyde and 2,3,5,6-tetramethylpyrazine in raw coffee seem to be associated with the presence of defects in general and their simultaneous detection may indicate the presence of black-immature defective beans. Potential marker compounds of moderately light roasted defective beans are pyrazine, 2,3-butanediol *meso*, 2-methyl-5-(1-propenyl)pyrazine, hexanoic acid, 2-methoxy-4-ethyl-phenol (4-ethyl-guayacol), 1-methyl-4-[(1-methylethyl)thio]benzene (isopropyl *p*-cresyl sulfide).

Considering the complexity of coffee aroma and that its volatile composition may vary according to genetics, soil composition, climate, agricultural practices, and roasting conditions, a larger number of samples need to be investigated to confirm the present results and identify new potential markers.

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