Influence of storage conditions on aroma compounds in coffee pads using static headspace GC–MS

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ABSTRACT

Static headspace gas chromatography coupled to mass spectrometry (SHGC–MS) was used to identify aroma compounds in coffee pad powder. Based on the peak areas of these aroma compounds, the influence of the type of original package on the time of evolution was studied. Statistical ANOVA indicated that coffee pads which were individually packed and hermetically sealed lost less aroma compounds than did pads which were enclosed together in an open package. In addition, coffee pads from an open package were stored in closed plastic bottles at two different temperatures. Storing the pads at 4 °C instead of keeping them at room temperature had a positive influence on the evolution of aroma compounds with time.

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1. Introduction

Coffee is one of the most widely consumed beverages in the world because it contains a wide range of aroma compounds, which is a very important factor in food quality (Kumazawa & Masuda, 2003). Coffee beans are obtained from the plants *Coffea arabica* and *Coffea canephora* (mainly variety robusta). The former is more valuable because its beans produce a better tasting beverage, which is therefore more expensive than the robusta coffee (Zambonin, Balest, De Benedetto, & Palmisano, 2005). During the roasting process of the green coffee beans, the aroma compounds are formed by a number of complex pyrolytic reactions, while different degrees of roasting (light, medium, dark) produce various aroma profiles (Mondello et al., 2005). Higher roasting temperatures result in darker coffee beans, as well as darker ground and brewed coffee. The roasting time, varying between 90 s and 40 min, also influences the reactions within the beans and thus the aroma characteristics of the coffee brew. Longer roasting times lead to a coffee with a bitter taste, whereas shorter periods produce a coffee with an underdeveloped aroma because not all pyrolytic reactions can be completed (Buffo & Cardelli-Freire, 2004).

The basic taste sensation of coffee is given by non-volatile compounds (e.g. caffeine, polysaccharides and chlorogenic acids), which determine bitterness, sourness and astringency. Furthermore, coffee contains over 800 volatiles that belong to different chemical families, including acids, alcohols, aldehydes, anisoles, esters, furans, ketones, pyrazines, pyridines, pyrroles, thiazoles and thiophenes, as well as phenolic and sulphur compounds (Buffo & Cardelli-Freire, 2004). But, as shown in previous studies (Lopez-Galilea, Fournier, Cid, & Guichard, 2006; Maeztu et al., 2001; Mayer, Czerny, & Grosch, 2000; Semmelroch & Grosch 1995), only a relatively small group of components is responsible for the coffee aroma (called key odorants). This aroma can be sensed either nasally (through the nose) or retronasally, i.e. the flavour obtained when the coffee is present in the mouth or has been swallowed, and the aroma compounds drift upward into the nasal passage.

Quantitative and qualitative analyses of aroma compounds in coffee are difficult, because they are mainly found at trace levels and are volatile (Costa Freitas, & Mosca, 1999). However, gas chromatography coupled with mass spectrometry (GC–MS) offers a sensitive analytical method that is commonly used for the analysis of coffee aroma. GC and MS complement each other; the former is known as an excellent tool for the separation of different components in a wide range of sample types and the latter is an established technique for the identification of unknown analytes (Grob & Barry, 2004).

For the GC–MS analysis of coffee aroma, the static headspace technique is predominantly used for sample preparation (Bicchi, Iori, Rubiolo, & Sandra, 2002; Maeztu et al., 2001; Sanz, Ansorena, Bello, & Cid, 2001). It is the most suitable method for studying volatiles because the prepared sample is near to a realistic representation of the coffee aroma perceived by the consumer (Mondello et al., 2005).

Most of the studies analyzing the aroma of conventional ground coffee and coffee brew were done in order to compare the effects of different sample preparation methods (Bicchi et al., 2002; Sanz et al., 2001). Other investigations have been focused on the aroma compounds of espresso coffee from different botanical varieties (Maeztu et al., 2001) and on the aroma differences in the brew caused by the preparation with a filter coffeemaker and an espresso machine, respectively (Lopez-Galilea et al., 2006). However, no work on the investigation of aroma compounds in coffee pads has been reported. This can be explained by the fact that the pads, and the required pad machine to prepare the brew, were introduced onto the market only about three years ago.

The first aim of this study was to identify the aroma compounds in coffee pad powder by using static headspace GC–MS. A further focus of attention was the change of aroma compounds under different storage conditions (time, temperature and packaging), based on the chromatographic peak areas.

2. Materials and methods

2.1. Coffee pad samples

Two different types of coffee pads ('strong' and 'Kachalu'), from the same brand, were obtained from a local store (Leuven, Belgium). The reproducibility of the aroma composition was evaluated by analyzing samples of three packages (A, B, C) of each type. In a first step, one sample from package A was analyzed. In order to evaluate the reproducibility between packages A, B, C and inside the pad (e.g. B1, B2), packages B and C were subsequently analyzed; two samples from each pad were taken.

2.2. Standards

The following standards of different compounds that were suspected to be present in the aroma of coffee pads were obtained from the chemical suppliers with source given in parentheses: butanal, 2,3-butanedione, 2-methylbutanal, 3-methylbutanal, methylpropanal and pyrazine (Acros Organics, Geel, Belgium); acetaldehyde, 2-acetylfuran and 2-ethylpyrazine (Sigma–Aldrich, St. Louis, MO, USA); 2,3-pentanedione (Merck, Darmstadt, Germany); 3-methylbutanoic acid (Janssen Chimica, Beerse, Belgium).

2.3. Static headspace GC–MS analyses

An AutoSystem XL Gas Chromatograph (PerkinElmer, Waltham, MA, USA) coupled to a TurboMass Gold Mass Spectrometer (PerkinElmer, Waltham, MA, USA) was equipped with a TurboMatrix 16 Headspace Sampler (PerkinElmer, Waltham, MA, USA). The GC–MS data were collected and handled by the Software TurboMass 4.4.0.

The samples were prepared from 400 (±5) mg of coffee powder that was taken out of the pads and placed in 22 ml headspace vials, which were sealed immediately with PTFE/butyl caps. Each vial was equilibrated at 60 °C for 15 min and 0.1 ml of the headspace sample was injected into the GC–MS instrument.

An Elite Wax capillary column (30 m × 0.25 mm × 0.25 μm film thickness; PerkinElmer, Waltham, MA, USA) with a polyethylene glycol stationary phase was used for the chromatographic analyses. The injector temperature of the GC was set at 230 °C and helium was the carrier gas with a column flow rate of 1.1 ml/min and a split flow rate of 10 ml/min. The oven temperature was held at 40 °C for 6 min and programmed to 190 °C at 3 °C/min.

The mass spectrometer operated in the electron ionisation mode (70 eV) with an ion source temperature of 200 °C. The full-mass-range mode was used for the analyses of the standards with a mass range of m/z 45–250 amu, a scan time of 0.2 s and an inter-scan

delay of 0.1 s. The SIM (single ion monitoring) mode was used for the analyses of coffee pad powder with a dwell time of 0.01 s and an inter-channel delay of 0.005 s (simultaneously full-mass-range mode with a scan time of 0.25 s and an inter-scan delay of 0.05 s).

2.4. Analyses of the standards

To analyse the available standards, a technique called total vapourization was used for the static headspace method. One microlitre of each standard was thermostatted for 10 min at 60 °C in the headspace vials in order to vapourize the entire sample; 0.02 ml of this headspace vapour was injected into the GC–MS system for the analysis.

2.5. Identification of aroma compounds in coffee pad powder

First, 400 (±5) mg of coffee pad powder of the two different types of coffee pads ('strong' and 'Kachalu') were analysed. To evaluate the reproducibility, one sample of package A, two samples of the same pad of package B and two samples of the same pad of package C were prepared for each type of coffee pad, resulting in the analysis of five samples for each coffee type.

After the headspace GC–MS analyses, a reverse searching with the NIST library was done for each aroma compound expected in the coffee pads. Furthermore, the retention times and mass spectra of the separated aroma compounds were compared with those of the standards. The identified peaks were integrated in order to determine their peak areas.

2.6. Investigation of the influence of storage conditions

To investigate the influence of the type of original package on aroma compounds, pads of both coffee types ('strong' and 'Kachalu') were stored in the original package at room temperature. It has to be mentioned that, in the original package, the coffee pads 'strong' were enclosed together, while those of the type 'Kachalu' were individually packed and hermetically sealed.

In addition, pads of the type 'strong' were removed from the original package and stored in closed plastic bottles at room temperature and at 4 °C, respectively.

Directly after opening the original package, as well as after 8, 14 and 21 days, one pad of each storage type was removed to analyze 400 (±5) mg of coffee pad powder with static headspace GC–MS.

The loss of aroma compounds influenced by the different storage conditions was evaluated semi-quantitatively, based on differences in peak areas. This was done by using a two-factor analysis of variance (ANOVA – General Linear Model) with the factor 'storage duration' as a covariant (fixed and quantitative; four storage durations). In the first part of this study, the time evolution of aroma compounds was compared for the pads 'strong' and 'Kachalu' stored at room temperature by using the factor 'original package' (fixed and qualitative; two original packages).

The second object was to evaluate the influence of storage packaging and temperature on the aroma compounds of the coffee type 'strong'. This was done by using, first the factor 'storage packaging' (fixed and qualitative; two packaging: original package and plastic bottle) and, second, the factor 'storage temperature' (fixed and qualitative; two temperatures: room temperature and 4 °C).

3. Results and discussion

3.1. Identification of aroma compounds in coffee pad powder

For the qualitative analysis of the two types of coffee pad powder ('strong' and 'Kachalu'), chromatograms with about 30 peaks

Table 1
Identified aroma compounds in the two types of coffee pad powder.

Compound	RT[a] [min]	Identification[b]	bp[c] [°C]
Aldehydes			
Acetaldehyde	1.73	A, B	21
Butanal	2.81	A, B	76
2-/3-Methylbutanal	3	A, B	92
Methylpropanal	2.14	A, B	64
Carboxylic acids			
3-Methylbutanoic acid	32.29	A, B	175–177
Furans			
2-Acetylfuran	25.55	A, B	167 (10 mmHg)
Dihydro-2-methyl-3(2H)-furanone	15.02	B	n/a
Ketones			
2,3-Butanedione	3.99	A, B	88
2,3-Pentanedione	6.35	A, B	110–112
Pyrazines			
2-Ethylpyrazine	18.16	A, B	152–153
Pyrazine	21.51	A, B	115–116
Sulfur compounds			
Methanethiol	1.71	B	6

[a] RT, retention time of the aroma compound.
[b] Identification is indicated by the following: (A) mass spectrum and retention time agreed with standard; (B) mass spectrum compared with NIST database.
[c] bp, boiling point of the aroma compound.

were obtained. Twelve of the 30 peaks were identified as aroma compounds by reverse searching with the NIST database and/or by comparing their mass spectra and their chromatograms with those of standards. The identified aroma compounds (Table 1) include four aldehydes, one carboxylic acid, two furans, two ketones, two pyrazines and one sulphur compound. These 12 compounds were found in both types of coffee pads.

3.2. Influence of different types of original packages

As the coffee pads 'Kachalu' and 'strong' have different types of original package, it was interesting to investigate differences in peak areas during storage at room temperature. Indeed, the 'Kachalu' pads were individually packed and hermetically sealed, while the 'strong' ones were enclosed together in the original package.

Figs. 1–3 show examples for the evolution of mean peak areas and standard deviations for some aroma compounds as a function of time for the two different types of original packages stored at room temperature.

According to ANOVA analysis, the compounds methylpropanal (Fig. 1), acetaldehyde, butanal, 2-/3-methylbutanal, 2,3-butanedione and 2,3-pentanedione show smaller decreases in peak areas with time for the pads 'Kachalu' than for the pads 'strong'. An explanation is that the aroma compounds in the type 'strong' could
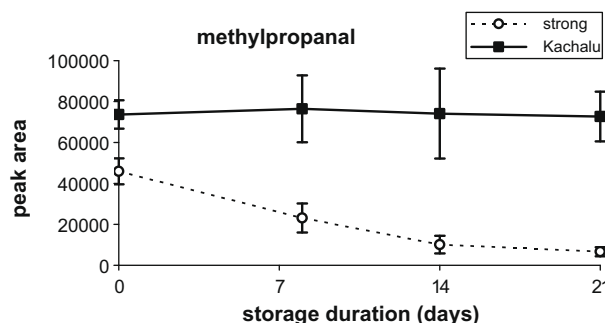

Fig. 1. Evolution of the peak areas of aroma compound methylpropanal as a function of storage duration for two different types of original packages.
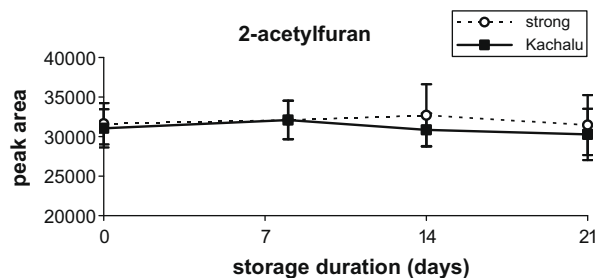

Fig. 2. Evolution of the peak areas of aroma compound 2-acetylfuran as a function of storage duration for two different types of original packages.
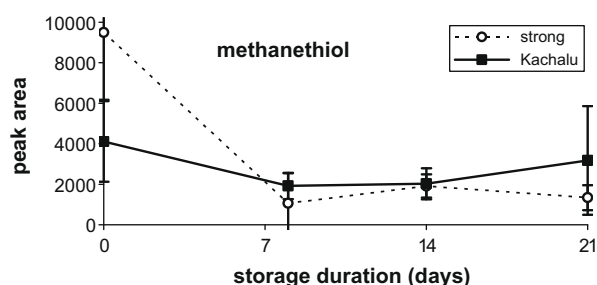

Fig. 3. Evolution of the peak areas of aroma compound methanethiol as a function of storage duration for two different types of original packages.

diffuse continuously into the atmosphere, leading to a greater loss. In addition, the boiling point of the six compounds named is below 112 °C (see Table 1). This supports their high volatilisation in pads of the type 'strong' stored at room temperature. As the volume of the gas phase inside the individual packages of 'Kachalu' pads is relatively small, the diffusion of volatile compounds from this powder into the gas phase is much lower and constant compared to that which occurs for 'strong' powder.

2-Acetylfuran (Fig. 2), 3-methylbutanoic acid, dihydro-2-methyl-3(2H)-furanone, 2-ethylpyrazine and pyrazine are aroma compounds that are not lost during storage of either coffee type. Their peak areas do not show a significant difference using ANOVA analysis. This is probably due to their higher boiling point (above 115 °C), hindering their diffusion into the gas phase at room temperature.

An exception is methanethiol (Fig. 3) as the peak areas decrease with time for both coffee types. The low boiling point of 6 °C can explain this loss of methanethiol during storage of the 'strong' type, as well as during weighing of the pad powder of both types.

3.3. Influence of different storage temperature and packaging

Part of the work investigated the influence of storage temperature and packaging on the aroma compounds identified in coffee pad powder of the type 'strong'.

The mean peak areas and standard deviations for some aroma compounds are shown in Figs. 4–6 for the three different storage conditions.

For acetaldehyde (Fig. 4), butanal, 2-/3-methylbutanal and methyl-propanal, ANOVA analysis indicated significantly different time evolutions for the three storage conditions. Compared to the storage of the pads in the original package, the storage in a plastic bottle had a positive influence on the aroma evolution of pads kept at room temperature. An explanation is that the plastic bottle was closed, allowing the volatile compounds to reach a state of equilibrium between the powder and the gas phase contained in-
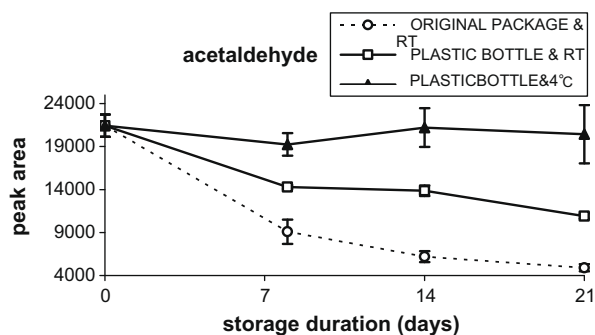
Fig. 4. Evolution of the peak areas of aroma compound acetaldehyde in 'strong' coffee pad powder as a function of storage duration under three different storage conditions.
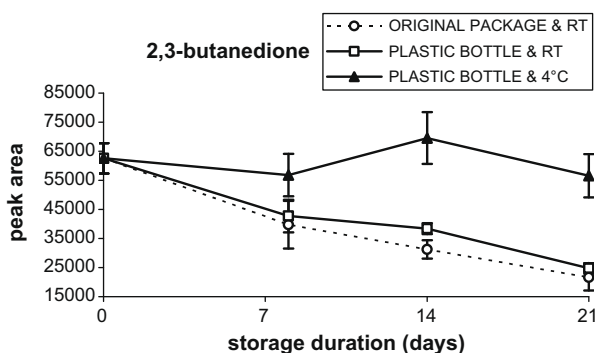

Fig. 5. Evolution of the peak areas of aroma compound 2,3-butanedione in 'strong' coffee pad powder as a function of storage duration under three different storage conditions.
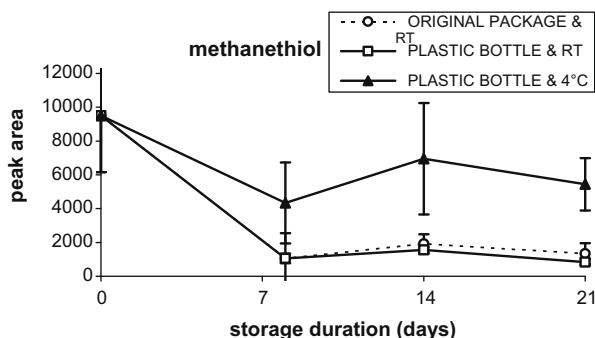

Fig. 6. Evolution of the peak areas of aroma compound methanethiol in 'strong' coffee pad powder as a function of storage duration under three different storage conditions.

side the plastic bottle. The original package was not closed and consequently the aroma compounds could diffuse continuously into the atmosphere. This causes a greater loss of aroma compounds for this storage type. The storage of the pads in a plastic bottle at 4 °C gives rise to the largest peak areas observed. Using a higher storage temperature causes a shift of equilibrium to the gas phase. Therefore, more aroma compounds are lost when storing the pads at room temperature than at 4 °C.

When comparing the storage of the pads at room temperature in the original package and in the plastic bottle, ANOVA analysis leads to the conclusion that there is no significant difference in peak areas for the aroma compounds 2,3-butanedione (Fig. 5),

dihydro-2-methyl-3(2H)-furanone, 2,3-pentanedione, pyrazine and methanethiol. However, the comparison of the storage in a plastic bottle at room temperature and at 4 °C indicates that significant differences in peak areas occur for these five aroma compounds. It can also be mentioned that methanethiol (Fig. 6) shows the largest decrease in peak areas, for all three storage conditions. This phenomenon can be explained by its low boiling point of 6 °C, which facilitates its volatilisation.

2-Acetylfuran and 2-ethylpyrazine show opposite behaviour. Indeed, the peak areas observed for the pads kept in the original package decrease less than those for the pads stored in a plastic bottle. Up to now, no explanation could be found for this phenomenon.

Furthermore, the aroma compound 3-methylbutanoic acid is not lost with time, whatever the storage conditions, since no significant differences in peak areas were found by ANOVA analysis. This is probably due to the very high boiling point of this compound (175–177 °C), which hinders its volatilisation at room temperature.

4. Conclusions

Twelve of the 30 peaks obtained by static headspace GC–MS were identified as aroma compounds in coffee pad powder. When comparing the peak areas of these compounds, under different storage conditions, it can be seen that storage in closed plastic bottles and at 4 °C decreases the loss of aroma compounds in coffee pads. Furthermore, this study showed that coffee pads should be individually packed and hermetically sealed in order to avoid loss of most of the aroma compounds identified in this work.

Acknowledgment

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