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Aroma simulation on the basis of the odourant composition of roasted coffee headspace†

Florian Mayer and Werner Grosch*

Deutsche Forschungsanstalt für Lebensmittelchemie, Lichtenbergstrasse 4, D-85748 Garching, Germany

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ABSTRACT: The concentrations of 22 potent odorants, including acetaldehyde, methylpropanal, 2- and 3-methylbutanal, 2,3-butanedione, 2,3-pentanedione, 2-furfurylthiol, 2-ethyl-3,5-dimethylpyrazine and 2,3-diethyl-5-methylpyrazine, were quantified in the headspace of roasted coffee powder. A model mixture containing these odorants was prepared on the basis of the results found in the headspace. When evaporated, the similarity of the aroma of this model mixture to that of the roasted coffee sample was scored 2.6 on a scale of 0 (no similarity) to 3.0 (identical). Also, after reduction of the model to the nine odorants mentioned above, the aroma was still scored 2.1. By determining headspace-concentrations of both freshly ground coffee and powdered coffee 15 min after grinding, and by preparing the corresponding aroma models, changes in the odour profile of a real coffee sample depending on the time passed after grinding could be reproduced. Results show this procedure to be suitable for establishing a composition of odorants causing the overall aroma of a food. Copyright © 2001 John Wiley & Sons, Ltd.

KEY WORDS: coffee flavour; headspace concentration; aroma simulation; quantitative analysis; isotope dilution assay

Introduction

As reviewed by Acree,[1] Grosch[6,7] and Schieberle,[18] the odorants that might cause the aroma of a food can be screened by Charm analysis or aroma extract dilution analysis (AEDA). The screened odorants are quantified and their odour activity values (OAV; ratio of concentration to odour threshold) are calculated. The odorants showing higher OAVs are used to formulate a synthetic blend (aroma model), which is compared with the real food product for similarity (or difference).

Preparation of aroma models is only simple for liquid foods, as it is easy to obtain a homogenous blend of odorants. Studies on the aroma of sour cream butter,[22] stewed beef juice,[9] coffee brew,[24] strawberry juice,[21] wine[8] and olive oil[16] are examples demonstrating that the suggested procedure leads to satisfactory results.

Difficulties arise, however, when aroma models are prepared for solid foods. In most cases it is not possible to imitate the composition and structure of the non-volatile part of the food and to simulate the distribution of the odorants in it. As a solution to this dilemma, different materials were compared with regard to their suitability for aroma models of solid foods, e.g. cellulose, sunflower oil and an oil/water mixture in a study on the character impact odorants of roasted coffee.[5] However, the aroma model for a solid food can only be improved when it is not affected by interactions with the material used as the base. This would be the case when the model reflects only the composition of the odorants in the headspace.

Zehentbauer and Grosch,[26] designed an apparatus based on the principle of dynamic headspace analysis to determine potent odorants released from French–type white breads (baguettes). Accurate quantitative data were obtained using stable isotopomers of the odorants as internal standards. By injecting known amounts of these compounds into the headspace of the food sample, they were collected by the dynamic procedure together with the analytes. On the basis of the results, a mixture of the odorants was prepared and its odour profile compared with that of the baguette, using the new apparatus as an olfactometer. The result was convincing, as the aroma of the synthetic blend was very similar to that of the original.

Comparing with the aroma of baguettes[26] polar odorants like guaiacol, 4-vinylguaiacol, alkylpyrazines and furanones are more important in the aroma of roasted coffee.[5] Therefore, whether these odorants can be

*Correspondence to: W. Grosch, Deutsche Forschungsanstalt für Lebensmittelchemie, Lichtenbergstrasse 4, D-85748 Garching, Germany. E-mail: Werner.Grosch@Lrz.tum.de
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accurately quantified in the headspace, so that a model aroma obtained from this quantification will match the odour profile of roasted coffee, is still unknown. The following study was carried out to explore this.

Materials and Methods

Coffee

Coffee beans (*Coffea arabica*) originating from Brazil and Colombia were roasted with a Neotec RFBS fluidized bed roaster, packed airtight in 300 g and 800 g portions, respectively, and stored at −35 °C. Beans from Brazil and Colombia had been roasted 3 years and 3 months prior to analysis, respectively. The degree of roast of the beans was characterized by colour values of 11.9 (Brazil) and 12.6 (Colombia, Color Tester LK 100; Dr Lange, Berlin, Germany). Initially, the beans were frozen in liquid nitrogen, ground, and sieved (diameter of the pores: 2 mm) with an ultracentrifugation mill (type ZM 1; Retsch, Haan, Germany). Particle size (μm) of the ground material was: < 200 (16–18%), 200–500 (59–60%), 500–800 (17–18%), and > 800 (6–7%).

Chemicals

Pure samples of the odorants listed in Table 1 and of the labelled internal standards used for the quantifications were obtained.[14]

Apparatus Used for Headspace Quantification and Sensory Evaluation

The apparatus (Figure 1; total volume 6.84 l) was designed, built, silylated, treated and prepared for analyses.[26]

Headspace Sampling

After grinding, coffee powder (0.1–10 g) was weighed onto 1–3 watchglasses (diameter 9 cm, maximum amount of powder per watchglass 3.33 g), quickly spread out on the glass and put in the middle of the tube (no. 10 in Figure 1), which was then sealed with a lid (no. 9). Valves no. 1, connected to a reservoir containing gaseous nitrogen under 30 kPa of pressure, and no. 2 were closed, while nos. 3 and 4 were opened.

Small volumes (10–200 μl) of solutions containing known amounts of the labelled internal standards in low-boiling organic solvents (diethyl ether, dichloromethane or methanol, except for labelled acetaldehyde, which was dissolved in water) were injected through the septum (no. 11) using a syringe and placed on the indentations of the glass finger (no. 12). This was heated to 80 °C using a hot water bath. The labelled methanethiol generated (concentration determined according to Mayer *et al.*[14]) was injected through the septum (no. 11) into the headspace of the apparatus with a gastight syringe (5–10 ml). Amounts of standards used varied between 0.3- and 3-fold concentrations of the odorant to be quantified. The coffee powder remained in the apparatus

Table 1. Concentrations of the odorants in the stock solutions and composition of the headspace aroma models of freshly ground Brazilian (I), of freshly ground Colombian coffee (II) and of Colombian coffee 15 min after grinding (III)

Odorant	Concentration of the stock solution (mg/ml) in pentane	Volume (μl) of the stock solution in aroma model[a]		
		I	II	III
Methanethiol (**1**)	Pure gas	930	1350	1350
Acetaldehyde (**2**)	Pure liquid	109	69	60
Methylpropanal (**3**)	53	100	113	38
2-Methylbutanal (**4**)	48	100	171	56
3-Methylbutanal (**5**)	30	100	147	57
2,3-Butanedione (**6**)	67	100	136	63
2,3-Pentandione (**7**)	65	100	138	68
(*E*)-ß-Damascenone (**8**)	0.14	100	214	229
2-Furfurylthiol (**9**)	3	100	127	150
Methional (**10**)	1.15	48	61	41
Guaiacol (**11**)	5.2	100	115	123
4-Ethylguaiacol (**12**)	1.5	147	100	87
4-Vinylguaiacol (**13**)	22	100	100	73
Vanillin (**14**)	3.15	200	250	206
2-Ethyl-3,5-dimethyl-pyrazine (**15**)	0.36	100	144	143
2,3-Diethyl-5-methyl-pyrazine (**16**)	0.13	108	100	115
2-Isobutyl-3-methoxy-pyrazine (**17**)	0.21	100	114	133
2-Ethenyl-3,5-dimethyl-pyrazine (**18**)	0.028	200	127	203
4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone (**20**)	11.2	321	179	143
2-Ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone (**21**)	2.0	135	100	65
3-Hydroxy-4,5-dimethyl-2(5*H*)-furanone (**22**)	0.3	87	67	87

[a] After mixing, the solution of the odorants was diluted with pentane to a volume of 10 ml.

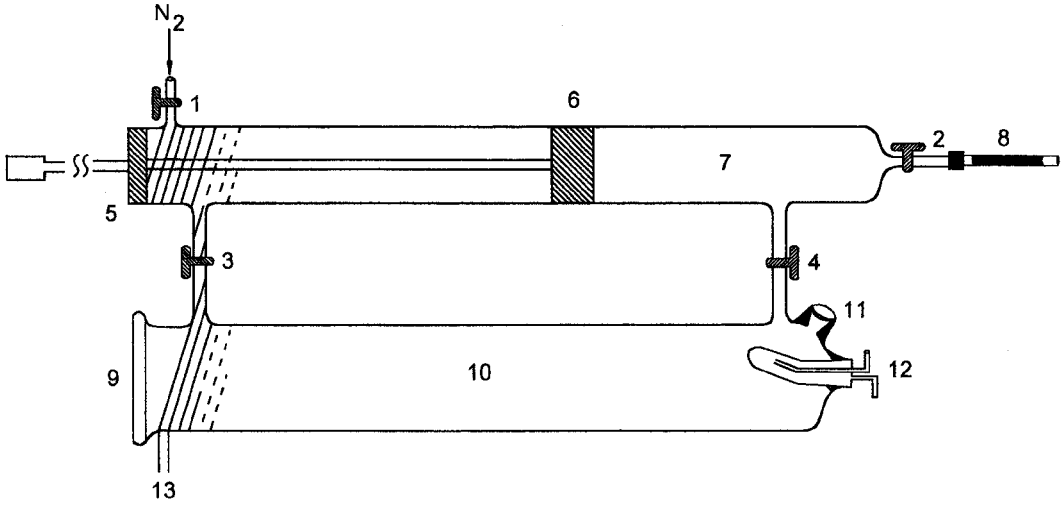

Figure 1. Apparatus used to determine odorants released from coffee powder into the headspace.[26] 1–4, Gastight valves; 5, lid; 6, piston; 7, upper tube; 8, Tenax trap; 9, lid; 10, lower tube; 11, septum; 12, heatable glass finger; 13, heating system

for 15 or 30 min. During this period the piston (no. 6) was pushed and pulled (10 motions/min) to accelarate the adjustment of a balance of the vapour phases in the tubes (nos. 7 and 10). After certain times, valves nos. 3 and 4 were closed and nos. 1 and 2 were opened. After opening, the gaseous nitrogen pressed the backdrawn piston (no. 6) and the headspace in tube no. 7 (ca. 2.7 l) into the Tenax trap (no. 8, glass-liner 160 × 4 mm, filled with Tenax TA, Chrompack, Frankfurt, Germany). In the case of the determination of acetaldehyde, a short glass column (10 × 0.5 cm) filled with $CaCl_2$ was placed between the outlet of tube no. 7 and the inlet of the Tenax trap (no. 8) to remove the water from the headspace. The low-volatile odorants **8–22** were trapped on a glass column, 30 × 0.5 cm, filled with Tenax TA (20–35 mesh, 0.5 g, Chrompack, Frankfurt, Germany) and rinsed with diethyl ether (freshly distilled, 100 ml) prior to use. The velocity of the gas leaving the outlet of the Tenax trap amounted to 200 ml/min at maximum.

After each run, the apparatus was cleaned in the following way: the lids (nos. 5 and 9) and the piston (no. 6) were removed, tube no. 7 was sealed with a cork, valve no. 4 was opened, and nos. 2 and 3 were closed. The walls of the apparatus were heated to 80 °C for 30 min using a heating tape (no. 13; HBSI, 15 m, 970 W, controlled by HT 51 NiCrNi-sensor; Horst, Bensheim, Germany), which was wrapped around the whole apparatus. During this time the apparatus was flushed with nitrogen from the reservoir, connected to valve no. 1.

Quantification

Quantification of the highly volatile odorants **1–7** in the headspace was performed with a CP-9001 gas chromatograph, interfaced to the purge and trap system TCT/PTI 4001 (Chrompack, Frankfurt, Germany). The TCT/PTI 4001 system was controlled via the keyboard of the gas chromatograph. After headspace sampling, the Tenax trap (no. 8) was put in the desorption heating block of the purge and trap system. The purge unit was operated in desorption mode for 10 min at 200 °C with helium (flow rate: 20 ml/min) as carrier gas sweeping the headspace sample into the trap (40 cm × 0.53 mm fused-silica capillary coated with CP-Sil 8 CB, film thickness 5 μm) precooled with liquid nitrogen at −110 °C for 2 min. To start the high-resolution gas chromatography (HRGC), the trap's temperature was raised rapidly to 200 °C. This was held for 1 min, and the sample flushed with helium (flow rate 2 ml/min) into the GC capillary (DB 5: 30 m × 0.32 mm, 0.25 μm film thickness; J&W Scientific, Folsom, USA). The initial GC temperature of 0 °C was held for 3 min and then raised to 250 °C at 6 °C/min. The capillary was connected to the mass spectrometer INCOS XL (Finnigan, Bremen, Germany) and mass chromatograms were recorded in chemical ionization mode (CI) at 115 eV, with methane as a reagent gas. The selected ions and the calibration factors used for quantification of the odorants were the same as reported previously.[14] After each run, the Tenax trap (no. 8) in the purge system was automatically cleaned (clean-up flow: 30 ml/min helium at 275 °C for 30 min). After this procedure, the trap had to be used for headspace sampling again within 24 h.

Quantification of the odorants **8–22** was performed by Multidimensional Gas Chromatography (MDGC; Fisons Instruments, Mainz-Kastell, Germany) as detailed by Mayer *et al.*[14] using the same modifications. The effluent of the first analytical GC-capillary (DB-FFAP: 30 m × 0.32 mm, 0.25 μm film thickness; J&W Scientific,

Table 2. Retention index range of the effluent from the first gas chromatography column (FFAP) that was cut out for the determination of the low volatile odorants via multidimensional gas chromatography (MDGC)

Odorant	Retention index (FFAP)	Retention index range for cut-out (FFAP)
2-Furfurylthiol (**9**)	1432	1400–1470
2-Ethyl-3,5-dimethylpyrazine (**15**)	1450	1420–1480
Methional (**10**)	1450	1420–1480
2,3-Diethyl-5-methylpyrazine (**16**)	1485	1450–1520
3-Isobutyl-2-methoxypyrazine (**17**)	1520	1490–1550
2-Ethenyl-3,5-dimethylpyrazine (**18**)	1553	1520–1580
2-Ethenyl-3-ethyl-5-methylpyrazine (**19**)	1585	1550–1620
(*E*)-ß-Damascenone (**8**)	1815	1780–1850
Guaiacol (**11**)	1850	1820–1880
4-Ethylguaiacol (**12**)	2032	2000–2070
4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone (**20**)	2035	2000–2070
2-Ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone (**21**)	2090	2060–2120
3-Hydroxy-4,5-dimethyl-2(5*H*)-furanone (**22**)	2200	2170–2230
4-Vinylguaiacol (**13**)	2205	2170–2240
Vanillin (**14**)	2560	2520–2600

Folsom, USA), eluting at the retention-index ranges shown in Table 2, was cut out. It was cryofocused in a trap cooled with liquid nitrogen and then transferred by flash heating (200 °C) onto a second analytical GC-column (DB 1701: 30 m × 0.32 mm, 0.25 μm film thickness; J&W Scientific, Folsom, USA). The odorants and the corresponding internal standards were recorded with an ion trap detector ITD 800 (Finnigan, Bremen, Germany), operated in chemical ionization mode at 70 eV, using methanol as a reagent gas. The selected ions and calibration factors for quantification were the same as reported by Mayer *et al.*[14] The carrier gas was helium with a flow rate of 2 ml/min. After headspace sampling, the Tenax trap containing the analytes and their labelled internal standards was eluted with diethyl ether (freshly distilled, 30 ml). The sample obtained was concentrated to 50 μl by distilling off the solvent on a Vigreux column, 40 × 1 cm, followed by microdistillation according to Bemelmans[2] and finally in a *Dünges* tube.[13] The samples (0.5 μl) were applied by the on-column injection technique at 35 °C. The initial temperature was held for 2 min; raised to 60 °C at 40 °C/min, held isothermally for 1 min, and finally raised to 240 °C at 6 °C/min. For the second GC capillary the initial temperature of 40 °C was held for 2 min, raised to 50 °C at 40 °C/min, held for 1 min and then raised to 230 °C at 6 °C/min and held for 10 min.

Quantification of the total amount of odorants in coffee powder was performed according to Mayer *et al.*[14]

Aroma Models

Concentrations of the Odorants

Pure samples of odorants **1** and **2** were directly used for preparing the model (Table 1). The amounts of the odorants **3–17** and **20–22** were determined by weight. The compounds were dissolved in pentane: in the case of **14**, **20** and **21** they were first dissolved in a small volume of diethyl ether, then filled up with pentane to prepare the stock solutions listed in Table 1. The concentration of odorant **18** was determined by high-resolution gas chromatography (HRGC), using a DB-1701 fused silica capillary (30 m × 0.32 mm, 0.25 μm film thickness; J&W Scientific, Folsom, USA) in a 5160 gas chromatograph (Carlo Erba, Hofheim, Germany) with flame ionization detector and the conditions (carrier gas flow, temperature programme) as reported above. 2,3-Diethyl-5-methylpyrazine was used without correction factor as the internal standard.[5]

Sensory Analysis

Assessors

The odour profile of the model was compared with that of the corresponding coffee powder sample. The panel, consisting of two women and four men aged 25–35 years, were trained in weekly sessions with 36 odorants representing different odour qualities in different concentrations varying in the factor above their odour threshold (Table 3). In each session the panelists evaluated the odour intensity of up to three known odorants on a category scale of 0 (not perceptible) to 3 (strongly perceptible), as well as the odour quality and intensity of up to six unknown odorants, with which the panelists had been acquainted in preceding sessions. In the latter test, the panelists had to identify the compounds on the basis of their odour quality. The six assessors were familiar with coffee flavour, as they had participated in at least one of our coffee studies quoted in the reference list.

Table 3. Reference stimuli for training the sensory panel

Odorant	Concentration of the odorants in water (μg/l)	Factor above the nasal odour threshold in water (μg/l)[a]	Odour quality
2-Acetyl-1-pyrroline	0.3–3	3–30	Roasty
2-Acetyl-2-thiazoline	5–40	5–40	Popcorn-like
p-Anisaldehyde	150–200		Anis-like
Benzaldehyde	1050–105 000		Almond-like
bis-(2-Methyl-3-furyl-)disulphide	$60–30\,000 \times 10^{-5}$	30–15 000	Meat-like
2,3-Butanedione	15–450	1–30	Butter-like
Butyric acid	20 000–80 000	20–80	Sweaty
S-(+)-Carvone	1000–1500		Carvon-like
(*E*)-ß-Damascenone	0.2–0.48	50–120	Honey-like, fruity
(*E*,*E*)-2,4-Decadienal	1.2–26	6–130	Fatty
Decanal	16.8–63	8–30	Orange-like, flowery
Dimethyl trisulphide	0.06–0.5	6–50	Sulphurous, cabbage-like
trans-4,5-Epoxy-(*E*)-decenal	0.15–0.3	10–20	Metallic, green
Ethylbutanoate	13.6–136	1–10	Fruity
2-Ethyl-3,5-dimethylpyrazine	3.2–19.2	20–120	Earthy, musty
2-Furfurylthiol	0.8–7	8–70	Coffee-like, roasty
Geraniol	250–650	50–130	Rose-like
Guaiacol	15–50	6–20	Smoky
Hexanal	5.8–1160	1–200	Green, leaf-like
(*E*)-2-Hexenal	500–1500	10–30	Apple-like
3-Hydroxy-4,5-dimethyl-2(5*H*)-furanone	6–30	20–100	Spicy
4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone	200–1200	20–120	Caramel-like
1-(*p*-Hydroxyphenyl)-3-butanone	100–300	10–30	Raspberry-like
ß-Ionone	0.35–3.5	50–500	Violet-like
Linalool	50–250	10–50	Flowery
3-Mercapto-3-methylbutylformate	0.28–1.05	80–300	Blackcurrant-like
Methional	3–16	15–80	Cooked potato-like
3-Methylbutanal	6–40	15–100	Malty
Naphthaline	15–100		Mothball-like
(*E*,*Z*)-2,6-Nonadienal	0.2–1	20–100	Cucumber-like
γ-Nonalactone	195–1950	3–30	Fruity, peach-like
(*E*)-2-Nonenal	2.4–40	3–50	Green, cucumber-like
δ-Octalactone	3200–20 000	8–50	Coconut-like
1-Octen-3-one	0.15–2	3–40	Mushroom-like
Phenylacetaldehyde	28–320	7–80	Honey-like, beeswax-like
Vanillin	500–6250	20–250	Vanilla-like

[a] According to Rychlik *et al.*[17]

Aroma Models

With the exception of 2-ethenyl-3-ethyl-5-methylpyrazine (**19**), stock solutions were prepared for 21 of the 22 odorants determined (Table 1). Pyrazine **19** was substituted by increasing the amount of pyrazine **15** as they both have the same odour quality and a similar odour threshold.[5] The volumes of the stock solutions detailed in Table 1 were pipetted together and filled to 10 ml with pentane.

Odour Profile Analysis

The apparatus for headspace sampling (Figure 1) was used as an olfactometer. Immediately and 15, 60 and 180 min after grinding, a coffee sample (2.5 g) was placed into the apparatus as described above. The Tenax trap (no. 8) was omitted; valves 1 and 2 were closed and valves 3 and 4 opened. To accelerate the equilibration of odorants in the apparatus, piston no. 6 was pushed and pulled 10 times/min. After 15 and 30 min, respectively, valves 3 and 4 were closed and valve 2 opened, and the back-drawn piston pushed slowly to produce a constant stream of odorants, perceived by an assessor, at the outlet of valve no. 2.

After cleaning the apparatus (see Headspace sampling), which lasted approximately 1 h, an aliquot (25 μl) of the aroma model was injected with a syringe through the septum (no. 11), placed on the indentations of the glass finger (no. 12) and heated to 80 °C. After accelerating the equilibration of the odorants in the apparatus by pushing and pulling the piston (no. 6) 10 times/min for 10 min, valves 3 and 4 were closed and valve 2 opened. Then the back drawn piston was pushed slowly to produce a constant stream of odorants perceived at the outlet of valve no. 2 by the assessor.

In the comparative odour profile analysis of the coffee powder sample and the model, the intensities of the odour qualities 'sweetish/caramel-like', 'earthy', 'roasty/sulphurous' and 'smoky' were scored on a category scale of 0 (not perceptible) to 3 (strongly perceptible) in increments of 0.5. These four attributes were determined by the sensory panel in previously performed

odour profile analyses of coffee powder and brew samples.[5,15] The panelists also rated the similarity of the odour of the model mixture headspace to the real coffee sample headspace on a category scale of 0 (no similarity) to 3 (identical). The results obtained by the six panelists were averaged, and the standard deviations calculated.

Results and Discussion

Detection of Odorants in the Headspace

To see whether the apparatus designed by Zehentbauer and Grosch[26] for the quantitative determination of odorants in the headspace of French baguette was also suitable for the quantification of odorants in the headspace of roasted coffee, an old sample of medium-roasted Arabica coffee from Brazil (roasted 3 years prior to this research) was used for the first set of experiments. Initially, odorants were detected by gas chromatography–mass spectrometry in the headspace of a roasted coffee powder sample allowing a quantitative determination using stable isotope dilution assays.[19] After 30 min in the apparatus at room temperature, 22 important odorants of roasted coffee were identified in the headspace of 10 g of coffee powder. High-volatile odorants, methanethiol, acetaldehyde, methylpropanal, 2- and 3-methylbutanal, 2,3-butanedione and 2,3-pentanedione were detected after thermal desorption from a Tenax-trap.[26] Low-volatile odorants **8–22**, especially those in lower concentrations, could only be detected after enrichment by solvent extraction from a Tenax-trap[20] and employing MDGC. Of the 28 potent odorants of coffee powder identified in dilution experiments by Holscher *et al.*,[11] Blank *et al.*,[3] Semmelroch and Grosch[23] and Czerny *et al.*[4] and quantified by Semmelroch *et al.*[25] and Mayer *et al.*[14] in Arabica and Robusta coffees, only the three sulphur-containing odorants, 2-methyl-3-furanthiol, 3-mercapto-3-methylbutylformate and 3-methyl-2-buten-1-thiol, as well as 5-ethyl-3-hydroxy-4-methyl-2(5H)-furanone, could not be detected due to too low concentrations in the headspace. Dimethyl trisulphide and propanal were not analysed.

Experiments on the Stability and Evaporability of the Standards

Using heat-labile 2-acetyl-1-pyrroline as an example, Zehentbauer and Grosch[26] examined the stability of the isotope-labelled internal standards when placed on the heated glass finger of the apparatus. As this compound was not degraded, they concluded that all internal standard compounds were stable during this step of analysis.

In the present study, the completeness of evaporation of low-volatile odorants from the heated glass finger into the headspace of the apparatus was tested using methional, 3-isobutyl-2-methoxypyrazine and vanillin as examples. After 30 min, only 0.25% of vanillin but no material of the two other compounds were found to be remaining on the glass finger. It would appear that the isotope-labelled internal standards evaporated quantitatively from the heated glass finger during the 30 min the coffee sample remained in the apparatus.

Table 4. Concentration of odorants in freshly ground Brazilian coffee and in its headspace[a]

Odorant	Total concentration (ng/g)	Headspace concentration[a] (ng/g)	FR-value (%)
Methanethiol (**1**)	4500	2000	44
Acetaldehyde (**2**)	131 000	85 400	65
Methylpropanal (**3**)	22 200	5300	24
2-Methylbutanal (**4**)	28 600	4800	17
3-Methylbutanal (**5**)	16 900	3000	18
2,3-Butanedione (**6**)	55 700	6700	12
2,3-Pentandione (**7**)	28 300	6500	23
(*E*)-ß-Damascenone (**8**)	245	14	5.7
2-Furfurylthiol (**9**)	1350	300	22
Methional (**10**)	148	55	37
Guaiacol (**11**)	3520	520	15
4-Ethylguaiacol (**12**)	1760	220	13
4-Vinylguaiacol (**13**)	45 000	2200	4.9
Vanillin (**14**)	2690	630	23
2-Ethyl-3,5-dimethyl-pyrazine (**15**)	363	34	9.4
2,3-Diethyl-5-methyl-pyrazine (**16**)	150	14	9.3
2-Isobutyl-3-methoxy-pyrazine (**17**)	84	21	25
2-Ethenyl-3,5-dimethyl-pyrazine (**18**)	55	5.5	10
2-Ethenyl-3-ethyl-5-methyl-pyrazine (**19**)	17	2.6	15
4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone (**20**)	113 000	3600	3.2
2-Ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone (**21**)	14 400	270	1.9
3-Hydroxy-4,5-dimethyl-2(5*H*)-furanone (**22**)	1030	26	2.5

[a] After an equilibration period of 30 min in the apparatus (Figure 1).

Brazilian Coffee — Quantitative Results

The result of the quantitative determination of the 22 odorants in the headspace of freshly ground Brazilian coffee powder released during 30 min, as well as the total content of these odorants in the powder, is shown in Table 4. The ratio of the concentration of the odorant in the headspace of the sample to the total concentration of the odorant in the sample was defined as the flavour release (FR) value. After 30 min, the high-volatile odorants had FR values between 12% (2,3-butanedione) and 65% (acetaldehyde). The FR-value of (*E*)-ß-damascenone amounted to approximately 6%, while for 2-furfurylthiol and methional it was between 22% and 37%, respectively. The phenolic compounds showed FR values from 5% for 4-vinylguaiacol to 23% for the high boiling vanillin. For the alkyl-pyrazines, the FR value was about 10%, while for 3-isobutyl-2-methoxypyrazine it was 25%. The FR values of the furanones were only around 2–3%. It is obvious that some of the higher-boiling odorants, such as vanillin or 3-isobutyl-2-methoxypyrazine, but also methional, had FR values similar to or even higher than those of lower-boiling odorants.

Brazilian Coffee — Aroma Simulation

To simulate the aroma of the Brazilian coffee sample, a highly concentrated model mixture of its headspace odorants in pentane (model I, Table 1) was prepared and injected into the apparatus. In previous experiments it was ascertained that small amounts of pentane (25 µL) were odourless when evaporated into the headspace of the apparatus and did not disturb the sensory evaluation of the models. A comparison of the odour profiles of freshly ground Brazilian coffee with model I (Figure 2), showed a parallel in earthy and roasty/sulphurous odour qualities. The sweetish/caramel-like note was scored higher and the smoky note scored lower in the model than in the real sample. Nevertheless, the overall similarity of the odour of model I compared with that of the real coffee sample was rated 2.5 (Table 5), indicating that the model mixture mimicked the odour of the freshly ground Brazilian coffee effectively.

Statistical evaluation of the individual scores of the six assessors for the different odour qualities in the real coffee samples, and in the corresponding models by an outlier test, according to Nalimov,[12] and the *t*-test according to Kaiser and Gottschalk,[12] revealed that there were no significant differences between the odour qualities of the model and those of the corresponding coffee sample. The reason for this is the homogenous distribution of the scores, showing no outliers but resulting in quite high standard deviations due to the limited number of assessors.

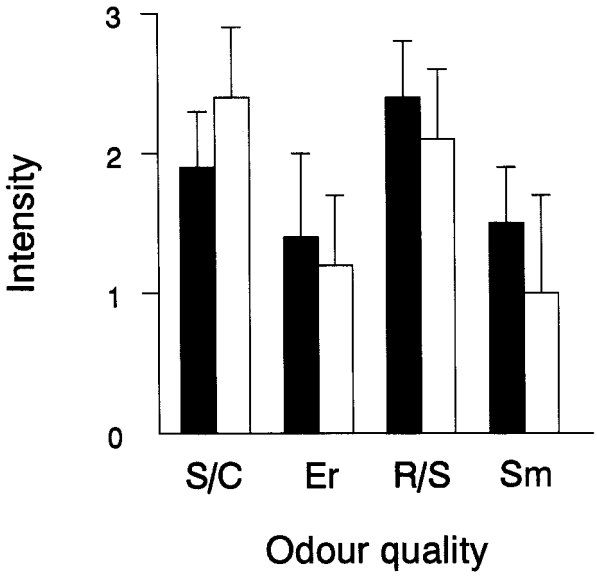

Figure 2. Odour profiles of ground Brazilian coffee and model I.[a] ■, Coffee sample; □, Model I.
[a]After 30 min in the apparatus (Figure 1) at room temperature. Odour quality: S/C, sweetish/caramel; Er, earthy; R/S, roasty/sulphurous; Sm, smoky. Intensity rating scale: 0 (not perceptible) to 3 (strongly perceptible); mean values of six assessors, standard deviation given as line

Table 5. Similarity of the aroma models to the original coffee samples

Comparison		Similarity score[a]
Model	Coffee	
I	Brazilian, freshly ground	2.5 (0.0)
II	Colombian, freshly ground	2.6 (0.3)
III	Colombian, 15 min after grinding	2.4 (0.3)
IV	Colombian, freshly ground	2.1 (0.3)

[a] The similarity was scored by six assessors on a scale from 0 (no similarity) to 3 (identical). The results were averaged; the standard deviations are given in parenthesis.

Colombian Coffee — Freshly Ground and 15 min after Grinding

Experiments were repeated with Colombian coffee. In particular, release of odorants causing changes in the odour profile of a coffee sample after grinding was investigated. As shown in Figure 3, the intensity of the sweetish/caramel-like odour quality of coffee powder was scored distinctly lower than that of freshly ground coffee 15 min after grinding. This decrease continued during the next 3 h. Additionally, the intensities of the earthy and smoky notes increased slightly, while those of the roasty/sulphurous notes remained constant.

Quantitative Results

To investigate the change of the odorant composition in the headspace of coffee powder depending on time

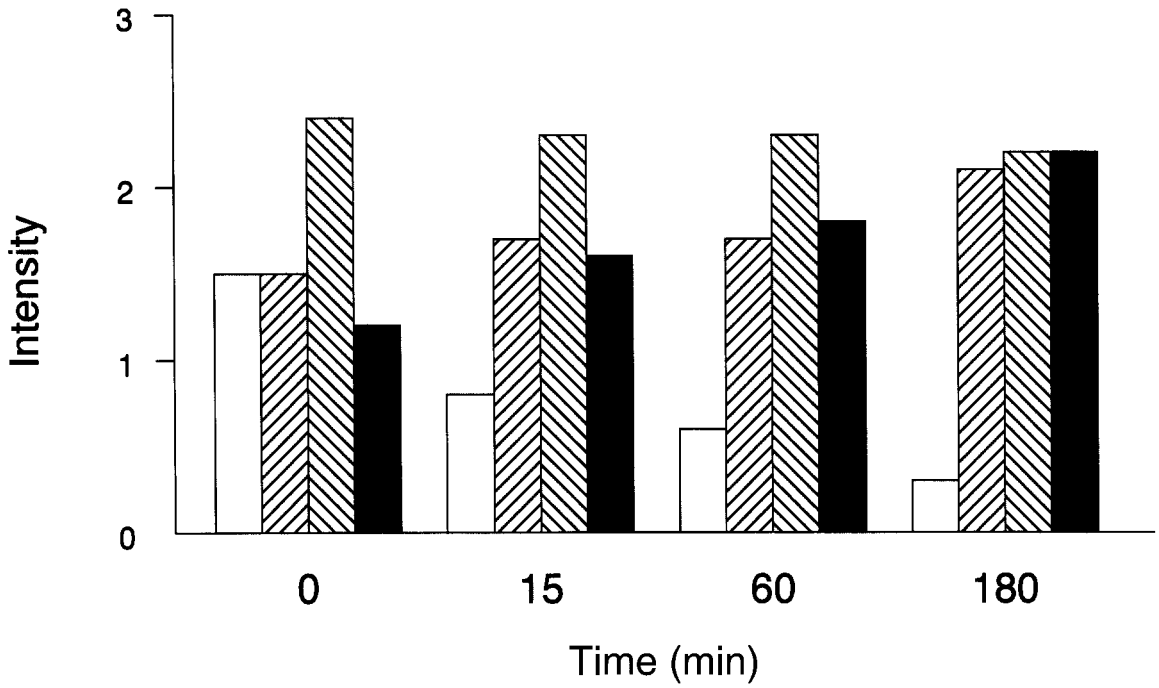

Figure 3. Changes in odour profile of roasted coffee depending on time passed after grinding. [a]After remaining in the apparatus for 15 min, intensities of odour qualities were scored on a category scale from 0 (not perceptible) to 3 (strongly perceptible). □, Sweetish/caramel; ▨, earthy; ▧, roasty/sulphurous; ■, smoky

after grinding, concentrations of the 22 MS-detectable odorants were determined for Colombian coffee powder, both freshly ground and 15 min after grinding. Table 6 shows the result of the headspace quantification and the calculated FR values. The FR value of methylpropanal (**3**) and 2- and 3-methylbutanal (**4**, **5**) decreased from 25–32% to 8–10%, of methional (**10**) from 29% to 19% and of 2,3-butanedione (**6**) and 2,3-pentanedione

Table 6. Concentration of odorants in freshly ground Colombian coffee and in its headspace before and after 15 min of storage

Odorant	Total concentration (ng/g)	Headspace concentration (ng/g)[a]		FR-value (%)	
		Freshly ground	15 min after grinding	Freshly ground	15 min after grinding
Methanethiol (**1**)	4400	2900	2900	66	66
Acetaldehyde (**2**)	118 000	54 000	47 000	45	40
Methylpropanal (**3**)	24 200	6000	2000	25	8.3
2-Methylbutanal (**4**)	25 800	8200	2700	32	10
3-Methylbutanal (**5**)	16 500	4400	1700	27	10
2,3-Butanedione (**6**)	48 800	9100	4200	19	8.6
2,3-Pentandione (**7**)	35 300	9000	4400	25	12
(*E*)-ß-Damascenone (**8**)	258	30	32	12	12
2-Furfurylthiol (**9**)	1650	380	450	23	27
Methional (**10**)	245	70	47	29	19
Guaiacol (**11**)	3420	600	640	18	19
4-Ethylguaiacol (**12**)	1780	150	130	8.4	7.3
4-Vinylguaiacol (**13**)	45 100	2200	1600	4.9	3.5
Vanillin (**14**)	4050	790	650	20	16
2-Ethyl-3,5-dimethyl-pyrazine (**15**)	401	50	49	12	12
2,3-Diethyl-5-methyl-pyrazine (**16**)	102	13	15	13	15
2-Isobutyl-3-methoxy-pyrazine (**17**)	117	24	28	21	24
2-Ethenyl-3,5-dimethyl-pyrazine (**18**)	53	3.5	5.6	6.6	11
2-Ethenyl-3-ethyl-5-methyl-pyrazine (**19**)	15	2.0	2.3	13	15
4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone (**20**)	144 000	2000	1600	1.4	1.1
2-Ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone (**21**)	15 900	200	130	1.3	0.8
3-Hydroxy-4,5-dimethyl-2(5*H*)-furanone (**22**)	1850	20	26	1.1	1.4

[a] The headspace concentrations were determined after an equilibration period of 30 min in the apparatus (Figure 1).

(**7**) from 19% and 25%, respectively, to 9% and 12%. The release of the other odorants was small (e.g. of furanones **20–22**) or was only slightly affected by the storage of 15 min. This suggested that the change in the odour profile during storage was mainly caused by a decrease in release of *Strecker* aldehydes **3**, **4**, **5** and **10** and of diones **6** and **7**.

Aroma Simulation and Aroma Changes

To simulate the aroma of freshly ground Colombian coffee and of the powder 15 min after grinding, aroma models II and III were prepared using the concentrations of the odorants listed in Table 1. The odour profiles of the two models were compared with those of the corresponding real coffee samples. The result of the freshly ground Colombian coffee presented in Figure 4 shows similarity in all four odour qualities. The overall similarity scored by the assessors was 2.6 (Table 5), indicating that model II was able to mimic the headspace odour of freshly ground coffee very well.

In a previous sensory experiment,[5] the 21 odorants reported here and a further six found in a medium-roasted Arabica coffee from Colombia were dissolved in a sunflower oil/water mixture (1:20, w/w). This aroma model reached a similarity score of 2.3. The lower score compared with the results reported here might be caused by the base, differing from the solid coffee matrix in the binding of the odorants. The higher similarity of the model presented here with the aroma of ground roasted coffee was achieved by elimination of the matrix. The concentrations of the odorants in the headspace were considerably lower than in the matrix as well as in the base. Hence, chemical reactions of the odorants are very unlikely.

Comparing the odour profile of the coffee powder 15 min after grinding and the corresponding model III (Figure 4), the intensity of the sweetish/caramel-like odour quality was scored higher and the roasty/sulphurous note was found to be slightly weaker in the model than in the real sample. The overall similarity of model III and the real coffee sample 15 min after grinding was rated 2.4 (Table 5).

The decrease in the intensity of the sweetish/caramel-like odour quality and the increase in the smoky note, observed in the odour profile above coffee powder depending on the time after grinding could be recognized when the sample remained in the apparatus for 15 (Figure 3) or 30 min (Figure 4). However, the intensity of the sweetish/caramel-like odour-quality was scored higher when freshly ground coffee was stored in the apparatus for the longer period. Also, in the corresponding models of freshly ground coffee powder (II) and of the powder 15 min after grinding (III) this decrease was perceptible (Figure 4). As discussed above, the decrease of the intensity of the sweetish/caramel-like odour quality from freshly ground coffee powder to coffee powder 15 min after grinding can be explained by the distinct decrease of the amounts of *Strecker* aldehydes and diones. The intensity of earthy and roasty/sulphurous notes was scored similarly in the headspace of freshly ground coffee powder and the powder 15 min after grinding. This agreed with the finding that the headspace concentrations of earthy-smelling

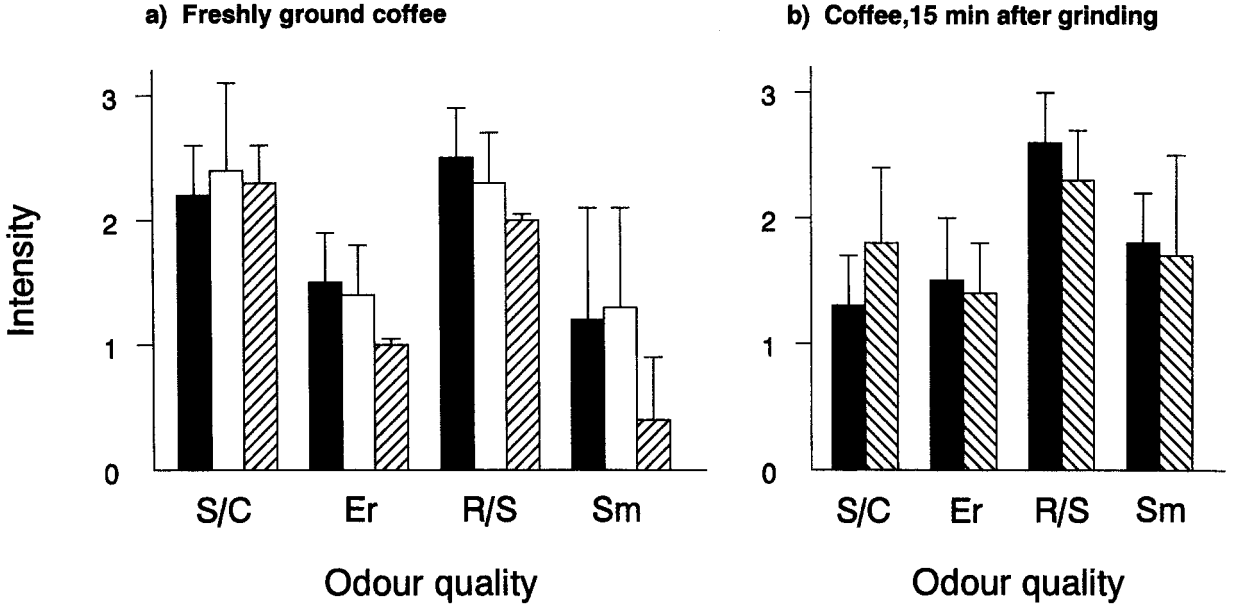

Figure 4. Odour profiles of freshly ground Colombian coffee and of Colombian coffee 15 min after grinding and of models II and III and the reduced model IV.[a] ■, Coffee sample; □, Model II; ▨, Model III; ▨, Model IV. [a]See footnote in Figure 2

pyrazines and roasty-smelling 2-furfurylthiol changed only in a small range during storage (Table 6). However, the smoky note of coffee powder was more intense 15 min after grinding (Figure 4). We assume that the odour contribution of volatiles like guaiacol (**11**), which might be responsible for this note, was reduced in the fresh coffee sample by higher headspace concentrations of the *Strecker* aldehydes and diones mentioned above.

Aroma Simulation with a Reduced Model

Finally, we tested whether it is possible to create a model for the odour of freshly ground roasted coffee powder with less than the 21 odorants. Therefore, models for freshly ground Colombian coffee that differed in the odorant composition were prepared and compared with the original (experiments not shown). This led to a reduced model (IV) that was able to simulate the odour of freshly ground coffee powder after 30 min in the apparatus. It consisted of only nine odorants: acetaldehyde, methylpropanal, 2- and 3-methylbutanal, 2,3-butanedione, 2,3-pentanedione, 2-furfurylthiol, 2-ethyl-3,5-dimethylpyrazine and 2,3-diethyl-5-methylpyrazine. As shown in Figure 4, only the intensity of the earthy and the smoky odour notes was smaller in the reduced than in the complete model II. This is not surprising, since there were only two of the five pyrazines in the model, and the phenols were absent. Nevertheless, the similarity of the reduced model IV to the complete model II was rated 2.5 and to the smell of the coffee powder 2.1 (Table 5). Addition of smoky-smelling guaiacol disturbed the flavour of model IV (data not shown). This negative effect was neutralized by addition of methanethiol, methional, 2-ethenyl-3,5-dimethylpyrazine and 4-vinylguaiacol. However, the similarity of this model, consisting of 14 odorants, to the original was not higher than that of model IV, containing only nine odorants.

Conclusion

The results confirm that the new analytical method is sufficient for an accurate quantification of the odorants occurring in the headspace of foods. The aroma of a complex solid food, like coffee, and its change during storage can be reproduced by preparing aroma models on the basis of headspace concentrations of potent odorants. The change of the odour profile of coffee powder within the first 15 minutes is mainly caused by the decrease in release of *Strecker* aldehydes and diones.

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