

JOURNAL OF FOOD COMPOSITION AND ANALYSIS

Journal of Food Composition and Analysis 20 (2007) 289-296

www.elsevier.com/locate/jfca

**Original Article** 

# Impact of "ecological" post-harvest processing on the volatile fraction of coffee beans: I. Green coffee

Oscar Gonzalez-Rios<sup>a</sup>, Mirna L. Suarez-Quiroz<sup>a</sup>, Renaud Boulanger<sup>b</sup>, Michel Barel<sup>b</sup>, Bernard Guyot<sup>b</sup>, Joseph-Pierre Guiraud<sup>c</sup>, Sabine Schorr-Galindo<sup>c,\*</sup>

> <sup>a</sup>Inst. Tecnol. de Veracruz, Miquel Angel de Ouevedo 2779, Apdo. Postal 539, Veracruz, Mexico <sup>b</sup>CIRAD-CP TA80/16, 34398 Montpellier Cedex 5, France <sup>c</sup>UMR-IR2B cc023 Université Montpellier-II, Place Bataillon, 34095 Montpellier Cedex 5, France

Received 16 January 2006; received in revised form 18 July 2006; accepted 19 July 2006

#### Abstract

Green coffees produced by three variants of the wet process and a new "ecological" process were characterised for their aroma using combined headspace solid-phase microextraction/gas chromatography-mass spectroscopy (HS-SPME/GC-MS) and headspace solidphase microextraction/gas chromatography-olfactometry (HS-SPME/GC-O). The effect of each post-harvest processing operation on the volatile fraction of the coffee produced was studied, particularly the effect of reducing the amount of water used in the process. The comparison of the green coffees from the different treatments revealed the importance of mucilage removal in distinguishing between the samples, and showed the merits of microbial mucilage removal in water to obtain coffees with a better aroma quality. These latter coffees were in fact characterised by pleasant and fruity aromatic notes, whereas those obtained after mechanical mucilage removal used in the ecological process were characterised by volatile compounds with an unpleasant note.

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Keywords: Green coffee; Post-harvest process; Aroma; Solid-phase microextraction (SPME); Gas chromatography-olfactometry (GC-O); Food safety

# 1. Introduction

The method chosen to prepare green coffee in producing countries depends on the species grown, and on the conditions and resources in each production region; the way a green coffee is obtained therefore differs. The dry method, generally used for Robusta, is technologically simpler than the wet method, which is generally used for Arabica coffee beans. Coffee preparation by the latter method consists in removing the pulp and skin from the cherries (or beans) while still fresh. This method comprises several stages. The first stage involves machine-pulping of the drupes; at this stage, the beans are still covered with remnants of pulp. They have to be washed in a series of concrete tanks or in appropriate machines. "Controlled" fermentation is then carried out, which eliminates any mucilage still stuck to the beans and helps to "improve beverage flavour" with the production of microbial volatile compounds and microbial metabolites which are precursor of volatile formed during roasting and also by limiting spontaneous fermentation due to incomplete mucilage removal (Finney, 1989; Barel and Jacquet, 1994; Mburu, 1999; Puerta-Quintero, 1999). In addition to the two main types of post-harvest process, dry or wet, different treatments exist for these two processes that are specific to each production region. As the wet process involves more stages than the dry process, it also has the largest number of variants. For example, in Mexico, conventional post-harvest coffee processing uses microbial mucilage removal under dry conditions (Bailly et al., 1992a), while in Kenya, fermentation is often carried out in water to prevent overfermentation of the mucilage (Vincent, 1971; Mburu, 1999). In fact, the wet process, as its name implies, consumes large amounts of water and is a major source of pollution in countries where it is used (Bailly et al., 1992b). To solve this problem, producers using the wet method are increasingly using post-harvest processes that use less

<sup>\*</sup>Corresponding author. Tel.: + 33 4 6714 4603; fax: + 33 4 6714 4292. E-mail address: galindo@univ-montp2.fr (S. Schorr-Galindo).

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water, introducing mechanical mucilage removal systems called "ecological" processes (Puerta-Quintero, 1999). Yet little is known about the impact of these new technologies on the quality of the coffee, or on its aroma potential. Not detecting the microbial fermentation stage is a risk that could result in physico-chemical and organoleptic modifications to the coffee. Scientific information on how new technologies affect the aroma quality of coffee beans and the brewed beverage is scarce and sometimes contradictory.

The purpose of this work was to study how three variants of the wet process and a new ecological method affected the aroma quality of green coffee. This study had the merits of identifying the volatile compounds of green coffee that were produced during post-harvest processing, or those present in the bean at the outset. In this way, it was possible to conclude how worthwhile the fermentation stage was, and see the effect of reducing the amount of water used during post-harvest processing on the amount of volatile compounds produced. Investigation of potent odorants from green coffees was performed using the headspace solid-phase microextraction (HS-SPME) in conjunction with gas chromatography-mass spectroscopy (GC-MS) and gas chromatography-olfactometry (GC-O). Vitzthum and Werkhoff were the first to use GC-O to analyse the volatile fraction of green coffee in 1976 (Clarke and Vitzthum, 2001; Grosch, 2001). HS-SPME on coffee was first utilised in 1994 for roasted coffee characterisation (Yang and Peppard, 1994). Even though these techniques have been applied separately to coffee samples since, our work was the first use of HS-SPM/GC-O for volatile compound characterisation in green coffee.

### 2. Material and methods

## 2.1. Biological material

The *Coffea arabica* samples used in this study came from the Veracruz production zone (Mexico). During the 2001–2002 harvest, ripe, defect-free coffee cherries were picked and divided into 40-kg batches of cherries.

# 2.2. Wet post-harvest processing treatments

Four wet post-harvest processing treatments were tested. They differed in the type of pulping and mucilage removal used. In treatments 1 and 2, pulping was carried out in

 Table 1

 Description of the wet post-harvest processing treatments used

water with a disc pulper, while in treatments 3 and 4 a vertical drum pulper (Penagos Hnos and CIA LTDA, Colombia) was used without water. The mucilage removal stage for treatments 1-3 was carried out microbially (natural fermentation). Mucilage removal in treatment 1 was carried out in water in  $0.5 \,\mathrm{m}^3$  polypropylene tanks. In treatments 2 and 3, microbial mucilage removal was carried out under dry conditions, in the same types of tanks as for treatment 1. The samples were washed as soon as the fermentation time had been judged sufficient: this was determined by assessing the breakdown of mucilage on the beans by touch (between 30 and 60 h). Treatment 4 used a vertical mechanical mucilage remover (Penagos Hnos and CIA LTDA, Colombia). Once the mucilage had been removed, the beans were dried in the sun on metal trays, in layers approximately 2 cm thick until a moisture content of about 12% was attained. The samples were frozen at -80 °C in plastic flasks pending their use. Table 1 summarises the wet processing treatments tested.

# 2.3. Preparation of coffee samples to study volatile compounds

Green coffee samples (100 g) from each post-harvest treatment were frozen 12 h at -80 °C prior to grinding. Grinding was carried out in a Perten<sup>®</sup> grinder (Laboratory Mill type 3600) on a 500 µm setting. After grinding, the ground coffee samples were frozen at -80 °C in plastic flasks pending their use.

# 2.4. Extraction of volatile compounds from the ground coffee by headspace-SPME

Ground coffee samples were brought to room temperature for 90 min prior to sampling for headspace analysis. A Carboxen/poly(dimethylsiloxane) (PDMS) (CAR/PDMS) type 75  $\mu$ m SPME fibre (Supelco Co., Bellefonte, PA, USA) was used to extract volatile constituents from the coffee headspace. One gram of ground coffee was placed in a 2 mL hermetically sealed flask, which corresponded to a headspace of 1/3 of the sampling flask. The flasks were placed for 30 min in an oven thermostatically regulated at temperatures of 25, 40 or 60 °C, to reach sample headspace equilibrium. Then, volatile compounds were extracted by placing the SPME fibre in contact with the headspace for 5–15 min at the equilibrium temperature. For compound

Treatment	Pulping	Mucilage removal	Water used <sup>a</sup>	Drying	Yield <sup>b</sup>
1	Disc pulper	Fermentation in water	13	Sun	$0.19 \pm 0.01$
2	Disc pulper	Dry fermentation	10	Sun	$0.19\pm0.02$
3	Vertical drum	Dry fermentation	5	Sun	$0.19 \pm 0.1$
4	Vertical drum	Mechanical mucilage removal	1.25	Sun	$0.22 \pm 0.01$

<sup>a</sup>l/kg of green coffees obtained.

<sup>b</sup>Weight of green coffees/weight of cherries.

# 2.5. HS-SPME/GC analysis

The chromatography analysis was performed with a Varian<sup>®</sup> 3300 chromatograph (Walnut Creek, CA, USA) equipped with a DB-WAX capillary column (J&W Scientific) measuring  $30 \text{ m} \times 0.32 \text{ mm}$  i.d., with  $0.25 \mu \text{m}$  phase coating. Injection was in splitless mode, at  $250 \,^{\circ}\text{C}$  with a Supelco specific SPME insert of 0.75 mm i.d. The carrier gas (hydrogen) flow was 1.5 mL/min. The column temperature was programmed from 44 to  $170 \,^{\circ}\text{C}$  at  $3 \,^{\circ}\text{C/min}$ , followed by a rise from  $170 \text{ to } 250 \,^{\circ}\text{C}$  at  $8 \,^{\circ}\text{C/min}$ . Detection was by a flame ionisation detector (FID) at  $300 \,^{\circ}\text{C}$ .

# 2.6. Combined gas chromatography-olfactometry

The aroma characteristics of the volatile compounds from each coffee sample were analysed by combined FID–olfactometry. A derivation with a deactivated column was used to bring half the effluents to an OD 01 sniffer system (SGE, Ringwood, Australia). The conditions used for olfactory perception were the same as those described above for HS-SPME/GC analysis. Detection was carried out independently by three judges and each detection was performed in triplicate on different days. For each odour stimulus, panellists gave odour description and recorded the detection time.

# 2.7. Combined gas chromatography-mass spectroscopy

The coffee SPME extracts were analysed on a GC–MS apparatus (HP-6890A GC connected to an HP-5973N MS) with a DB-WAX capillary column (J&W scientific) measuring  $30 \text{ m} \times 0.32 \text{ mm}$ , with a  $0.25 \mu \text{m}$  phase coating. Column temperature programming was identical to that described for GC-FID. Injection was in splitless mode for 4 min at 250 °C with a specific SPME insert. The mass range scanned was from 40 to 350 amu at a scanning rate of 2.89 scans/s. The transfer line temperature was 260 °C. The carrier gas (Helium) flow rate was 1.5 mL/min. The ionisation method used was electronic impact with an ionisation energy of 70 eV.

# 2.8. Identification of volatile compounds

The volatile constituents of the headspace were identified by comparing their calculated relative retention indexes with those given in the literature, and their mass spectra with those in the database (Wiley Mass Spectral Data). The relative retention indexes were calculated from the retention times of the compounds and of the linear alkanes (Retention Index Standard, Sigma). The aromatic notes of the compounds perceived by olfactometry were also used as identification criteria by comparing them to references in the literature.

# 2.9. Statistical analysis

In order to distinguish between green coffees from four post-harvesting processes, a principal components analysis (PCA) was applied to the means of data items from the olfactometry analysis (area of group note) by the Statistica software package (v6, Statsoft).

# 3. Results and discussion

## 3.1. Development of the HS-SPME extraction method

The headspace SPME method was used to extract volatile compounds because it is a simple solvent-free extraction/concentration method appropriated to characterise and discriminate coffee sample (Yang and Peppard, 1994; Bicchi et al., 1997, 2002; Costa-Freitas et al., 2001a, b; Akiyama et al., 2003). The CAR/PDMS 75 µm fibre was chosen because of its affinity for all classes of aroma compounds found in coffee, in order to gain a clearer picture of the differences between treatments (Roberts et al., 2000; Bicchi et al., 2002; Akiyama et al., 2003). An optimisation stage was performed beforehand based on the influence of the extraction temperature and duration. Extraction times of 5, 10, and 15 min were tested at temperatures of 25, 40 and 60 °C after an equilibrium time of 30 min at the given temperatures. Fig. 1 gives the evolution profiles for the total quantities of volatile compounds extracted under these conditions. It can be seen that a temperature of 40 °C gave the best extraction right from 5 min in terms of quantity with a higher total FID area. Furthermore, the number of compounds extracted is not modified with the increase of the temperature. Lengthening the extraction time did not modify extraction at 40 °C, but did lead to a loss of compounds at 60 °C, and to an increase of the extracted quantities at 25 °C with highest standard deviations. The extraction conditions chosen to give the best result in the shortest time were therefore a sample headspace equilibrium time of 30 min, and 5 min of fibre contact with the headspace at 40 °C.

# 3.2. Identification of volatile compounds

Table 2 gives a list of the 62 volatile compounds identified by HS-SPME/GC–MS. This is quite a large number of compounds, given that some 230–300 compounds have been detected in green coffee in recent years when the HS-SPME extraction method is used (Holscher and Steinhart, 1995; Cantergiani et al., 2001; Clarke and Vitzthum, 2001; Grosch, 2001; Flament, 2002). Moreover, studies conducted on green coffee have demonstrated between 30 and 50 compounds of interest with a majority of aldehydes (Czerny and Grosch, 2000; Yeretzian et al., 2002; Akiyama et al., 2003). It is known that the volatile fraction of coffee beans develops primarily in the form of alcohols, acids, esters and aldehydes (Barel et al., 1976;



Fig. 1. Variation in the total quantities of volatile compounds extracted by HS-SPME depending on temperature and time.

Table 2		
Volatile compounds identified in	green coffee by	HS-SPME/GC-MS

Peak	Compounds	RI exp. <sup>a</sup>	RI ref. <sup>b</sup>	Peak	Compounds	RI exp. <sup>a</sup>	RI ref. <sup>b</sup>
1	Acetaldehyde		690	32	Nonanal	1391	1385
2	Dimethylsulphide	_		33	1,3-Dichloro benzene	1434	
3	2-Propanone	814		34	Acetic acid	1452	1450
4	Methyl acetate	824	813	35	Furfural	1457	1449
5	4-Methyl octane	849		36	1-Octen-3-ol	1460	1441
6	2-Methyl furane	868		37	Heptanol	1464	1447
7	2,4-Dimethyl heptane	876		38	Benzaldehyde	1514	1502
8	Ethyl acetate	886	872	39	Propanoic acid	1541	1559
9	2-Butanone	903	908	40	2,3-Butanediol	1549	1583
10	2-Methyl butanal	909	910	41	5-Methylfurfural	1565	1563
11	3-Methyl butanal	912	910	42	Dimethylsulphoxide	1570	
12	Ethanol	944	929	43	γ-Valerolactone	1597	
13	Pentanal	978	935	44	y-Butyrolactone	1607	1632
14	2-Butanol	1027	1024	45	4-Methyl Benzaldehyde	1636	
15	Toluene	1031	1042	46	Butanoic acid	1636	1634
16	Propanol	1038	1037	47	Furfuryl alcohol	1664	1689
17	Ethyl isovalerate	1069	1060	48	Isovaleric acid	1672	
18	Hexanal	1087	1072	49	Hexanoic acid	1848	1828
19	Isobutyl alcohol	1105	1099	50	2,4 Dimethylbenzaldehyde	1853	
20	Ethyl benzene	1125		51	Guaiacol	1859	1840
21	2-Pentanol	1129	1118	52	Benzyl alcohol	1874	1858
22	1,3-Dimethyl benzene	1132		53	2-Phenyl ethanol	1903	1873
23	1-Methyl pyrrole	1133		54	Maltol	1952	
24	1-Butanol	1151	1145	55	2-Acetyl pyrrole	1970	1949
25	Pyridine	1185	1180	56	phenol	1998	1984
26	Isoamyl alcohol	1214	1208	57	γ-Decalactone	2121	2101
27	2-Pentyl furane	1229		58	γ-Undecalactone	2185	2210
28	1-Pentanol	1259	1240	59	4-Vinyl guaiacol	2185	2182
29	3-Hydroxy-2-butanone	1282	1273	60	Decanoic acid	2223	2253
30	3-Methyl-2-buten-1-ol	1329		61	Benzoic acid	2430	2399
31	1-Hexanol	1362	1360	62	5-Hydroxy 2-methyl furfural	2505	

<sup>a</sup>Experimental Kovacs indexes of green coffee calculated on a DB-WAX capillary column (J&W scientific). <sup>b</sup>Reference Kovacs indexes (Holscher et al., 1990; Cantergiani et al., 2001; Sanz et al., 2001). Full et al., 1999) during post-harvest processing. Two types of compounds are formed in this way, namely those derived from thermal reactions during drying, such as some aldehydes formed by the Maillard reaction between sugars and amino acids; and those that result from the fermentation stage, such as alcohols and esters. Acids and aldehydes may be of both origins. Some compounds known to play a role in aroma development during fermentation were identified in our samples: ethyl acetate, 2-phenylethanol, 2,3-butanediol, acetic and butanoic acids, 2 and 3-methylbutanal. The two latter compounds may also have a thermal origin by transamination and decarboxylation of amino acids, and through thermal degradation and oxidation of butanol (Spadone et al., 1990; Cantergiani et al., 2001).

#### 3.3. Comparison of the different treatments

#### 3.3.1. Chemical classes

It can be seen from Table 2 that the volatile compounds encountered in our green coffee samples were divided into 14 chemical classes. There were 14 alcohols, 8 aldehydes, 7 acids, 5 furans, 5 hydrocarbons, 4 lactones, 4 benzene compounds, 3 esters, 3 phenol compounds, 3 ketones, 2 sulphur compounds, 2 pyrroles, 1 pyridine and 1 pyrone. The number of volatile compounds identified in green coffee was reduced when compared to those identified in roasted coffee; the aroma of thermal origin was less welldeveloped in green coffee, as it had been produced only during drying. Worth noting is the absence of pyrazines along with the presence of furanes, ketones, phenols and pyridine. However, pyrazines were previously identified in green coffee (Czerny and Grosch, 2000; Cantergiani et al., 2001); their absence in this study was probably due to the use of the HS-SPME with the CAR/PDMS fibre chosen for its affinity for compounds in trace form or with low molecular weights (Roberts et al., 2000; Akiyama et al., 2003). As could be expected, the compounds of the acid, alcohol, aldehyde and ester chemical classes, which apparently come from the fermentation stage or were initially present in the bean, were present in larger numbers and quantities. These results were in agreement with those of Cantergiani et al. (2001), who identified 219 compounds in Mexican green coffee with a majority of alcohol and acids in terms of numbers and quantities. To date, more than 300 volatile compounds have been identified in green coffee, and more than 850 have been found in roasted coffee (Flament, 2002). However, a dynamic analysis of the headspace of green coffee identified 41 compounds of interest constituted by 15 aldehydes, 14 alcohols, 7 acids, 4 ketones and 1 hydrocarbon (Yeretzian et al., 2002). These results are similar to our results for these classes of compounds, but SPME allowed additional compounds of interest for the comparison of coffee aroma quality to be detected, especially esters, lactones, furans and sulphur compounds.

Fig. 2 shows the quantities of the different chemical classes of compounds in green coffees derived from the four post-harvest processes. Coffee from process 1 was richest in volatile compounds, notably alcohols, aldehydes, ketones and esters. The drier the microbial treatment, the less rich was the coffee in volatile compounds. The profiles of the green coffees in processes 2 and 3 were very similar. The majority of compounds in process 1 were also found in smaller quantities in processes 2 and 3, but there were very high hydrocarbon contents. The green coffee in process 4, which was the ecological process and the driest treatment, did not involve a fermentation stage, but it nonetheless displayed compounds thought to be of fermentation origin. However, these green coffees were less rich in esters and alcohols than in the microbial treatments, but sulphur compounds were more abundant. This result might have been due to spontaneous fermentation (not desired in the process) due to incomplete mucilage removal, confirmed by the higher weight of green coffee yield compared to the bean weight in this process (Table 1).

The fermentation stage therefore gave coffees richer in volatile compounds, and even more so if fermentation was



Fig. 2. Contents of the different chemical classes of the volatile compounds in green coffees produced by four post-harvest processes.

carried out in water. The fermentation stage is therefore important for ensuring the aroma quality of green coffees.

# 3.3.2. Odour compounds

To confirm the previous results and validate the positive effect of microbial treatments on the aroma quality of green coffees, an olfactory analysis was carried out on samples from the four processes. Table 3 gives a list of compounds that were detected by olfactometry with a comparison of the experimental notes and the reference notes for the characterised compounds. The olfactory impact of 27 compounds was perceived. These were mostly esters, alcohols and aldehydes. The olfactory notes were quite varied, mixing pleasant (fruity, floral, sweet, caramel and jam) and unpleasant odours (acrid, cabbage, pungent, sour, and burnt). Only a few studies have been published on the aroma characterisation of green coffee by GC-O, and some of our descriptors have already been cited in these studies as buttery, green, vegetable, earthy, pungent, fruity and floral (Spadone et al., 1990; Holscher and Steinhart, 1995; Czerny and Grosch, 2000; Sarrazin et al., 2000; Cantergiani et al., 2001). The use of headspace solidphase microextraction/gas chromatography-olfactometry (HS-SPME/GC-O) could not identify significant potent

Table 3Odour compounds identified in green coffee

Compound	Reference notes <sup>a</sup>	Sniffing notes
Acetaldehyde	Acrid, pervasive	Acrid/egg
Dimethylsulphide	Vegetable, cabbage	Cabbage
2-Propanone	Pervasive (H), sweet (L)	Lemon
Methyl acetate	Pleasant	Pleasant
Ethyl acetate	Fruity	Fruity
Ethanol	Alcohol	Sweet
Toluene	Solvent	Bitter
Ethyl isovalerate	Fruity	Fruity
Hexanal	Fruity/green	Green
Isobutyl alcohol	Unpleasant	Unpleasant
Isoamyl alcohol	Acrid, pungent	Pungent
1-Pentanol		Green
3-Hydroxy-2-butanone	Buttery	Buttery
Acetic acid	Sour	Sour
Furfural	Bitter almond	Bitter
1-Octen-3-ol	Earthy, herbaceous	Herbaceous
Benzaldehyde	Bitter almond	Bitter
2,3-Butanediol	Buttery, unpleasant	Unpleasant
5-Methylfurfural	Caramel	Caramel
Dimethylsulphoxide	Vegetable	Vegetable
γ-Butyrolactone	Pleasant	Pleasant
Furfurylalcohol	Burnt	Burnt
Isovaleric acid	Unpleasant	Unpleasant
2-Phenyl ethanol	Floral	Floral
Guaiacol	burnt (H), sweet (L)	Burnt
Maltol	Jam	Sweet
4-Vinyl guaiacol	Clove	Bitter

(H) high concentration.

(L) low concentration.

odorants like linalool, sotolon, vanillin or pyrazines (Czerny and Grosch, 2000). On the other hand, this method allows the determination of compounds not identified by a solvent method using solvents such as acetaldehyde, dimethylsulphide, methyl acetate and ethyl acetate, which had quite low detection thresholds and could make it possible to discriminate among samples from different post-harvest treatment. In order to facilitate the distinction, compounds with identical or similar odour were grouped. There were 15 olfactory notes, making it possible to characterise and distinguish between the four processes by their presence or their different quantities, as shown in Table 4 (the quantities corresponding to the sum of the peak areas for each component in the olfactory group). It is essential to mention that the peak area of a volatile compound is not necessarily connected with its contribution to the overall flavour, because the threshold value of the compound plays the major role. This first approach based only on the area of compounds is used to see if it is possible to use the volatile compound to differentiate coffee from various post-harvest treatments. The coffee from process 1 was richest in odorant compounds, notably esters with a fruity note such as ethyl acetate and ethyl isovalerate, or pleasant such as methyl acetate. This coffee was also richest in alcohol, notably ethanol, characterised by the sweet note and in 2phenylethanol with a floral aromatic note. These 2 chemical classes, which made up the largest proportion of volatile compounds in this coffee (see Fig. 2) also gave quality aromatic notes. This coffee was also the only one to be characterised in olfactory terms by maltol which was qualified as sweet. The second richest coffee in olfactory compounds was the one from process 4, the ecological process. However, it was less characterised by esters and alcohols, and more characterised by defective compounds such as the sulphur compounds, dimethylsulphide and dimethylsulphoxide with a cabbage aromatic note. It also contained abundant butan-2,3-diol with an unpleasant note and acetic acid with a sour note. These results back the hypothesis of undesired spontaneous fermentation due to incomplete mucilage removal, so it can be deducted that mechanical mucilage removal, although more ecological, leads nonetheless to off-aromas in green coffee.

# 3.3.3. Multivariate analysis

The olfactory analysis data (each sample was analysed in triplicate) were processed by a PCA (Fig. 3) to display the distinction between the four processes. A combination of principal components PC 1 and 2 accounts for 89% of the information and distinguishes between the processes based on the identified and grouped olfactory variables. The green coffee from process 1 was characterised by the most pleasant notes such as fruity, pleasant and sweet. However, the green coffee from process 4 gave stronger, more unpleasant aromatic notes such as sour, cabbage and bitter. The coffees from processes 2 and 3 were very similar and characterised only by caramel notes. The essential

<sup>&</sup>lt;sup>a</sup>Furia and Bellanca (1992), Czerny and Grosch (2000), and Cantergiani et al. (2001).

Table 4 Quantities<sup>a</sup> of odour compounds of Table 3 grouped by similar aromatic note<sup>b</sup> for green coffees from the four processes (values are means  $\pm$  sp; n = 3)

Notes	Compounds <sup>c</sup>	Process				
		1	2	3	4	
Acrid	1	$2.24 \pm 0.13 \times 10^{5}$	$1.76 \pm 0.16 \times 10^{5}$	$1.62 \pm 0.15 \times 10^5$	0	
Cabbage	2	$6.90 \pm 0.02 \times 10^4$	$3.25 \pm 0.02 \times 10^4$	$2.57 \pm 0.01 \times 10^4$	$5.26 \pm 0.01 \times 10^5$	
Fruity	3	$14.65 \pm 0.05 \times 10^5$	$9.59 \pm 0.04 \times 10^5$	$8.44 \pm 0.04 \times 10^5$	$4.00 \pm 0.03 \times 10^5$	
Pleasant	2	$5.91 \pm 0.03 \times 10^5$	0	0	0	
Sweet	2	$4.18 \pm 0.05 \times 10^5$	$2.13 \pm 0.03 \times 10^5$	$2.00 \pm 0.03 \times 10^5$	$2.52 \pm 0.03 \times 10^5$	
Green	2	$3.51 \pm 0.02 \times 10^5$	$7.68 \pm 0.16 \times 10^4$	$8.47 \pm 0.01 \times 10^5$	$1.68 \pm 0.03 \times 10^5$	
Buttery	1	$3.35 \pm 0.03 \times 10^4$	0	0	0	
Sour	2	$6.50 \pm 0.02 \times 10^4$	$7.50 \pm 0.02 \times 10^4$	$1.12 \pm 0.03 \times 10^5$	$3.00 \pm 0.01 \times 10^5$	
Herbaceous	1	$9.00 \pm 0.23 \times 10^3$	0	0	0	
Unpleasant	3	$1.21 \pm 0.02 \times 10^5$	$9.82 \pm 0.39 \times 10^4$	$5.25 \pm 0.24 \times 10^4$	$3.52 \pm 0.03 \times 10^5$	
Caramel	1	$7.50 \pm 0.50 \times 10^3$	$3.35 \pm 0.04 \times 10^4$	$2.06 \pm 0.26 \times 10^4$	$4.35 \pm 0.65 \times 10^3$	
Burnt	2	$1.47 \pm 0.71 \times 10^4$	$2.97 \pm 0.81 \times 10^4$	0	$1.68 \pm 0.26 \times 10^4$	
Floral	1	$2.13 \pm 0.25 \times 10^4$	$1.23 \pm 0.17 \times 10^3$	$4.35 \pm 0.22 \times 10^3$	$1.99 \pm 0.43 \times 10^4$	
Bitter	4	$3.15 \pm 0.67 \times 10^4$	$1.40 \pm 0.32 \times 10^4$	$4.16 \pm 0.49 \times 10^4$	$4.49 \pm 0.35 \times 10^4$	
Pungent	1	$1.48 \pm 0.06 \times 10^{5}$	$3.99 \pm 0.37 \times 10^4$	$5.17 \pm 0.41 \times 10^4$	$1.27 \pm 0.03 \times 10^{5}$	
Total	27	$3.57 \pm 0.06 \times 10^{6}$	$1.75 \pm 0.04 \times 10^{6}$	$1.60 \pm 0.04 \times 10^{6}$	$2.21\pm0.03\times10^6$	

<sup>a</sup>Means of peak areas for 3 analyses (arbitrary units).

<sup>b</sup>Sums of peak areas of compounds with similar aromatic note given in Table 3 (arbitrary units).

<sup>c</sup>Number of compounds of Table 3 with similar note.



Fig. 3. Principal components analysis of the aroma profiles for the four green coffees studied (three analyses per sample, noted a-c).

stage in post-harvest processing on which distinction was based was therefore mucilage removal. The mechanical treatment (4) gave coffees with more off-aromas and stood out from the microbial treatments. Among these, dry mucilage removal (2 and 3) gave similar coffees in aroma level despite different pulping, which confirms the importance of mucilage removal for discrimination. Moreover, these coffees were neutral when compared to those obtained with natural mucilage removal in water (1), which gave green coffees with excellent aroma quality.

#### 4. Conclusions

Given the results obtained from an analysis of volatile compounds, olfactory criteria provided enough information to distinguish between green coffees obtained by different processes. A reduction in the amount of water used in the processes decreased the aroma quality of green coffees. The new ecological process which was the driest process using pulping and mechanical mucilage removal gave green coffees with the most off-aromas. It clearly stood out from the processes using microbial mucilage removal, among which the wettest process using pulping and mucilage removal in water gave green coffees with an excellent aroma quality. The ecological advantage of the reduction of water in the process decreases, however, the aromatic quality of the green coffee obtained. These observations should be confirmed by roasted coffee analysis with the same analytical method to show how the change in aroma composition occurs during roasting and if differences between processes persist.

## References

- Akiyama, M., Murakami, K., Ohtani, N., Iwatsuki, K., Sotoyama, K., Wada, A., Tokuno, K., Iwabuchi, H., Tanaka, K., 2003. Analysis of volatile compounds releases during the grinding of roasted coffee beans using solid-phase microextraction. Journal of Agricultural and Food Chemistry 51 (7), 1961–1969.
- Bailly, H., Sallée, B., García-García, S., 1992a. El mejoramiento de la Calidad del Café en la Zona Xalapa-Coatepec (México). Café Cacao Thé XXXVI, 55–66.
- Bailly, H., Sallée, B., García-García, S., 1992b. Proyecto de Tratamiento de aguas residuales de benefícios húmedos. Café Cacao Thé XXXVI, 129–136.
- Barel, M., Jacquet, M., 1994. La qualité du café: ses causes, son appréciation, son amélioration. Plantations, recherche développement 1, 5–13.
- Barel, M., Challot, F., Vincent, J.-C., 1976. Contribution à l'Étude des Fèves de Café Défectueuses. Café Cacao Thé XX, 129–134.
- Bicchi, C.P., Panero, O.M., Pellegrino, G.M., Vanni, A.C., 1997. Characterization of roasted coffee and coffee beverages by solid phase microextraction-gas chromatography and principal component analysis. Journal of Agricultural and Food Chemistry 45, 4680–4686.
- Bicchi, C., Iori, C., Rubiolo, P., Sandra, P., 2002. Headspace sorptive extraction (HSSE), stir bar sorptive extraction (SBSE) and solid phase microextraction (SPME) applied to the analysis of roasted Arabica coffee and coffee brew. Journal of Agricultural and Food Chemistry 50, 449–459.
- Cantergiani, E., Brevard, H., Krebs, Y., Feria-Morales, A., Amadò, R., Yeretzian, C., 2001. Characterisation of the aroma of green Mexican coffee and identification of mouldy/earthy defect. European Food Research and Technology 212, 648–657.
- Clarke, R.J., Vitzthum, O.G. (Eds.), 2001. Coffee. Recent Developments. Blackwell Science Ltd, London, UK.
- Costa-Freitas, A.M., Parreira, C., Vilas-Boas, L., 2001a. Comparison of two SPME fibers of differentiation of coffee by analysis of volatile compounds. Chromatographia 54, 9–10.
- Costa-Freitas, A.M., Parreira, C., Vilas-Boas, L., 2001b. The use of an electronic aroma-sensing device to assess coffee differentiation-

comparison with SPME gas chromatography-mass spectrometry aroma patterns. Journal of Food Composition Analysis 14, 513-522.

- Czerny, M., Grosch, W., 2000. Potent odorants of raw Arabica coffee. Their changes during roasting. Journal of Agricultural and Food Chemistry 48 (3), 868–872.
- Finney, A., 1989. Technologie de Traitement du Café Arabica "Fully Washed". Café Cacao Thé XXXIII, 117–125.
- Flament, I., 2002. Coffee Flavour Chemistry. Wiley, New York, USA, pp. 79–99.
- Full, G., Lonzarich, V., Suggi-Liverani, F., 1999. Differences in chemical composition of electronically storted green coffee beans. In: Proceedings of the 19th International Conference on Coffee Science, Helsinki, Finland, Association Scientifique International du Café.
- Furia, T.E., Bellanca, N., 1992. Fenaroli's handbook of flavor ingredients, second edition. CRC Press, Boston.
- Grosch, W., 2001. Chemistry III: volatile compounds. In: Clarke, R.J., Vitzthum, O.G. (Eds.), Coffee. Recent Developments. Blackwell Science, London, UK, pp. 68–89.
- Holscher, W., Vitzhum, O.G., Steinhart, H., 1990. Identification and sensorial evaluation of aroma-impact-compounds in roasted coffee. Café cacao thé XXXIV 205–212.
- Holscher, W., Steinhart, H., 1995. Aroma compounds in green coffee. In: Charalambous, G. (Ed.), Food Flavors—Generation, Analysis and Process Influence. Elsevier Science, Amsterdam, pp. 785–803.
- Mburu, J.K., 1999. Notes on coffee processing procedures and their influence on quality. Kenya Coffee 64, 2861–2867.
- Puerta-Quintero, G.I., 1999. Influencia del Proceso de Beneficio en la Calidad del Café. Cenicafé 50, 78–88.
- Roberts, D.D., Pollien, P., Milo, C., 2000. Solid-phase microextraction method development for headspace analysis of volatile flavor compounds. Journal of Agricultural and Food Chemistry 48, 2430–2437.
- Sanz, C., Ansorena, D., Bello, J., Cid, C., 2001. Optimizing headspace temperature and time sampling for identification of volatile compounds in ground roasted arabica coffee. Journal of agricultural and food chemistry 49, 1364–1369.
- Sarrazin, C., LeQuéré, J.-L., Gretsch, C., Liardon, R., 2000. Representativeness of coffee aroma extracts: a comparison of different extraction methods. Food Chemistry 70, 99–106.
- Spadone, J.-C., Takeoka, G., Liardon, R., 1990. Analytical investigation of Rio off-flavor in green coffee. Journal of Agricultural and Food Chemistry 38 (1), 226–233.
- Vincent, J.-C., 1971. Essais comparatifs de Méthodes rapides de préparation du café Arabica. Café Cacao Thé XV, 49–54.
- Yang, X., Peppard, T., 1994. Solid phase microextraction for flavour analysis. Journal of Agricultural and Food Chemistry 42, 1925–1930.
- Yeretzian, C., Jordan, A., Badoud, R., 2002. From the green bean to the cup of coffee: investigating coffee roasting by on-line monitoring of volatiles. European Food Research and Technology 214, 92–104.