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Influence of Water Quench Cooling on Degassing and Aroma Stability of Roasted Coffee

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Coffee roasting experiments with air cooling versus water quench cooling were carried out on laboratory scale with a fluidized-bed hot air roasting system (200 g batch size) and on production scale with a rotating bowl roaster (320 kg batch size). Two series of coffees with different water contents resulted, which were stored at 25 °C under normal atmospheric conditions. Carbon dioxide desorption was followed and stability of selected aroma compounds was tested with headspace solid-phase microextraction−gas chromatography−mass spectrometry (SPME-GC-MS) and stable isotope labeled compounds as internal standards. Degassing is faster in water-quenched coffees with higher moisture content, but pore size distribution in the different coffee samples did not correlate with degassing behavior. Bean firmness, which increases with increasing moisture content, might have an influence on degassing. Air- and water-quenched coffees exhibit similar stability of most aroma compounds despite different degassing behavior. However, evolution of dimethyl trisulfide was different in coffees with increased water content. This suggests higher thiol oxidation rates, a factor that is cited to be related to a faster loss of freshness attributes.

KEYWORDS: Coffee; roasting; water quenching; solid-phase microextraction; flavor stability; carbon dioxide; coffee structure

INTRODUCTION

Once the desired degree of roast is achieved, fast quenching of coffee beans is necessary in order to avoid overroasting and to stop exothermic reactions within the beans. In industrial coffee roasting, air and water quench cooling are applied. Air cooling implies the use of large quantities of cold air for several minutes (*1*) and is relatively slow. Therefore, exothermic reactions within coffee beans may continue during the first 15 s of the cooling process (*2*). Water quenching cools down coffee faster, and temperature drops from 230 to 100 °C in less than 1 s are reported (*2*). When bean temperature falls below 100 °C, exothermic moisture condensation occurs and coffee beans can take up moisture. Eggers (*2*) distinguishes three types of water quenching. During spray quenching, coffee beans are cooled rapidly by the evaporation enthalpy of water droplets on the bean surface. In immersion quenching, coffee beans are immersed in water and cooled by bulk boiling. In film quenching, water is poured over coffee beans. Spray quenching is judged as the most efficient method due to high evaporation rates and intensive recurring contact of water with surface of coffee beans. Generally cold water quenching is more efficient than hot water quenching, which is slower but results in a better water uptake into coffee beans (*2*).

Water quenching is generally associated with loss of coffee quality, although explicit experimental data are lacking. Illy and Viani (*1*) mention possible oxidation reactions on the surface of coffee beans as well as the opening of pores, which allows stripping of volatile substances off the bean. These authors relate water quench cooling to cell wall cracking and more pronounced structure collapse leading to faster degassing and aroma loss. However, Geiger et al. (*3*) showed that carbon dioxide loss rates during roasting greatly exceed degassing rates during storage. Furthermore, near the end of roasting, volatile organic compounds and many individual aroma compounds are emitted at considerably higher rates than after quenching (*4*, *5*).

In studies on degassing of roasted coffee, Radtke (*6*) found that between 40% and 50% of the entrapped carbon dioxide is released during fine grinding, whereas loss of carbon dioxide during coarse grinding is low. Radtke concluded that the main part of carbon dioxide is entrapped in the fine pores of the coffee bean tissue and not in large cavities from where entrapped CO_2 is probably lost already during the roasting process through relatively large fissures. When internal carbon dioxide pressure is calculated on the basis of the amount of entrapped CO_2 in coffee beans, values up to 8 bar are found (*4*, *6*). Shimoni and Labuza (*7*) suggested that the major part of carbon dioxide in coffee powder is in a sorption/desorption equilibrium and only a minor part is entrapped in collapsed structure. However, neither the mechanisms of CO_2 entrapping and sorption nor the

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driving forces and mechanisms of degassing within coffee beans are fully understood.

Spadone and Liardon (*8*) studied staling of coffee aroma during storage of roasted coffee with high and low water content under high and low oxygen storage conditions. Concentrations of hexanal, several branched aldehydes, ketones, and alkylfurans in coffee cooled by air and by water quenching changed in a similar way during storage. As the two cooling methods resulted in different moisture content, the authors concluded that lipid oxidation and at least some chemical reactions involved in coffee aging were independent of water content in roasted coffee. Clinton (*9*) examined consumer and expert evaluations of stored roast and ground coffee and found that higher water content and higher oxygen conditions in packaging lead to faster product deterioration. Hinman (*10*) showed that the reaction of roast and ground coffee with oxygen can be considerably accelerated by effect of temperature, moisture, and coffee density.

Nicoli et al. (*11*) examined the correlation between volatiles and carbon dioxide release in roasted coffee beans and ground coffee at different temperatures. They concluded that, during storage, evolution of carbon dioxide is always related to an equal behavior of volatile compounds. However, the authors measured headspace concentrations and results were given as total peak area without the use of internal standards. Therefore, volatile substances that were bound to the coffee matrix were not taken into account.

The aim of this study was to determine whether water quench cooling with and without increase of water content implies significant effects on aroma stability, degassing, oxidative stability, and roast coffee structure. In addition, the transferability of the results from laboratory roasting trials to industrial roasting processes was to be verified.

MATERIALS AND METHODS

A. Roasting Process and Process Characterization: *1. Raw Material.* Wet-processed *Coffea arabica* Linn. variety from Colombia was obtained from a Swiss roasting company for laboratory trials. For industrial trials, a commercial 100% Arabica blend of the same company was roasted.

2. Color Measurement. Roast degree was determined from the lightness value (L^*) of the $L^*a^*b^*$ color space. Coffee was ground and gently pressed to form an even surface, and color was measured with a colorimeter CR-310 (Minolta, Japan).

3. Moisture Content. Roasted coffee was ground in a disk grinder (Buehler-Miag 4000, Bühler Ltd., Milano, Italy), and weight loss of 5 g of ground coffee at 103 °C during 5 h was determined gravimetrically.

4. Laboratory Roasting Trials. Batches (200 g) of green coffee beans were roasted with a fluidized-bed hot-air laboratory roaster (G. W. Barth AG, Freiberg/Neckar, Germany) by a low-temperature long-time process [LTLT, 228 °C, 12 min (*3*)]. The roaster has been described in detail by Schenker (*12*) and Geiger et al. (*3*). Bean color of roasted coffee was $L^* = 21-22$ (passive cooling) and $L^* = 22-23$ (all others). Four different cooling methods were applied. Air-cooled coffee was cooled with an ambient air stream of 1.4 $m^3\ min^{-1}$ during 4 min as described by Schenker (*12*), resulting in a water content of 1.9 g/100 g on a wet basis (wb). In spray cooling, 8.7 g of water was sprayed through a hollow cone nozzle into the cooling chamber during 20 s. This cooling method was slightly faster than air cooling, but final water content was nearly as low as in air-cooled coffee (2.1 g/100 g wb). The second water cooling method (film cooling) consisted of pouring 35 g of water directly on the coffee during the first 12 s of the cooling process. Significant higher end water content of coffee resulted from this method (4.2 g/100 g wb). In addition to the air and the two water quenching techniques, slow cooling was applied, whereas coffee beans were cooled for 45 min in a wide steel container at ambient temperature without air stream. Due to the slow decrease in temperature, the degree of roast of slowly cooled coffee was somewhat higher than in the other coffees, whereas water content was slightly lower (1.7 g/100 g wb).

5. Industrial Roasting Trials. Coffee was roasted on a RZ 3500Y rotating bowl roaster (Probat, Emmerich, Germany) with batch size of 320 kg. Inlet air temperature was 307 ± 2 °C, and coffee was roasted to a final bulk temperature of 222 ± 1 °C, resulting in roasting times of about 275 s and a bean color of $L^* = 29-30$. Due to safety considerations water cooling had to be applied on all batches, but the amount of water was varied (38, 35, 25, 15, or 5 L), resulting in end water contents of 5.3, 4.8, 3.8, 3.2, and 2.4 g/100 g on a wet basis.

6. Firmness. Firmness of coffee beans was determined by a shearing test in a Kramer cell using a force deformation testing equipment (Z010/TH2S, Zwick, Ulm, Germany). A single layer of roasted coffee beans ($n = 50-60$) was placed in the cell and the maximum force was measured at a deformation rate of 100 mm/min. After roasting and quenching, coffee beans were stored at room temperature for 24 h, and then at −80 °C until firmness measurements took place.

7. Gas Desorption Measurement. Batches (80 g) of coffee beans or finely ground coffee powder (Ditting KFA 1403 disk mill, level 2; Ditting, Bachenbülach, Switzerland) were placed in 500 mL septum flasks immediately after roasting and quenching. Headspace pressure was measured periodically. The flasks were vented after each measurement. Results were adjusted to 100 g dry mass.

8. Mercury Intrusion Porosimetry. Porosimetry was carried out using mercury porosimeters Pascal 140 and 440 (Thermo Electron Corp., Waltham, MA) as described by Schenker et al. (*13*).

B. Aroma Analysis: *1. Chemicals.* Isotopically labeled standards were obtained from Dr. Ehrenstorfer GmbH, Augsburg, Germany ([$^2H_6$]-dimethyl sulfide, [$^2H_5$]pyridine, and [$^2H_2$]-3-methylbutanal), Witega Laboratorien, Berlin, Germany ([$^2H_3$]-4-vinylguaiacol), and Toronto Research Chemicals, North York, Canada ([$^2H_6$]-2-ethyl-3,5-dimethylpyrazine). The following substances were synthesized at Nestlé Research Center (Lausanne, Switzerland): [$^2H_2$]hexanal (*14*), [$^2H_6$]-dimethyl trisulfide (*15*), [$^{13}C_4$]-2,3-butanedione, and [$^{13}C_2$]-2,3-pentanedione (*16*).

2. SPME-GC-MS Analysis and Quantification of Coffee Aroma Compounds. Samples of coffees roasted at laboratory scale were taken directly after roasting and then after 1, 8, 15, 23, 35, 56, and 133 days of storage. Coffee samples from industrial roasting trials were taken after roasting and quenching (12 h equilibration time) and then after 8, 15, 23, 35, 56, and 126 days of storage. Coffee beans were stored in open containers in the dark at 25 °C.

Three aldehydes (2-methylbutanal, 3-methylbutanal, and hexanal), two ketones (2,3-butanedione and 2,3-pentanedione), two sulfides (dimethyl sulfide and dimethyl trisulfide), one pyridine (pyridine), six alkylpyrazines (2-ethyl-3-methylpyrazine, 2-ethyl-5-methylpyrazine, 2-ethyl-6-methylpyrazine, 2,3,5-trimethylpyrazine, 2-ethyl-3,5-dimethylpyrazine, and 2-ethyl-3,6-dimethylpyrazine), and one phenolic compound (4-vinylguaiacol) were analyzed (**Table 1**).

Ground coffee (5 g for the first group of compounds, **3**, **6**−**11**, and **14**; 1 g for the second group of compounds, **1**, **2**, **4**, **5**, **12**, **13**, and **15**)

Table 1. Analytes and Standards Used in GC-MS Analyses

analyte (A)	selected ion (*m/z*) of A	internal standard (IS)	selected ion (*m/z*) of IS
2-methylbutanal (**1**)	86	[$^2H_2$]-**2**	88
3-methylbutanal (**2**)	71	[$^2H_2$]-**2**	73
hexanal (**3**)	56	[$^2H_2$]-**3**	58
2,3-butanedione (**4**)	43	[$^{13}C_4$]-**4**	45
2,3-pentanedione (**5**)	100	[$^{13}C_2$]-**5**	102
2-ethyl-3-methylpyrazine (**6**)	121	[$^2H_6$]-**10**	141
2-ethyl-5-methylpyrazine (**7**)	121	[$^2H_6$]-**10**	141
2-ethyl-6-methylpyrazine (**8**)	121	[$^2H_6$]-**10**	141
2,3,5-trimethylpyrazine (**9**)	122	[$^2H_6$]-**10**	141
2-ethyl-3,5-dimethylpyrazine (**10**)	135	[$^2H_6$]-**10**	141
2-ethyl-3,6-dimethylpyrazine (**11**)	135	[$^2H_6$]-**10**	141
pyridine (**12**)	79	[$^2H_5$]-**12**	84
4-vinylguaiacol (**13**)	150	[$^2H_3$]-**13**	153
dimethyl sulfide (**14**)	62	[$^2H_6$]-**14**	68
dimethyl trisulfide (**15**)	126	[$^2H_6$]-**15**	132

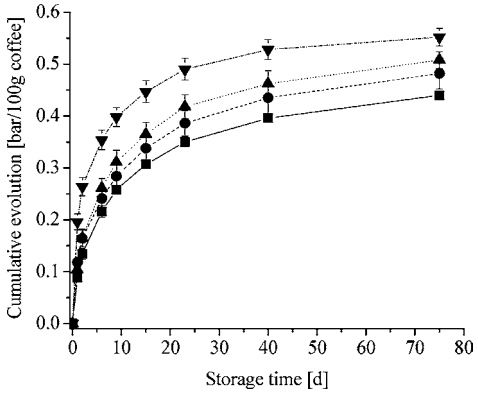

Figure 1. Degassing of whole coffee beans: passively cooled (■, 1.7 g of H_2O/100 g wb), air-cooled (●, 1.9 g of H_2O/100 g wb), spray-cooled (▲, 2.1 g of H_2O/100 g wb), and film-cooled coffee (▼, 4.2 g of H_2O/100 g wb) [bar/100 g dm].

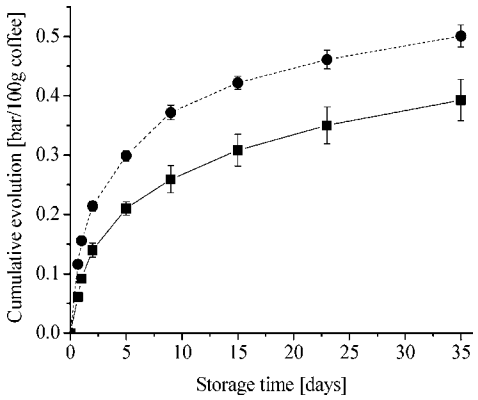

Figure 2. Degassing of air-cooled coffee (■) and remoistened air-cooled coffee (●) [bar/100 g dm].

was weighed in a 100 mL flask and extracted with 100 mL boiling water for 10 min under constant stirring. During extraction, the flasks were kept closed to avoid evaporation and loss of volatile compounds. After cooling, the coffee solution was spiked with definite amounts of the isotopically labeled internal standards [$^2H_2$]-**3**, [$^2H_6$]-**10**, and [$^2H_6$]-**14** (for the first group) and [$^2H_2$]-**2**, [$^{13}C_4$]-**4,** [$^{13}C_2$]-**5**, [$^2H_5$]-**12**, [$^2H_3$]-**13**, and [$^2H_6$]-**15** (for the second group). The coffee solution was subsequently stirred for 10 min, and 7 mL was transferred to a 20 mL headspace vial.

Coffee aroma compounds were sampled with solid-phase microextraction (SPME) at 40 °C for 10 min by use of a Supelco 50/30 μm StableFlex divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (Supelco, Buchs, Switzerland). Injection was done at 240 °C in the splitless mode with a splitless time of 240 s. Separation was carried out on a 60 m × 0.25 mm × 0.25 μm medium polar ZB-1701 column (Phenomenex, Aschaffenburg, Germany) on a Fisons 8000Series gas chromatograph (GC) (Thermo Electron, Allschwil, Switzerland) with the following temperature programs: 40 °C (6 min), 4 °C/min, 135 °C (0 min), 40 °C/min, 240 °C (5 min) for compounds **3**, **6**−**11**, and **14**; 40 °C (4 min), 4 °C/min, 140 °C (0 min), 40 °C/min, 240 °C (5 min) for compounds **1**, **2**, **4**, **5**, **12**, **13**, and **15.** Helium 5.6 was used as carrier gas at a constant column head pressure of 135 kPa. Detection of aroma compounds was done on a quadrupole mass spectrometer (MS) SSQ710 (Finnigan MAT, San Jose, CA) with single-ion monitoring (SIM) in the EI mode with an ionization potential of 70 eV. All SPME-GC-MS measurements were run in triplicate.

RESULTS AND DISCUSSION

Gas Desorption and Physical Structure. Initial gas desorption of whole coffee beans is markedly higher in coffees with higher water content, as shown for the coffees obtained from the laboratory roasting trials (**Figure 1**). However, after 1 week of storage, no marked difference in degassing rate is found anymore. In addition, **Figure 1** shows that coffees with same roast degree and comparable water content exhibit similar degassing rates throughout storage, unaffected by cooling methods. To evaluate the influence of water content on degassing and at the same time exclude any influence of cooling method, one batch of air-cooled coffee was divided in two parts. One part was remoistened to a water content of 5 g/100 g immediately after cooling. The second part was left untreated. Degassing of the remoistened coffee is very similar to degassing

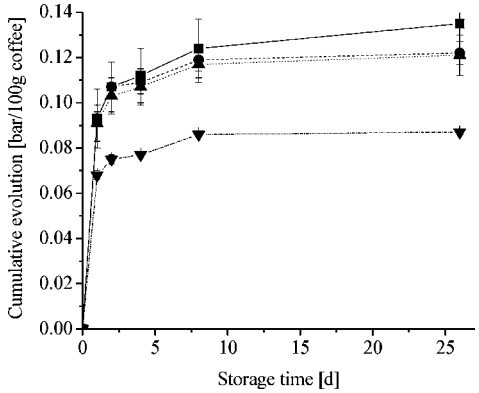

Figure 3. Degassing of ground coffee: passively cooled (■, 1.7 g of H_2O/100 g wb), air-cooled (●, 1.9 g of H_2O/100 g wb), spray-cooled (▲, 2.1 g of H_2O/100 g wb), and film-cooled (▼, 4.2 g of H_2O/100 g wb) [bar/100 g dm].

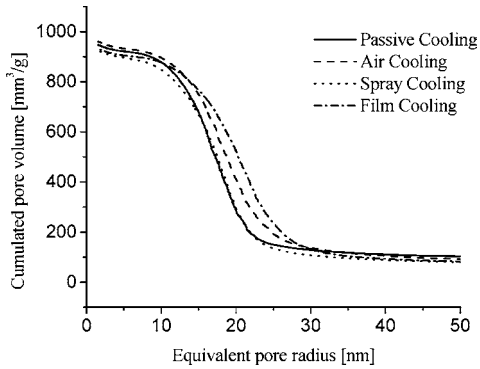

Figure 4. Cumulated intruded mercury volume in coffees from laboratory roasting trials.

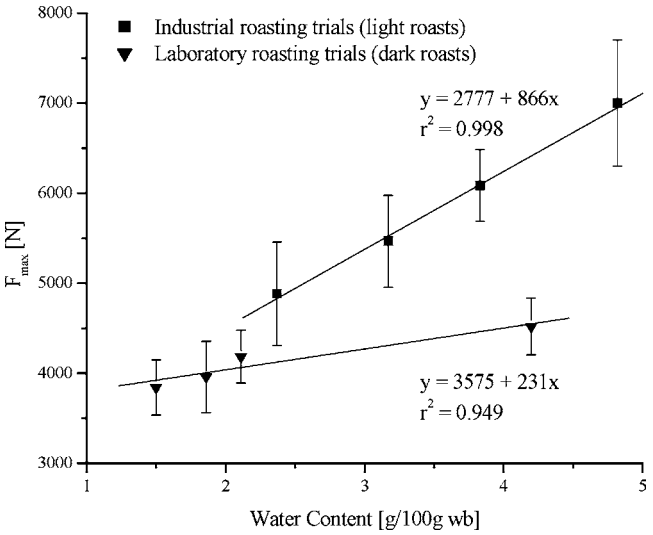

Figure 5. Firmness of coffee beans roasted in laboratory and industrial trials.

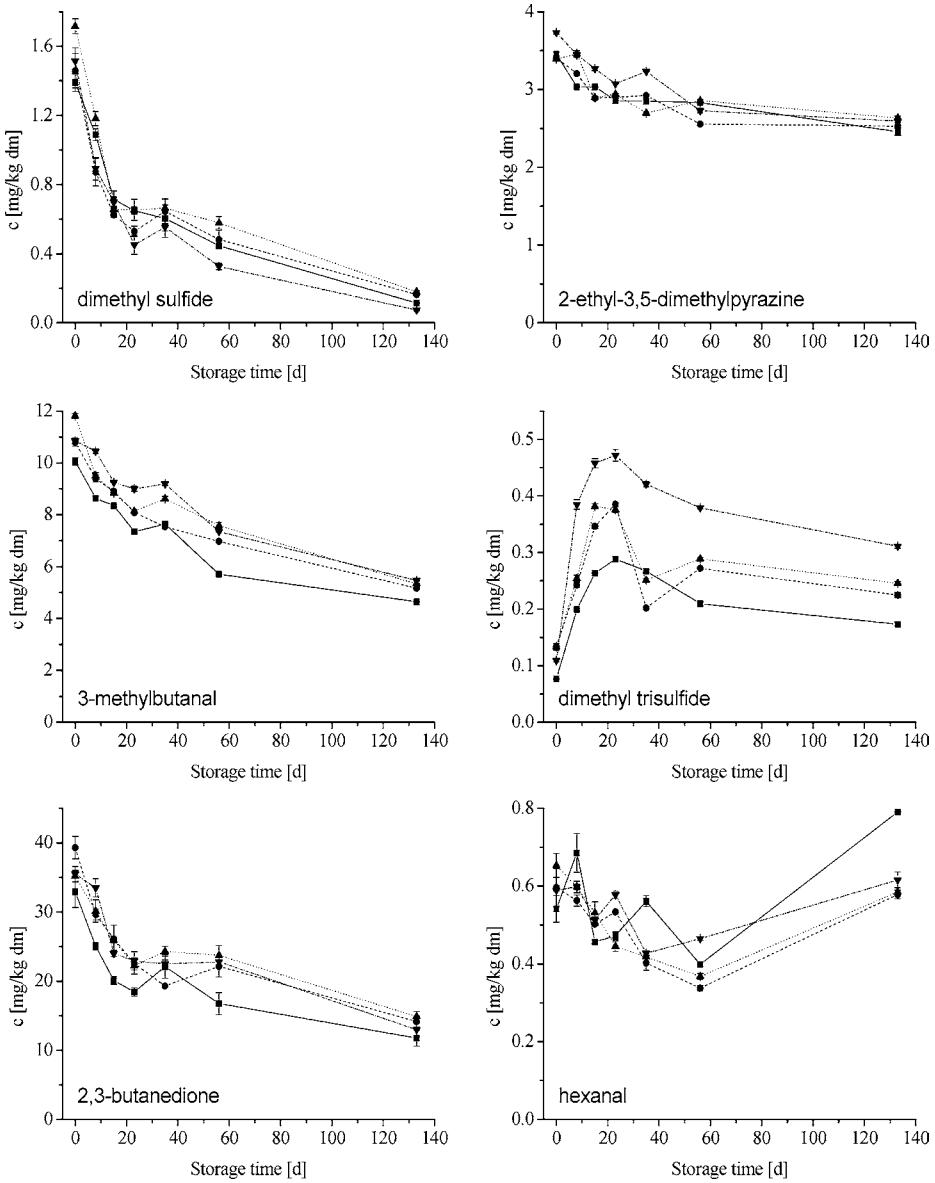

Figure 6. Alteration of selected coffee aroma compounds in passively cooled coffee (■, 1.7 g of H_2O/100 g wb), air-cooled coffee (●, 1.9 g of H_2O/100 g wb), spray-cooled coffee (▲, 2.1 g of H_2O/100 g wb), and film-cooled coffee (▼, 4.2 g of H_2O/100 g wb).

of film-cooled coffee (**Figure 2**), which gives rise to the assumption that fast degassing of coffees with high water content is due to remaining moisture only and is unaffected by the specific cooling method.

In a further experiment, coffee was ground immediately after roasting, and degassing of coffee powder was measured. Degassing was noticeably decreased in ground coffee with higher water content (**Figure 3**). Apparently, CO_2 loss during grinding is higher in coffee beans with increased water content, and less CO_2 is available for degassing during storage.

It is known from research on carbon dioxide diffusion kinetics of roast and ground coffee (*7*, *17*) that diffusion is very complex and likely to be a combination of various mechanisms including Knudsen and transition-region diffusion, pressure-driven viscous flow, surface diffusion, and interactions between carbon dioxide molecules and coffee matrix. Results of these studies suggest indeed that at least two mechanisms control the degassing process. In the early stage of degassing, carbon dioxide desorption is fast and large differences in degassing behavior can be seen between coffees with different water contents.

For water-quenched coffee beans, the assumption was made that fast degassing is linked to opening of pores during the cooling step (*1*). Schenker et al. (*13*) showed that mercury intrusion porosimetry is a suitable method to determine the internal pore structure of roasted coffee beans and found significant differences in average pore size between fast- and slow-roasted coffees. The assumption that water-quenched coffees have higher porosity than air-quenched coffees was not corroborated by porosimetry measurements of the laboratory roasting trials, where no correlation between internal pore structure and degassing behavior was found (**Figure 4**). It must be noted, though, that mercury intrusion porosimetry gives insight into the intracellular pore system but does not provide information about surface porosity (*12*). The origin and structure of the micropore system within coffee cell walls still remains unclear, and the question of how gas and oil are transferred from the bean core to the outside is not yet answered satisfactorily.

Even if carbon dioxide was transported through the intracellular micropore system, transfer through the outer cell barrier

Table 2. Percent Retention of Aroma Compounds after 56 Days of Open Storage (Laboratory Trials)

	quenching method[a]			
	passive cooling, 1.7 g of H_2O	air cooling, 1.9 g of H_2O	spray cooling, 2.1 g of H_2O	film cooling, 4.2 g of H_2O
dimethyl sulfide	32	33	34	22
dimethyl trisulfide	272	204	216	347
hexanal	74	57	56	79
2-methylbutanal	63	67	61	70
3-methylbutanal	57	65	64	68
4-vinylguaiacol	93	91	85	76
pyridine	84	82	88	88
2,3-butanedione	51	56	67	64
2,3-pentanedione	55	62	62	65
2-ethyl-5-methylpyrazine	85	80	81	76
2-ethyl-6-methylpyrazine	80	76	80	75
2-ethyl-3-methylpyrazine	78	78	77	73
2,3,5-trimethylpyrazine	79	77	89	76
2-ethyl-3,5-dimethylpyrazine	82	75	84	73
2-ethyl-3,6-dimethylpyrazine	77	74	73	70

[a] Water content is expressed as grams of H_2O per 100 g wet basis for each method.

(epidermis) might be limiting. Therefore it is hypothesized that in a first stage of gas desorption, when carbon dioxide pressure is equal throughout the coffee bean, transport through epidermis is limiting. In a second stage, when CO_2 pressure becomes lower and a pressure gradient from the bean core to the outer cells is further built up, carbon dioxide transfer from the bean core to the outer cell barrier will be an additional limiting factor. As pore size distribution is similar in all investigated coffees, no major differences are expected in degassing during this second stage. Differences in gas desorption between coffees with different water contents are found particularly in the first stage; therefore the assumption is made that due to higher water content the outer cell walls are more permeable to carbon dioxide. Higher permeability in the outer cell wall may also be caused by higher solubility of carbon dioxide in higher water contents.

The fact that tissue and cell wall structure of coffee beans is influenced by water content, which in turn influences degassing behavior, is also evident from firmness measurements (**Figure 5**). An almost linear relationship between water content and maximum force upon shearing coffee beans in the Kramer cell was found. Light-roasted coffee beans are less brittle than dark-roasted beans, and the increase of maximum force with water content is less pronounced in dark-roasted coffee. The detailed relationship between bean firmness, porosity, and degassing behavior would have to be explored further.

Aroma Stability. Odorants for the assessment of coffee shelf life were chosen on the basis of studies that linked analytical to sensory data (*18*, *19*). In addition to impact compounds identified in the before-mentioned studies, dimethyl sulfide was used as an additional freshness marker, hexanal was chosen as a secondary product of lipid oxidation, and pyridine was selected as a relatively stable marker substance.

Storage trials with roasted coffee beans obtained from laboratory trials revealed substantial changes in aroma profile (**Figure 6** and **Table 2**). After 133 days of storage, concentrations of volatile substances like 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, and 2,3-pentanedione decreased to 40−50% of the initial value. Reduction of dimethyl sulfide was especially distinct: after 133 days of storage, about 10% of the initial concentration was left. 4-Vinylguaiacol, pyridine, and pyrazines were less affected by long-term storage; reduction of these compounds was in the region of 25%.

Table 3. Percent Retention of Aroma Compounds after 56 Days of Open Storage (Industrial Trials)

	2.37 g of H_2O[a]	3.17 g of H_2O[a]	3.83 g of H_2O[a]	4.82 g of H_2O[a]	5.26 g of H_2O[a]
dimethyl sulfide	35	31	39	28	37
dimethyl trisulfide	339	447	582	608	511
hexanal	97	104	141	131	132
2-methylbutanal	60	55	66	55	66
3-methylbutanal	54	55	61	57	61
4-vinylguaiacol	96	96	103	96	94
pyridine	106	88	84	102	107
2,3-butanedione	61	67	62	71	71
2,3-pentanedione	55	55	57	60	64
2-ethyl-5-methylpyrazine	70	66	67	70	75
2-ethyl-6-methylpyrazine	73	69	72	76	79
2-ethyl-3-methylpyrazine	76	75	80	82	80
2,3,5-trimethylpyrazine	82	80	81	80	97
2-ethyl-3,5-dimethylpyrazine	94	81	94	93	99
2-ethyl-3,6-dimethylpyrazine	108	95	107	93	107

[a] Water content is expressed as grams of H_2O per 100 g wet basis.

Table 2 shows retention of aroma compounds after 56 days of storage, while **Figure 6** shows aroma alteration during storage of selected compounds. Despite different degassing behavior of the examined coffees, no substantial differences in loss of 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, and 2,3-pentanedione was observed. Among the highly volatile compounds, dimethyl sulfide probably exhibited a somewhat faster reduction rate in film-cooled coffee. Evolution of 4-vinylguaiacol, pyridine, and all examined pyrazines was comparable in all coffees. Since degassing in film-cooled coffee was markedly higher than in the other coffees, these findings suggest that loss of aroma compounds is not directly linked to degassing behavior. Therefore, in whole roasted coffee beans, aroma stripping due to degassing is a negligible effect compared to chemical degradation, which is primarily affected by temperature and ambient oxygen content. Hexanal contents showed that during the first weeks of storage no difference in lipid oxidation was induced by different cooling methods or water content. After 133 days, however, coffee beans that were cooled slowly exhibited noticeably higher amounts of hexanal. As hexanal is a suitable marker substance for lipid oxidation reactions, this is evidence of faster lipid oxidation in slowly cooled coffee. However, it has to be noted that lipid oxidation should not be a key problem in coffee storage, as after 133 days of storage, roasted coffee beans already underwent major aroma alterations. Arackal and Lehmann (*20*) indicate that after 6−8 weeks of open storage of roasted coffee beans, significant aroma alteration and staleness is perceived by consumers.

Large differences in alteration of dimethyl trisulfide were found in coffees cooled with different methods (**Figure 6**). Directly after roasting, around 100 μg of dimethyl trisulfide/kg dry mass was present. During the first 21 days of storage, dimethyl trisulfide content increased up to 430% (film cooling), 370% (passive cooling), 290% (air cooling), and 280% (spray cooling) of the initial value. The observed buildup of dimethyl trisulfide was most likely due to oxidation of methanethiol to dimethyl disulfide and dimethyl trisulfide (*21*, *22*). Water-quenched coffee with increased moisture content as well as slowly cooled coffee possibly underwent faster degradation of methanethiol. As loss of methanethiol may be linked to loss of the characteristic freshness of coffee flavor (*23*), water-quenched coffee with increased moisture content probably exhibits an accelerated loss of freshness attributes.

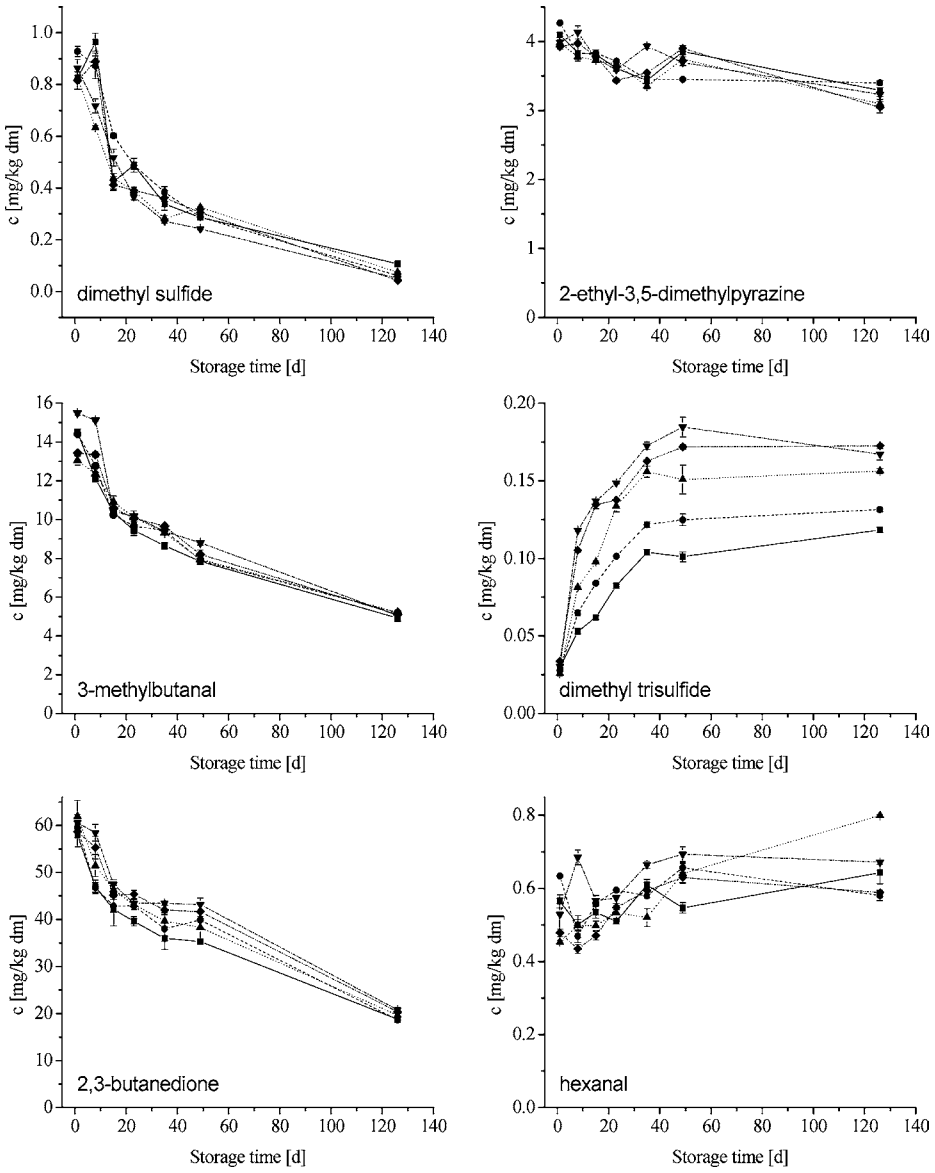

Figure 7. Alteration of selected coffee aroma compounds in coffees from industrial roasting trials with 2.4 g of H_2O/100 g wb (■), 3.2 g of H_2O/100 g wb (●), 3.8 g of H_2O/100 g wb (▲), 4.8 g of H_2O/100 g wb (▼), and 5.3 g of H_2O/100 g wb (◆).

The series of industrial roasting trials showed very similar behavior to the laboratory trials. Due to the lighter roast degree and due to differing raw material, some initial contents of aroma compound were different. Industrial roastings exhibited markedly higher contents of 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, and 2,3-pentanedione, whereas concentrations of pyridine, dimethyl sulfide, dimethyl trisulfide, and 2-ethyl-3,5-dimethylpyrazine were lower. The other compounds were at roughly equal concentrations in both roasting series. Similarly to the laboratory roasting trials, no basic differences in aroma alteration upon storage of the coffees with differing water content were observed (**Figure 7** and **Table 3**), although degassing was noticeably higher in coffees with higher water content (results not shown). Namely, dimethyl sulfide, 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, 2,3-pentanedione, 4-vinylguaiacol, pyridine, and all examined pyrazines exhibited very similar alterations throughout storage in all coffees. Again, the major variation between these coffees was found in the storage alteration of dimethyl trisulfide, where coffee beans with higher water content showed a higher increase during storage. As mentioned before, this could be a sign of faster oxidation of methanethiol and hence an indication of faster decay of freshness attributes.

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LITERATURE CITED

(1) Illy, A.; Viani, R. *Espresso Coffee: the Chemistry of Quality*; Academic Press Ltd.: London, 1995.
(2) Eggers, R. Zum Wärme- und Stofftransport bei der Röstung von Kaffeebohnen. In *Jahresbericht*; FEI (Forschungsvereinigung der Ernährungsindustrie): Bonn, Germany, 2004; pp 11−28.
(3) Geiger, R.; Perren, R.; Kuenzli, R.; Escher, F. Carbon dioxide evolution and moisture evaporation during roasting of coffee beans. *J. Food Sci.* **2005**, *70* (2), E124−E130.
(4) Clarke, R. J.; Macrae, R. *Coffee. Volume 2: Technology*; Elsevier Science Publishers Ltd: Essex, U.K., 1987.

(5) Dutra, E. R.; Oliveira, L. S.; Franca, A. S.; Ferraz, V. P.; Afonso, R. J. C. F. A preliminary study on the feasibility of using the composition of coffee roasting exhaust gas for the determination of the degree of roast. *J. Food Eng.* **2001**, *47*, 241−246.

(6) Radtke, R. Das Problem der CO_2-Desorption von Röstkaffee unter dem Gesichtspunkt einer neuen Packstoffentwicklung. In *7th International Scientific Colloquium on Coffee*, Hamburg, Germany, 1975; Association Scientifique Internationale pour le Cafe: Paris, France.

(7) Shimoni, E.; Labuza, T. P. Degassing kinetics and sorption equilibrium of carbon dioxide in fresh roasted and ground coffee. *J. Food Process Eng.* **2000**, *23* (6), 419−436.

(8) Spadone, J. C.; Liardon, R. Analytical study of the evolution of coffee aroma compounds during storage. In *13th International Scientific Colloquium on Coffee*, Paipa, Colombia, 1989; Association Scientifique Internationale pour le Cafe: Paris, France; pp 145−157.

(9) Clinton, W. P. Consumer and expert evaluations of stored coffee products. In *9th International Scientific Colloquium on Coffee*, London, 1980; Association Scientifique Internationale pour le Cafe: Paris, France; pp 273−285.

(10) Hinman, D. C. Rates of oxidation of roast and ground coffee and the effect on shelf-life. In *14th International Scientific Colloquium on Coffee*, San Francisco, CA, 1991; Association Scientifique Internationale pour le Cafe: Paris, France; pp 156−164.

(11) Nicoli, M. C.; Innocente, N.; Pittia, P.; Lerici, C. R. Staling of roasted coffee: volatile release and oxidation reactions during storage. In *15th International Scientific Colloquium on Coffee*, Montpellier, France, 1993; Association Scientifique Internationale pour le Cafe: Paris, France; pp 557−565.

(12) Schenker, S. R. Investigations on the hot air roasting of coffee beans. Dissertation 13620, Eidgenoessische Technische Hochschule (ETH), Zuerich, Switzerland, 2000.

(13) Schenker, S.; Handschin, S.; Frey, B.; Perren, R.; Escher, F. Pore structure of coffee beans affected by roasting conditions. *J. Food Sci.* **2000**, *65* (3), 452−457.

(14) Lin, J. M.; Welti, D. H.; Vera, F. A.; Fay, L. B.; Blank, I. Synthesis of deuterated volatile lipid degradation products to be used as internal standards in isotope dilution assays. 1. Aldehydes. *J. Agric. Food Chem.* **1999**, *47* (7), 2813−2821.

(15) Milo, C.; Grosch, W. Changes in the odorants of boiled salmon and cod as affected by the storage of the raw material. *J. Agric. Food Chem.* **1996**, *44* (8), 2366−2371.

(16) Schieberle, P.; Hofmann, T. Evaluation of the character impact odorants in fresh strawberry juice by quantitative measurements and sensory studies on model mixtures. *J. Agric. Food Chem.* **1997**, *45* (1), 227−232.

(17) Anderson, B. A.; Shimoni, E.; Liardon, R.; Labuza, T. P. The diffusion kinetics of carbon dioxide in fresh roasted and ground coffee. *J. Food Eng.* **2003**, *59* (1), 71−78.

(18) Audouin, V. P. Sensory importance and interactions of character impact compounds in brewed coffee model systems. Ph.D., University of Minnesota, Minneapolis/St. Paul, MN, 2002.

(19) Czerny, M.; Mayer, F.; Grosch, W. Sensory study on the character impact odorants of roasted Arabica coffee. *J. Agric. Food Chem.* **1999**, *47* (2), 695−699.

(20) Arackal, T.; Lehmann, G. Messung des Quotienten 2-Methylfuran/2-Butanon von ungemahlenem Röstkaffee während der Lagerung unter Luftausschluss. *Chem. Mikrobiol. Technol. Lebensm.* **1979**, *6*, 43−47.

(21) Chin, H. W.; Lindsay, R. C. Ascorbate and Transition-Metal Mediation of Methanethiol Oxidation to Dimethyl Disulfide and Dimethyl Trisulfide. *Food Chem.* **1994**, *49* (4), 387−392.

(22) Parliment, T. H.; Kolor, M. G.; Rizzo, D. J. Volatile Components of Limburger Cheese. *J. Agric. Food Chem.* **1982**, *30* (6), 1006−1008.

(23) Holscher, W.; Steinhart, H. Investigation of Roasted Coffee Freshness with an Improved Headspace Technique. *Z. Lebensm.-Unters. Forsch.* **1992**, *195* (1), 33−38.

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