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COFFEE ROASTING AND QUENCHING TECHNOLOGY – FORMATION AND STABILITY OF AROMA COMPOUNDS

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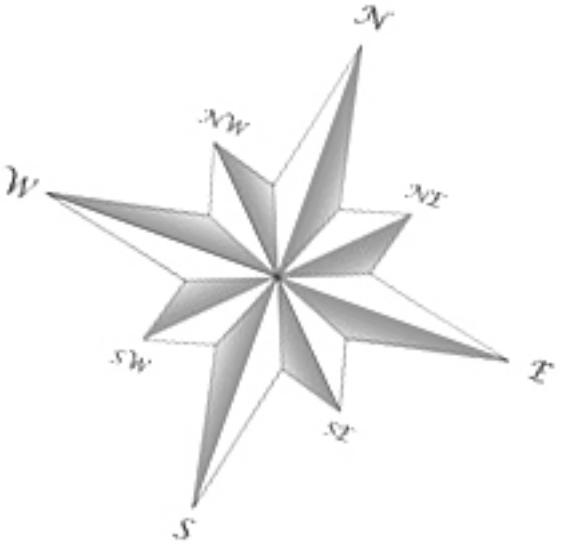
Quelli che s'innamorano della pratica
senza scienza sono come un nocchiere che
conduce una nave senza timone o bussola e
non ha mai certezza di dove sta andando.

Leonardo da Vinci



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Abbreviations

CIE	commission internationale d'éclairage
CZ	cooling zone
dm	dry mass
DVB	divinylbenzene
EDMP	2-ethyl-3,5-dimethylpyrazine
EI	electron ionization
GC	gas chromatography
HTST	high temperature–short time
IDA	isotope dilution assay
LTLT	low temperature–long time
m/z	mass-to-charge ratio
MMBF	3-mercapto-3-methylbutyl formate
MS	mass spectrometry
n.a.	not available
n.d.	not detected
PDMS	polydimethylsiloxane
PTR	proton transfer reaction
RZ	roasting zone
SIM	single ion monitoring
SPME	solid-phase microextraction
TMP	2,3,5-trimethylpyrazine
wb	wet basis

Summary

Coffee is one of the world's most popular beverages. Roasting presents the key step in coffee processing to develop the characteristic flavor properties for which coffee is appreciated. In addition, roasting induces major physical changes within the coffee beans and determines their behavior in storage, grinding, and brewing. In the present dissertation, the impact of the roasting parameters roasting time, roasting temperature, moisture content, quenching method, and roaster design, on aroma formation, aroma stability, and grinding properties of roasted coffee were investigated.

Coffee was roasted on a laboratory scale using a fluidized-bed hot air roaster with batch size from 100 to 200 g, and on production scale using horizontal drum, semi-fluidized bed, rotating bowl, and tangential roasters with batch sizes of 20 to 170 kg. In laboratory scale roasting, hot air velocity, bean core temperature, bulk temperature, hot air temperature, as well as cooling air temperature and amount of quenching water were monitored during the roasting trials. Industrial scale roasting trials were carried out where results complementary to laboratory trials were needed under realistic industrial roasting conditions, in particular regarding the level of energy transfer. The industrial trials were less controllable, and usually only bulk pile temperatures were recorded during the process. Structural and physical changes during roasting of coffee were monitored using weight, color, density, firmness, porosity, and degassing behavior. In addition, the particle size distribution and extraction properties were determined for the elucidation of the impact of grinding on product properties.

Emphasis of product characterization was put on the analysis of aroma compounds. For this purpose, headspace solid-phase microextraction (HS-SPME) was coupled to

gas chromatography–mass spectrometry. The quantification of aroma compounds was carried out with stable isotope labeled standard substances.

Time-temperature conditions are decisive for the generation of aroma compounds during coffee roasting. At the same degree of roast, physical properties and concentrations of aroma compounds can differ considerably as a function of the applied time-temperature combinations. If similar time-temperature profiles are applied on different roasting equipments, e.g. horizontal drum roaster and fluidized-bed roaster, similar aroma profiles are obtained. When coffees with different initial water content are roasted, differences in the evolution of the degree of roast and aroma formation are observed in light roasts because of the slower temperature increase in coffees with high moisture content. Steam treatment of coffee prior to roasting leads to changes in the aroma profile of roasted coffee because of the partial extraction of precursor compounds.

Quenching of coffee, which can be carried out with air or water, has a major impact on the aroma stability during storage of the roasted coffee. When coffee is water-quenched, water uptake is possible. In turn, the increased moisture content affects bean firmness and grinding behavior, accelerates degassing in whole coffee beans, and influences loss and degradation of aroma compounds. Open stored coffee beans and roast and ground coffees lose dimethyl sulfide, 3-mercapto-3-methylbutyl formate, and *N*-methylpyrrole faster with increasing moisture content, while the accumulation of dimethyl trisulfide is faster and quantitatively more important. This suggests that degradation reactions are faster in coffees with higher moisture content. If roast and ground coffee is packaged under protective atmosphere, also other compounds, such as Strecker aldehydes and α-diketones, degrade faster with increasing moisture, and differences are particularly distinct. It is therefore recommended to store coffee at low moisture level to extent shelf-life.

During grinding of roasted coffee, a part of the volatile fraction is released and can be trapped when grinding is carried out under water. The resulting coffee suspension can be used directly for extraction, and a promising two-step process would result for producing coffee beverages.

Zusammenfassung

Kaffee ist nicht nur eines der beliebtesten Getränke, sondern auch ein wichtiges Welthandelsgut. Für die Entwicklung des charakteristischen Aromas und Geschmacks stellt die Röstung den entscheidenden Schritt in der ganzen Verarbeitungskette von der Kaffeekirsche am Baum zum Röstkaffee dar. Beim Rösten werden nicht nur die Aromastoffe gebildet, es finden auch strukturelle Veränderungen im Innern der Bohne statt, die unter anderem die Lagerfähigkeit, das Mahlverhalten und die Extraktion beeinflussen. In der vorliegenden Dissertation wurde untersucht, welchen Einfluss die Röstparameter Röstzeit, Rösttemperatur, Wassergehalt, Kühlmethode und Röster-design auf die Bildung von Aromastoffen und deren Stabilität während der Lagerung haben. Ausserdem wurden die Einflüsse der Rösttechnologie auf das Mahl- und Extraktionsverhalten untersucht.

Röstversuche wurden mit einem Heissluft-Fliessbettröster mit einer Kapazität von 100 bis 200 g pro Charge, sowie auf industriellen Röstanlagen durchgeführt. Diese wiesen Batchgrössen von 20 bis 170 kg auf und waren von verschiedenster technischer Ausführung: Trommelröster (horizontal), Semi-Fliessbettröster, Zentrifugalröster und Tangentialröster. Im Labormassstab konnten Heissluft-Geschwindigkeit, Heissluft-Temperatur, Kühlluft-Temperatur, Haufen- und Bohnenkern-Temperaturen, sowie die Menge des eingesetzten Kühlwassers präzise bestimmt und verfolgt werden. Bei Röstungen im Industriemassstab war eine derart genau Kontrolle der Prozessparameter nicht möglich. Dennoch wurden ergänzende Industrieröstungen durchgeführt, um einen energetisch realistischen Wärmetransfer auf die Bohnen zu erzielen, was im Labormassstab nur beschränkt möglich war. Die physikalischen Änderungen der Kaffeebohne während des Röstens wurden via Röstverlust, Farbe,

Dichte, Zähigkeit, Porosität, Entgasungsverhalten, Partikelgrössenverteilung beim Mahlen und Extraktionsfähigkeit des gemahlenen Kaffees verfolgt.

Den Hauptakzent der Produktcharakterisierung bildete die Analyse der Aromastoffe. Diese wurden mittels Kopfraum-Festphasen-Mikroextraktion (HS-SPME) extrahiert, anschliessend gaschromatographisch aufgetrennt und durch Isotopenverdünnungs-analyse im Massenspektrometer quantifiziert.

Für die Ausbildung des Kaffeearomas ist das Zeit-Temperatur-Profil während der Röstung entscheidend. Unterschiedliche Kombinationen von Zeit und Temperatur führen bei gleichem Röstgrad zu unterschiedlichen physikalischen Eigenschaften und Aromastoffkonzentrationen. Werden andererseits ähnliche Zeit-Temperatur-Profile auf unterschiedlichen Röstsystemen verwendet, sind auch die daraus resultierenden Aromaprofile ähnlich. Variationen im Ausgangswassergehalt führen bei hellen Röstungen zu abweichenden Aromaprofilen, da die Entwicklung eines Röstgrades in Abhängigkeit des Wassergehaltes unterschiedlich schnell verläuft. Bei dunklen Röstungen hingegen sind diese Differenzen kaum noch ausgeprägt. Wird der Kaffee vor der Röstung mit Dampf behandelt, ändert sich das Aromaprofil des gerösteten Kaffee deutlich aufgrund partialer Extraktion von Präkursoren der Aromabildung.

Die Kühlung des Kaffees nach dem Rösten erfolgt mit Kaltluft oder einer Kombination von Kaltluft und Wasser. Wird Wasser eingesetzt, lässt sich der Wassergehalt des gerösteten Kaffees erhöhen. Allerdings führt ein erhöhter Wassergehalt zu grösserer Zähigkeit und unterschiedlichem Mahlverhalten, erhöhter Austragung von Kohlendioxid und schnellerem Verlust von Aromasubstanzen. Dimethylsulfid, 3-Mercapto-3-methylbutylformat und *N*-Methylpyrrol werden in Kaffeebohnen und gemahlenem Kaffee schneller abgebaut bei höherer Restfeuchte, während Dimethyltrisulfid in stärkerem Masse zunimmt. Wird gemahlener Kaffee unter Schutzatmosphäre verpackt, wird die Abbaugeschwindigkeit weiterer Substanzen, beispielsweise α-Diketone und Strecker-Aldehyde, ebenfalls von höherer Restfeuchte beeinflusst, und die Unterschiede in Abhängigkeit des Wassergehaltes treten besonders deutlich hervor. Aus diesem Grund wird empfohlen, dass zur

Verlängerung der Haltbarkeit gerösteten Kaffees der Wassergehalt möglichst gering gehalten werden soll.

Wird Kaffee gemahlen, geht ein Teil der Aromafraktion verloren, der aber aufgefangen werden kann, wenn die Mahlung unter Wasser erfolgt. Die daraus resultierende Kaffeesuspension kann mit einem Zwei-Stufen-Prozess direkt zur Herstellung von Kaffeegetränken genutzt werden.

1 Introduction

Coffee is one of the most appreciated beverages worldwide and its annual trade volume accounts for around 7 million tons of green coffee. The popularity of coffee is not based on nutritional value or potential health benefits, but, besides the slight stimulating effect, simply on its characteristic flavor properties.

The flavor of coffee is generated virtually exclusively during roasting and consists of an immense spectrum of substances with various concentrations. Around 1000 volatile compounds have been identified in roasted coffee, whereof a minority of around 30 compounds is responsible for the main impression of coffee odor.

Coffee flavor is influenced by agricultural and technological factors. The coffee bean variety and its provenance, green coffee processing and storage of processed coffee are the main determinants of green coffee quality. However, the roasting process alone decides how much of the potential of a green coffee bean is transformed in roasted coffee flavor. Despite the longtime experience, roasting is still an empirical standard technology. There are different ways to roast coffee, starting from grandmother's roasting pan all the way to industrial batch roasters of different design and continuous roasting systems with large product throughput. In addition, various pre-treatments related to roasting claim to improve roasted coffee quality, such as preheating and steam treatment.

Roasted coffee is a product of very limited shelf-life. To prevent the rapid deterioration of coffee flavor, roasted coffee needs to be stored under protective conditions. The oxygen concentration in storage atmosphere and the impact of temperature have been identified as the major sources of coffee staling [1-4]. Moisture

also has a negative effect on coffee flavor stability [2]. The impact of moisture on product stability is particularly interesting with regard to coffee roasting technology because the water content of the final product may be controlled by quenching techniques at the end of the roasting process.

The project presented in this dissertation deals with the role of roasting technology in aroma formation and aroma stability of roasted coffee. As the methodology of aroma analysis is critical for any such investigation, a separate chapter is devoted to the experimental development of the respective analytical methods. Six chapters cover the main experimental topics: impact of time-temperature conditions and initial moisture content on aroma formation during roasting, the effects of water quenching on degassing, storage stability, and grinding behavior of roasted coffee, and aroma recovery from roasted coffee by wet grinding methods. A short review of the extensive literature so far published and a general conclusion and outlook frame these chapters.

2 Background

2.1 Coffee roasting

Coffee is roasted by dry heat treatment to a bean core temperature beyond 200 °C, which is atypically high for a food product. The generation of the characteristic flavor, the development of brown to dark brown color, and the increase of coffee bean volume are the most obvious changes from green to roasted coffee. The green coffee bean exhibits a cellular structure and, therefore, may be regarded as an aggregation of small reactor units, which withstand a large pressure buildup during roasting, because of the comparatively thick cell walls. So far there has not been any evidence of cell wall rupture in roasted coffee [5], and it is assumed, that coffee cell walls change from a glassy to a more elastic rubbery state during roasting [6, 7]. The impact of elevated temperatures for a given roasting time leads to the development of a degree of roast with regard to color, roast loss, flavor, and chemical changes in selected components [8]. Color is frequently used as a measure of the degree of roast, and it was suggested that color is directly related to the final roasting temperature [9, 10]. However, a series of roasting trials on a production scale did not corroborate this assumption [5]. Several methods for indirect determination of the degree of roast have been proposed, using the ratios of free amino acids [11], alkylpyrazines [12], the content of chlorogenic acids [9], and the analysis of roasting exhaust gases by PTR-MS [13] and by a chemosensor array [14].

The quality of raw material is most important for the quality of roasted coffee, while process temperature, hot air humidity, and air-to-bean ratio have been identified as important process factors [5]. The conventional roasting technology uses a horizontal rotating drum, a vertical drum with paddles, or a rotating vertical bowl to keep the coffee beans moving, while hot air flows through the roasting device. Roasting times are generally around 10 min. Shorter roasting times are realized by using fluidized-

bed roasting equipment where beans are kept in motion by the high velocity of hot air. While heat transfer in conventional roasting is mostly convective and partially conductive, heat transfer in fluidized-bed roasting is practically exclusively convective. Fast roasting is reported to result in higher amount of soluble solids, less degradation of chlorogenic acids, lower loss of volatiles and lesser burnt flavor [15]. In addition fast roasting leads to larger volume increase, larger carbon dioxide desorption and higher oil migration [5].

Extensive research on hot air roasting of coffee beans, structure development, and the impact of different process parameters was carried out by Schenker [5] and Geiger [6]. Detailed comprehensive reviews on coffee roasting technology were written by Eggers and Pietsch [16] and Clarke [8].

2.2 Generation of aroma compounds during roasting

Maillard reactions have been identified to be the major pathway in the formation of volatile compounds in coffee roasting [17]. In the Maillard reaction, reducing sugars such as glucose or fructose react with free amino acids to form *N*-substituted glycosylamine adducts, which are then rearranged to aminoketones and aminoaldoses by Amadori and Heynes rearrangements. A complex reaction cascade of Amadori and Heynes rearrangement products leads to numerous volatile compounds and complex melanoidins. These reactions, i.e. the Strecker degradation, condensation reactions, rearrangements, and others, were summarized in the now so-called Hodge scheme [18]. Other compounds present in raw coffee, e.g. nitrogen containing substances, chlorogenic acids, and lipids, are also involved in reactions which lead to the generation of aroma compounds. A simplified reaction scheme for coffee flavor compounds was presented by Yeretzian and coworkers [19]. Reviews on flavor generation in coffee worth reading are available from Flament [20], Reineccius [21], and Shibamoto [17]. Only about 30 of the several hundred identified aroma compounds are mainly responsible for the characteristic coffee odor (Table 2.1). Grosch [22] summarized their evaluation by gas chromatography–olfactometry and

the identification of the most important odorants within the group of character impact odorants by omission experiments. 2-furfurylthiol, 4-vinylguaiacol, the alkylpyrazines and furanones listed in Table 2.1, acetaldehyde, propanal, methylpropanal, and 2- and 3-methylbutanal were found to be the odorants with the highest impact on coffee aroma.

The reaction conditions within coffee beans during the roasting process are different to those usually applied to model systems in aqueous solution, and, therefore, results from model reactions have to be interpreted with care. It was shown by Schieberle [23] that fundamentally different reaction pathways might occur depending on the water content of the reaction mixtures, such as in the reaction of glucose with L-proline. In coffee beans, high temperature is accompanied by a considerable pressure buildup, and reactions may take place in the gas phase or at the surfaces of cell walls. As described before, due to their specific microstructure, coffee beans are compartmentalized during roasting in cellular microreactor units, giving rise to very specific reaction conditions. Using thermo-gravimetric measurements, it was shown that roasting of green coffee powder and green coffee bean fragments is different to the roasting of whole coffee beans [24]. Roasting experiments with ground green coffee or fragments of beans are therefore of limited value. The most promising approach to mimic the specific conditions has been undertaken by Müller, Lang and Hoffmann [25, 26], who used extracted green coffee bean shells as a matrix for model reactions.

Table 2.1 Character impact odorants of roasted coffee as described by Grosch [22].

1	Acetaldehyde
2	Propanal
3	Methylpropanal
4	2-Methylbutanal
5	3-Methylbutanal
6	2,3-Butanedione
7	2,3-Pentanedione
8	Methanethiol
9	Dimethyl trisulfide
10	3-Methyl-2-buten-1-thiol
11	2-Methyl-3-furanthiol
12	2-Furfurylthiol
13	3-(Methylthio)propanal (Methional)
14	3-Mercapto-3-methylbutyl formate
15	4-Hydroxy-2,5-dimethyl-3(2H)-furanone
16	5-Ethyl-3-hydroxy-4-methyl-2(5H)-furanone
17	3-Hydroxy-4,5-dimethyl-2(5H)-furanone
18	5-Ethyl-3-hydroxy-4-methyl-2(5H)-furanone
19	(E)-β-Damascenone
20	2-Methoxyphenol (Guaiacol)
21	2-Methoxy-4-ethylphenol (4-Ethylguaiacol)
22	2-Methoxy-4-vinylphenol (4-Vinylguaiacol)
23	3-Methoxy-4-hydroxybenzaldehyde (Vanilline)
24	2-Ethyl-3,5-dimethylpyrazine
25	2-Ethenyl-3,5-dimethylpyrazine
26	2,3-Diethyl-5-methylpyrazine
27	2-Ethenyl-3-ethyl-5-methylpyrazine
28	3-Isobutyl-2-methoxypyrazine

2.3 Aroma stability and staling of roasted coffee

Storage related changes of coffee aroma are generally referred to as staling. Steinhart and Holscher [27] proposed a two phase model for staling: loss of volatile compounds by aroma stripping short time after roasting, which is overlapped by chemical degradation reactions at longer storage times. From their results, the authors concluded that the aroma freshness of roasted coffee was mainly composed of the impact of some low-boiling odorants, mainly sulfur compounds, Strecker aldehydes and α-diketones, with methanethiol being the most important indicator. The perceived changes in coffee aroma may originate from the emergence of new off-flavor compounds or from a disturbance of the aroma balance caused by different degradation kinetics of the individual odorants. However, investigations on the evolution of odorants during storage of roasted coffee suggest that off-flavor does not result from newly formed compounds [28]. Oxygen, temperature, and moisture have been identified as the major factors influencing aroma staling [1-4, 29, 30]. In addition, Hinman [30] showed that staling of coffee might be accelerated by oxidative reactions which take place before packaging. Aroma deterioration is considerably faster in ground coffee because of the increased surface and the shorter pathways for oxygen diffusion. Mayer and Grosch [31] demonstrated that immediately after grinding, the aroma profile starts to change. The sweetish/caramel-like notes decreased, and the intensity of roasty, sulfurous, and smoky notes increased within minutes.

2.4 Solid-phase microextraction (SPME)

Solid-phase microextraction (SPME) is a solvent-free sampling technique and makes use of the sorption of analytes on polymeric organic material coatings on a silica fiber. Fiber coatings can consist of either solid adsorbents like divinylbenzene (DVB) or carboxen (CAR), or of polymers that are liquid at room temperature like poly-dimethylsiloxane (PDMS). For sampling, the SPME fiber is introduced in the headspace above a sample or immersed in a liquid sample. A scheme of headspace sampling is presented in Figure 2.1. The analytes are extracted and concentrated on

the fiber coating, transferred to the analytical instrument, and thermally desorbed. SPME has found a large number of applications and a wide acceptance as a tool for sample preparation since its introduction by Pawliszyn in 1989 [32-34]. A broad range of books and reviews on principles and applications are available. Stashenko and coworkers [35] provide a comprehensive overview.

For the analysis coffee aroma compounds, SPME has been applied extensively because of its simplicity of use and the fast, solvent-free sample preparation [36-39]. Concerning the choice of fiber, Roberts and coworkers [38] found that PDMS/DVB coatings had highest overall sampling sensitivity and were especially adapted for guaiacol, 4-ethylguaiacol and 4-vinylguaicol, whereas CAR/PDMS was the most advisable coating for acids and small molecules. Because of the large differences in structure and polarity of coffee aroma impact compounds [40], a three-component fiber (DVB/CAR/PDMS) might be the best choice.

Although the method is simple, the physical chemistry behind SPME is complex and quantitative measurements with SPME are not straightforward. The amount adsorbed on the fiber depends not only on the concentration, but also on the partition coefficients between coffee solution and headspace on the one hand, and between headspace and fiber on the other hand [41]. In addition, some analytes may reach equilibrium faster than others and compete for adsorption on the fiber coating. There are several examples reported for this competition effect [42-47]. Competition effects can be minimized by using short fiber exposure time, which allows to remain in the linear range for all analytes [38, 42, 43, 45, 47].

The fact that reproducibility in CAR/DVB/PDMS fibers may be a problem presents a further challenge in quantitative SPME analysis [48]. The main difficulty in the quantification with internal standards is that small chemical differences between molecules can have a large impact on adsorption. Blank and coworkers [41] showed that even for very similar analytes like guaiacol, 4-ethylguaiacol, and 4-vinylguaiacol, the adsorption behavior can be fundamentally different. The same authors showed that the limitations of SPME, i.e. small linear range and competition effects, can be overcome by the use of stable isotope labeled compounds as internal standards.

Isotope dilution assays (IDA) with labeled standards for quantification were first used in aroma analysis in 1987 by Schieberle and Grosch [49] for the analysis of *N*-heterocyclic odorants in wheat bread crust and have been applied to coffee by various authors [38, 40, 50-53].

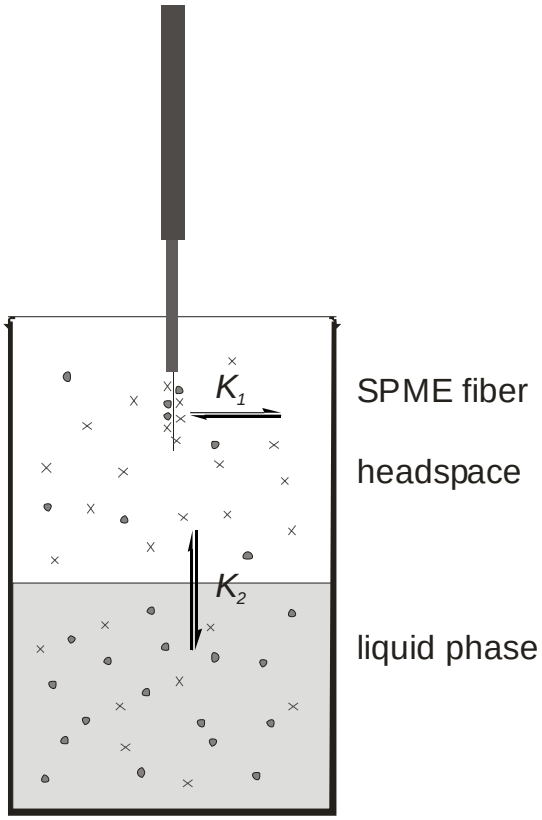

Figure 2.1 Schematic representation of the headspace SPME sampling of a liquid sample. K_1 and K_2 are the fiber coating/headspace and the liquid phase/headspace partition coefficients, respectively. In this example, compound 1 (•) exhibits larger K_1 and K_2 than compound 2 (×).

3 Aspects of analytical methodology

3.1 Introduction

The aim of this chapter on general aspects of analytical methodology is to summarize the approach for aroma analysis applied in the present research project. The numbering of odorants is kept consistent throughout the dissertation (Table 3.1). The performance of the analytical method with regard to parameters such as repeatability and robustness was determined. Some parameters of the analytical method, such as investigated odorants, GC stationary phase, temperature programs and instrument types changed in the course of the project. These changes are specified in the "Materials and methods" sections of the following chapters.

3.2 Materials and methods

3.2.1 Green coffee and coffee roasting

Green *Coffea Arabica Tip.* variety from Sumatra (Mandheling, S-795, Kartika 1), supplied by Rast Ltd. (Ebikon, Switzerland) with a moisture content of 10.04 g/ 100 g wb was roasted on the fluidizing-bed laboratory roaster described in chapter 4 at 228 °C for 11 min if not stated otherwise.

The roasted coffee was stored at -80 °C and ground in frozen state immediately before the aroma analysis.

3.2.2 Standards

Methanethiol (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
Dimethyl sulfide (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
Dimethyl disulfide (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
Dimethyl trisulfide (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
3-Mercapto-3-methylbutyl formate (Oxford Chemicals Ltd., Hartlepool, UK)
2-Furfurylthiol (Aldrich, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
Methylpropanal (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
2-Methylbutanal (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
3-Methylbutanal (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
Hexanal (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
2,3-Butanedione (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
2,3-Pentanedione (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
N-Methylpyrrole (Aldrich, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
Pyridine (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
4-Vinylguaiacol (Aldrich, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
2,3,5-Trimethylpyrazine (Aldrich, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)
2-Ethyl-3,5-dimethylpyrazine and 2-Ethyl-3,6-dimethylpyrazine (Aldrich, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland)

[$^{2}H_3$]-Methanethiol (Sigma-Aldrich Ltd., St. Louis, MO, USA)
[$^{2}H_6$]-Dimethyl sulfide (Dr. Ehrenstorfer GmbH, Augsburg, Germany)
[$^{2}H_6$]-Dimethyl disulfide (Cambridge Isotope Laboratories Inc., Andover MA, USA)
[$^{2}H_6$]-Dimethyl trisulfide (Synthesis [54] at Nestlé Research Center, Lausanne, Switzerland)
[$^{2}H_6$]-3-Mercapto-3-methylbutyl formate (AromaLAB, München, Germany)
[$^{2}H_2$]-2-Furfurylthiol (Toronto Research Chemicals, North York, Canada)
[$^{2}H_7$]-Methylpropanal (AromaLAB, München, Germany)
[$^{2}H_2$]-3-Methylbutanal (Dr. Ehrenstorfer GmbH, Augsburg, Germany)
[$^{2}H_2$]-Hexanal (Synthesis [55] at Nestlé Research Center, Lausanne, Switzerland)
[$^{13}C_4$]-2,3-Butanedione (AromaLAB, München, Germany and synthesis [56] at Nestlé Research Center, Lausanne, Switzerland)
[$^{13}C_2$]-2,3-Pentanedione (AromaLAB, München, Germany and synthesis [56] at Nestlé Research Center, Lausanne, Switzerland)
[$^{2}H_3$]-*N*-Methylpyrrole (Cambridge Isotope Laboratories Inc., Andover MA, USA)
[$^{2}H_5$]-Pyridine (Dr. Ehrenstorfer GmbH, Augsburg, Germany)
[$^{2}H_3$]-4-Vinylguaiacol (Witega Laboratorien, Berlin, Germany)
[$^{2}H_{9\text{-}10}$]-2,3,5-Trimethylpyrazine (Toronto Research Chemicals, North York, Canada)
[$^{2}H_6$]-2-Ethyl-3,5-dimethylpyrazine (Toronto Research Chemicals, North York, Canada)

3.2.3 Identification of aroma compounds

All investigated odorants were identified by comparison of their retention indices (RI) on two stationary phases (ZB-Wax and ZB-1701, Phenomenex, Aschaffenburg, Germany) as well as their mass spectra to those of standard compounds.

3.2.4 Sample preparation and aroma analysis

Sample preparation and aroma analysis consisted of grinding, hot-water extraction of coffee, addition of isotope labeled standards, equilibrating, headspace solid-phase microextraction followed by separation by gas chromatography, and quantification with mass spectrometry in the single ion monitoring mode.

The method was carried out as follows:

1. Grinding of roasted coffee beans. If not stated otherwise a Bühler-Miag 4000 grinder (Bühler Ltd., Milano, Italy, level 3) was used.

2. Weighing and extraction of 5 g or 1 g of ground coffee with 95 g (5% total solids) or 99 g (1% total solids) boiling water respectively in closed 100 mL flasks for 10 min under constant stirring.

3. Cooling of the flasks under tap water.

4. Addition of deuterated and ^{13}C-labeled standards (Table 3.1, structures are displayed in Figure 3.1) and stirring for 10 min. The amount of added standards was chosen so as to obtain roughly equal concentration of standard and analyte in the coffee brew.

5. Sampling and transfer of 7 mL of the supernatant liquid phase to 20 mL headspace vials.

6. Headspace solid-phase microextraction.

7. Separation and quantification of odorants by means of GC-MS.

Due to the differences in concentrations of odorants, and in order to minimize interferences between the degradation products of analytes and standards (e.g. methanethiol and dimethyl disulfide), aroma compounds were divided into two groups for the analysis. Group 1 contained methanethiol (**1**), dimethyl sulfide (**2**), 3-mercapto-3-methylbutyl formate (**5**), 2-furfurylthiol (**6**), hexanal (**10**), 2,3,5-trimethylpyrazine (**16**), and 2-ethyl-3,5-dimethylpyrazine (**17**). For the analysis of group 1, 5 g of roast and ground coffee were extracted with 95 g boiling water (5% total solids). Group 2 included dimethyl disulfide (**3**), dimethyl trisulfide (**4**), methylpropanal (**7**), 2-methylbutanal (**8**), 3-methylbutanal (**9**), 2,3-butanedione (**11**), 2,3-pentanedione (**12**), *N*-methylpyrrole (**13**), pyridine (**14**), and 4-vinylguaiacol (**15**). 1 g of roast and ground coffee was extracted with 99 g boiling water (1% total solids).

Table 3.1 Analytes and standards used for the quantitative analysis of aroma compounds by GC-MS.

Analyte (A)	Selected ion (*m/z*) of A	Internal standard (IS)	Selected ion (*m/z*) of IS [a]
Methanethiol (**1**)	48	[$^2H_3$]-**1**	51
Dimethyl sulfide (**2**)	47	[$^2H_6$]-**2**	50
Dimethyl disulfide (**3**)	94	[$^2H_6$]-**3**	100
Dimethyl trisulfide (**4**)	126	[$^2H_6$]-**4**	132
3-Mercapto-3-methylbutyl formate (**5**)	102	[$^2H_6$]-**5**	108
2-Furfurylthiol (**6**)	114	[$^2H_2$]-**6**	116
Methylpropanal (**7**)	72	[$^2H_7$]-**7**	79
2-Methylbutanal (**8**)	86	[$^2H_2$]-**9**	88
3-Methylbutanal (**9**)	71	[$^2H_2$]-**9**	73
Hexanal (**10**)	56	[$^2H_2$]-**10**	58
2,3-Butanedione (**11**)	43	[$^{13}C_4$]-**11**	45
2,3-Pentanedione (**12**)	100	[$^{13}C_2$]-**12**	102
N-Methylpyrrole (**13**)	81	[$^2H_3$]-**13**	84
Pyridine (**14**)	79	[$^2H_5$]-**14**	84
4-Vinylguaiacol (**15**)	150	[$^2H_3$]-**15**	153
2,3,5-Trimethylpyrazine (**16**)	122	[$^2H_{9\text{-}10}$]-**16**	131 & 132
2-Ethyl-3,5-dimethylpyrazine (**17**)	135	[$^2H_{9\text{-}10}$]-**16**	131 & 132

[a] The appropriate response factors were determined with standard solutions of the unlabeled compounds.

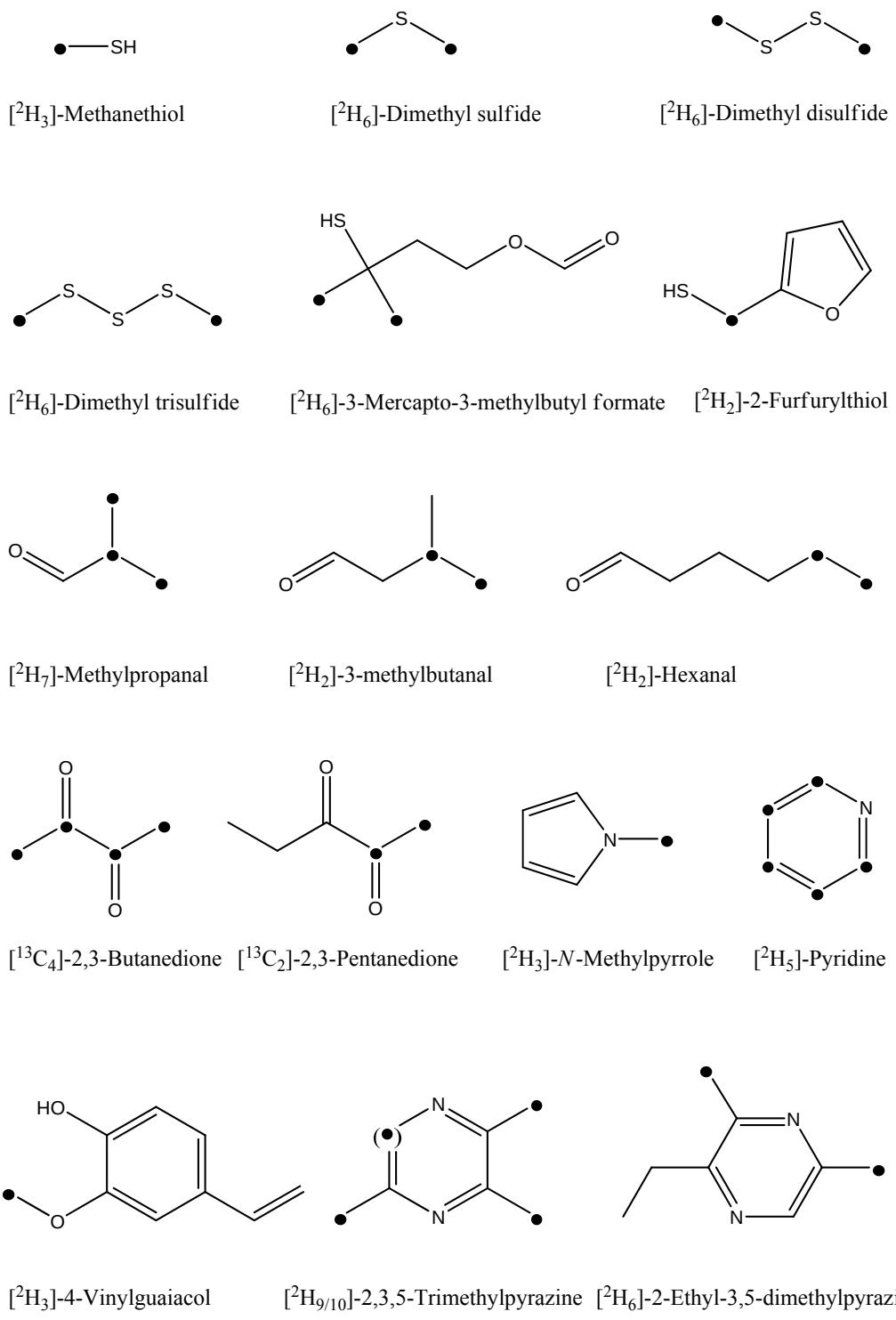

Figure 3.1 Structure of ^2H and ^{13}C labeled standards used for isotope dilution assays (position of labels: •). [$^2H_6$]-2-Ethyl-3,5-dimethylpyrazine was used for the quantification of pyrazines in chapters 6 and 9.

Coffee aroma compounds were sampled with solid-phase microextraction at 40 °C for 10 min with a 50/30 µm StableFlex DVB/CAR/PDMS fiber (Supelco, Buchs, Switzerland). The injection was carried out at 240 °C in the splitless mode with a splitless time of 240 s. Compounds **3, 4, 7-9** and **11-15** were separated on a 60 m × 0.25 mm × 0.25 µm ZB-Wax column (Phenomenex, Aschaffenburg, Germany) with a Fisons 8000 Series gas chromatograph (Thermo Electron, Allschwil, Switzerland) with the following temperature program: 40 °C (6 min), 4 °C/min, 120 °C (0 min), 40 °C/min, 240 °C (5 min). Helium 5.6 was used as carrier gas at a constant column head pressure of 135 kPa. The gas chromatograph was coupled to a quadrupole mass spectrometer SSQ710 (Finnigan MAT, San Jose, California), where mass spectra were recorded in the single ion monitoring (SIM) mode using electron ionization and an ionization potential of 70 eV. Compound **1** was quantified using the same set-up with the following temperature program: 40 °C (6 min), 40 °C/min, 240 °C (5 min). Compounds **2, 5, 6, 10, 16,** and **17** were separated on a 60 m × 0.25 mm × 0.25 µm ZB-1701 column (Phenomenex, Aschaffenburg, Germany) in a 2000 series TRACE GC gas chromatograph (Thermo Quest CE Instruments, Milano, Italy) with 40 °C (6 min), 4 °C/min, 120 °C (0 min), 40 °C/min, 240 °C (5 min) as temperature program**.** Helium 5.6 was used as carrier gas at a constant flow of 1.5 mL/ min. The GC was coupled to a TSQ triple quadrupole mass spectrometer (Finnigan MAT, San Jose, California) with Q1 operating in the RF-only mode. Spectra were recorded in the single ion monitoring mode. Electron ionization with an ionization potential of 70 eV was used. All SPME-GC-MS measurements were run in triplicate.

Typical total ion chromatograms of aroma analyses of groups 1 and 2 are presented in Figures 3.2 and 3.3

3.2.5 Statistical analysis

Student's *t*-test was applied to the results with a level of significance of 95%.

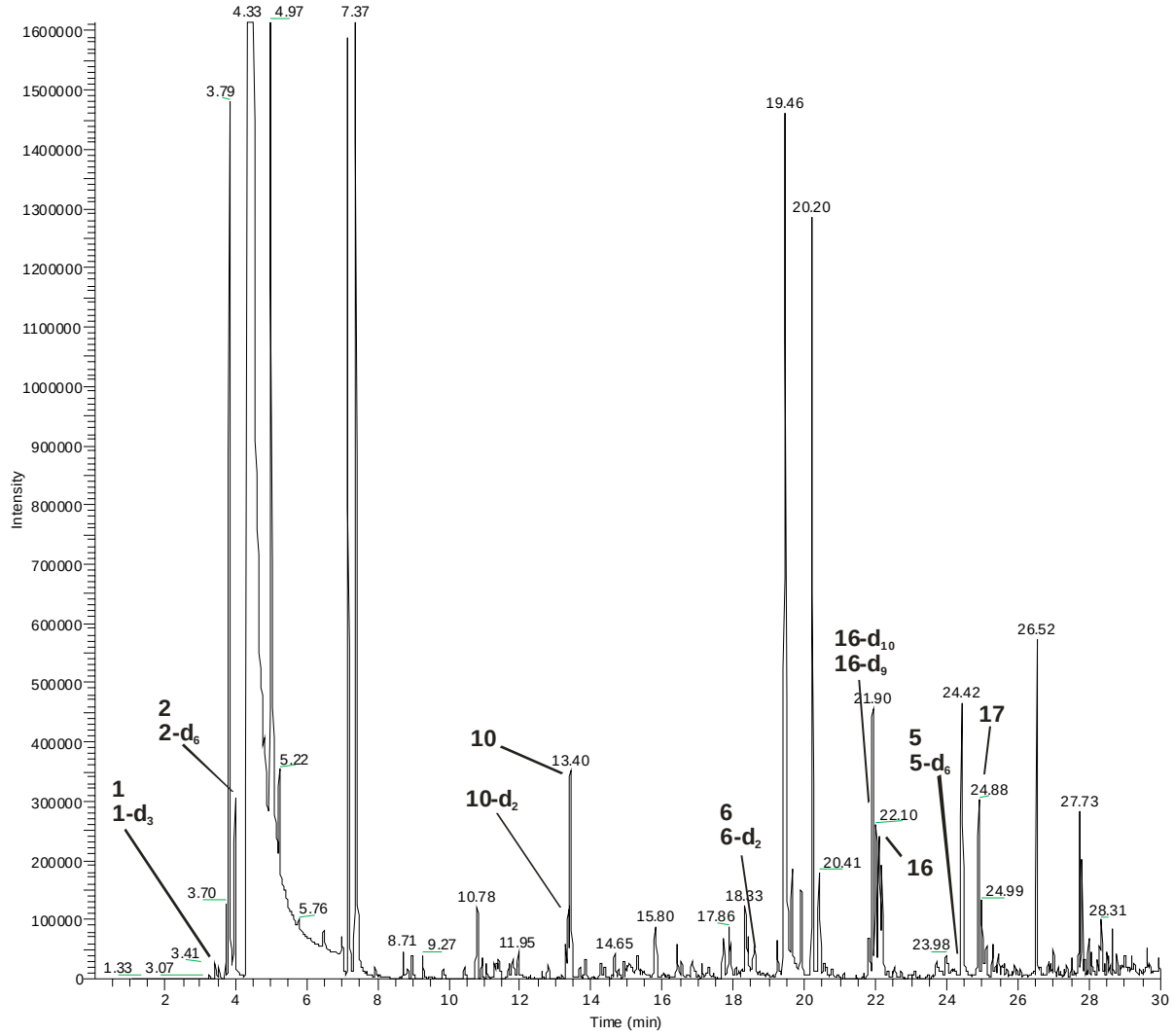

Figure 3.2 Total ion chromatogram of the aroma analysis of a coffee sample (Group 1).

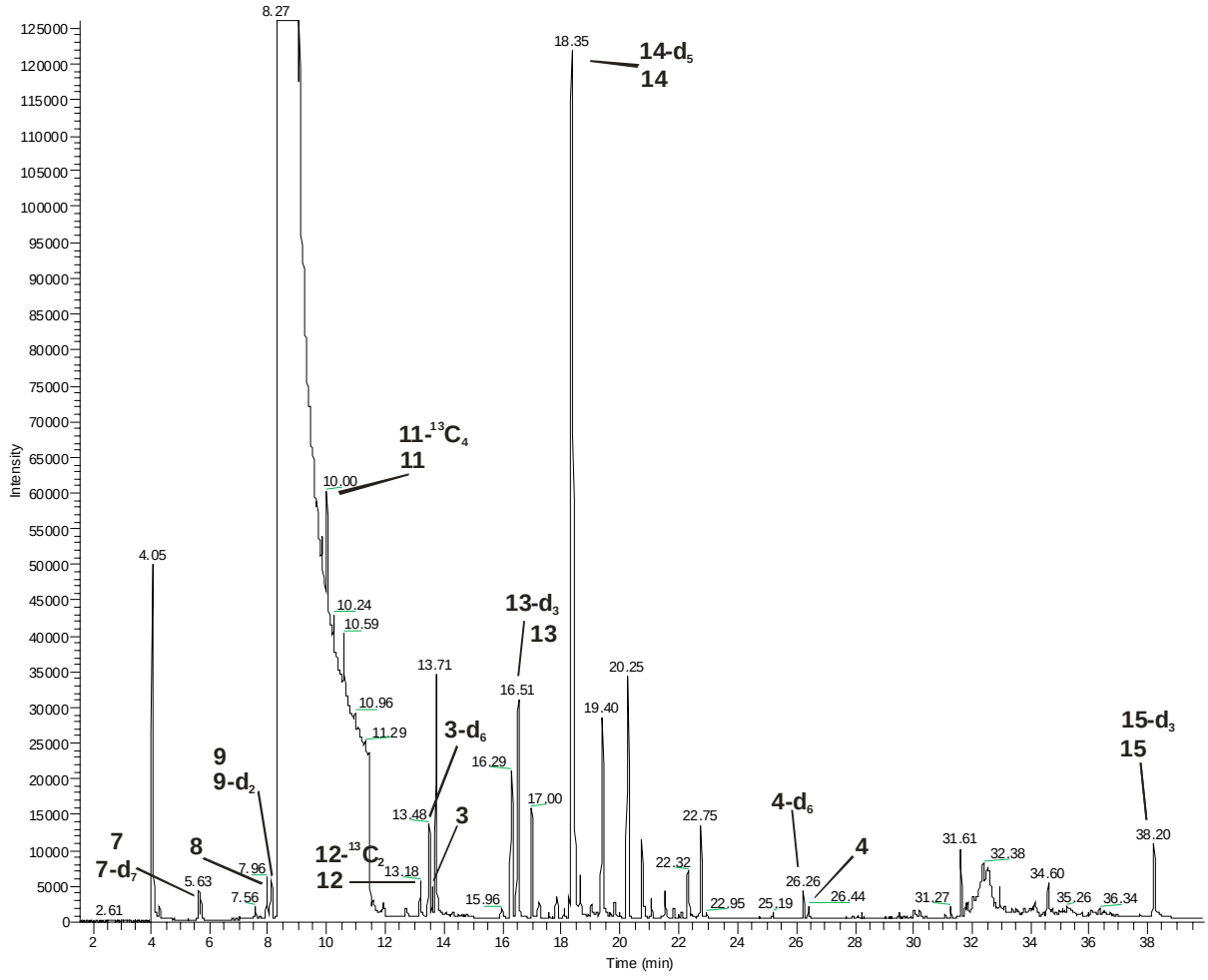

Figure 3.3 Total ion chromatogram of the aroma analysis of a coffee sample (Group 2).

3.3 Repeatability

The repeatability of the whole sample preparation and aroma analysis (grinding, extraction, cooling, addition of standards, headspace solid-phase microextraction, GC-MS analysis) was generally in an acceptable range. Standard deviations were rarely higher than 10%, and often below 5%. Relative standard deviations of a series of roasting trials are displayed in Table 3.2. Sample preparations were carried out in triplicates, and each preparation was subjected to triplicate headspace SPME–GC–MS analysis.

3.4 Robustness of the analytical method

The definition of the term robustness according to the United States Pharmacopeia (USP) and the International Conference on Harmonisation of Technical Requirements for the Registration of Pharmaceuticals for Human Use (ICH) is cited in Dejaegher and Vander Heyden [57]: "The robustness of an analytical procedure is a measure of its capacity to remain unaffected by small, but deliberate variations in method parameters and provides an indication of its reliability during normal usage." There is high similarity between the terms *robustness* and *ruggedness*. The USP distinguishes between them, while the ICH designates them as synonyms [57].

With each step of the sample preparation and analysis being a potential source of variation, the robustness of the method with regard to several method parameters was investigated by using the one-variable-at-a-time (OVAT) procedure.

Table 3.2 Standard deviation (%) of sample preparation and headspace SPME-GC-MS analyses of roasted coffee (3 sample preparations and 3 SPME-GC-MS analyses per sample preparation).

Sample [a]	A0	A1	A2	A3	A4	A5	A6	A7
Roasting Time at 228 °C [s]	*120*	*240*	*420*	*600*	*660*	*720*	*840*	*1140*
Lightness [L]* [b]	*36.2*	*27.1*	*22.8*	*21.4*	*21.0*	*20.8*	*20.3*	*19.5*
	Standard deviation (n = 3) [%]							
Methanethiol (**1**)	2.5	8.6	4.6	7.8	8.4	3.9	4.8	5.4
Dimethyl sulfide (**2**)	9.7	17.5	4.5	6.3	4.0	9.6	6.2	1.7
Dimethyl disulfide (**3**)	21.6	8.6	6.0	3.9	1.7	4.8	6.3	6.7
Dimethyl trisulfide (**4**)	5.2	6.9	8.9	2.8	2.0	9.5	8.7	9.3
3-Mercapto-3-methylbutyl formate (**5**)	5.8	4.3	3.2	0.9	3.8	10.4	4.6	6.1
2-Furfurylthiol (**6**)	9.0	5.2	10.5	3.0	0.8	12.0	5.4	11.1
Methylpropanal (**7**)	14.2	6.3	10.2	6.8	4.3	9.8	4.2	5.0
2-Methylbutanal (**8**)	5.2	9.3	13.8	10.1	0.9	5.4	4.7	2.1
3-Methylbutanal (**9**)	2.1	9.6	15.1	10.3	2.4	2.4	6.6	2.5
Hexanal (**10**)	2.9	12.8	7.6	0.8	4.3	19.9	3.4	5.5
2,3-Butanedione (**11**)	2.8	4.5	4.4	4.3	0.7	3.8	3.6	5.0
2,3-Pentanedione (**12**)	1.9	6.1	3.2	6.1	1.5	1.4	8.0	3.4
N-Methylpyrrole (**13**)	4.6	10.7	5.5	8.1	3.0	1.2	8.4	3.6
Pyridine (**14**)	5.2	8.7	6.0	4.1	0.5	2.6	7.6	1.2
4-Vinylguaiacol (**15**)	1.4	0.9	2.0	2.9	5.2	1.9	2.2	1.9
2,3,5-Trimethylpyrazine (**16**)	2.0	6.2	5.4	5.4	4.3	1.9	2.8	3.3
2-Ethyl-3,5-dimethyl-pyrazine (**17**)	8.1	13.6	10.7	5.9	6.0	0.5	10.3	1.9

[a] The samples correspond to the LTLT roasting trials as described in chapter 4.

[b] The method for the determination of L*-values is described in chapter 4.

Table 3.3 Losses of odorants during resting time between grinding and extraction.

Odorant	Concentration of odorants [mg/ kg dm] after resting time between grinding and extraction (n = 3)			Loss of odorant [%]	
	0 min	*5 min*	*15 min*	*0-5 min*	*0-15 min*
1	$2.2^{a} \pm 0.2$	$1.83^{b} \pm 0.09$	$2.0^{a,b} \pm 0.2$	19	12
2	$3.0^{a} \pm 0.1$	$2.4^{b} \pm 0.1$	$1.7^{c} \pm 0.1$	18	42
3	$0.374^{a} \pm 0.02$	$0.311^{b} \pm 0.002$	$0.34^{a} \pm 0.01$	17	9
4	$0.052^{a} \pm 0.01$	$0.045^{a} \pm 0.001$	$0.046^{a} \pm 0.003$	14	11
5	$0.125^{a} \pm 0.002$	$0.121^{b} \pm 0.002$	$0.112^{c} \pm 0.003$	4	11
6	$3.9^{a} \pm 0.6$	$3.5^{a} \pm 0.3$	$3.21^{a} \pm 0.08$	11	18
7	$10.9^{a} \pm 0.9$	$8.6^{b} \pm 0.4$	$9.0^{a,b} \pm 1.1$	21	18
8	$23.6^{a} \pm 1.1$	$16.8^{b} \pm 0.6$	$15.9^{b} \pm 0.3$	29	32
9	$11.0^{a} \pm 0.4$	$8.0^{b} \pm 0.1$	$7.4^{c} \pm 0.2$	27	32
10	$1.2^{a} \pm 0.1$	$1.13^{a} \pm 0.03$	$1.02^{a} \pm 0.06$	8	17
11	$15.2^{a} \pm 0.8$	$11.9^{b} \pm 0.7$	$11.8^{b} \pm 0.4$	22	23
12	$4.77^{a} \pm 0.07$	$3.7^{b} \pm 0.1$	$3.37^{c} \pm 0.08$	23	29
13	$3.5^{a} \pm 0.1$	$2.7^{b} \pm 0.1$	$2.61^{b} \pm 0.07$	22	25
14	$175^{a} \pm 2$	$159^{b} \pm 5$	$153^{b} \pm 1$	9	12
15	$18.1^{a} \pm 0.3$	$17.3^{b} \pm 0.3$	$18.2^{a} \pm 0.4$	4	0
16	$4.47^{a} \pm 0.06$	$4.4^{a} \pm 0.1$	$4.43^{a} \pm 0.05$	2	1
17	$1.34^{a} \pm 0.06$	$1.35^{a} \pm 0.03$	$1.34^{a} \pm 0.09$	0	0

$^{a, b, c}$ Different letters indicate statistically significant differences ($p < 0.05$).

3.4.1 Period between grinding and extraction

Losses of odorants may occur in the period between grinding of roasted coffee and extraction with boiling water. Three series of analyses were carried out, i.e., one with immediate extraction after grinding, the others with a period of 5 and 15 min between grinding and extraction (Table 3.3). 5 min of standing time prior to extraction were already sufficient to lose significant amounts of methanethiol (**1**), dimethyl sulfide (**2**), dimethyl disulfide (**3**), methylpropanal (**7**), 2-methylbutanal (**8**), 3-methylbutanal (**9**), 2,3-butanedione (**11**), 2,3-pentanedione (**13**), *N*-methylpyrrole (**13**), pyridine (**14**), and 4-vinylguaiacol (**15**). The largest losses (>20%) were found for methylpropanal, 2-methylbutanal, 3-methylbutanal, *N*-methylpyrrole, 2,3-butanedione, and 2,3-pentanedione. The decrease of pyridine and 4-vinylguaiacol was lower. No significant decrease of 2-furfurylthiol (**6**), dimethyl trisulfide (**4**), hexanal (**10**), 2,3,5-trimethylpyrazine (**16**), and 2-ethyl-3,5-dimethylpyrazine (**17**) was found after 5 and 15 min resting time before extraction. A significant difference between the 5 and 15 min periods between grinding and extraction was found for 2.3-pentanedione and 3-methylbutanal only. It can be concluded that considerable amounts of odorants were lost during the first 5 min after grinding. Similar results were obtained by Mayer and Grosch [31]. The reduction to a minimum of the time between grinding and extraction is therefore important to reduce losses of odorants.

3.4.2 Cooling period after extraction

Approximately 15 min were necessary to cool down the samples to room temperature after extraction and to prepare them for the addition of the stable isotope labeled standards. However, in practice, several samples were prepared at once, so that some of them were exposed to considerable longer cooling times of up to 35 min. As during longer cooling time, loss of odorants by degradation was possible, its effect on final results was investigated. A series with three periods (15, 25, 35 min) between end of extraction and addition of standards was analyzed (Table 3.4). The effect of the cooling time on the final result is very limited. Only dimethyl sulfide (**2**), 3-mercapto-3-methylbutyl formate (**5**), hexanal (**10**), pyridine (**14**), and 2,3,5-trimethylpyrazine (**16**) exhibited a slightly significant decrease of concentration between 15 and 25 min.

Table 3.4 Effect of the cooling time between extraction and addition of standards.

Odorant	Concentration of odorants [mg/ kg dm] after cooling time between extraction and addition of standards (n = 3)		
	15 min	*25 min*	*35 min*
1	$1.64^{a} \pm 0.08$	$1.7^{a} \pm 0.2$	$1.7^{a} \pm 0.1$
2	$8.3^{a} \pm 0.2$	$7.36^{b} \pm 0.06$	$8.4^{a,b} \pm 0.7$
3	$0.45^{a} \pm 0.04$	$0.45^{a} \pm 0.02$	$0.48^{a} \pm 0.03$
4	$0.06^{a} \pm 0.01$	$0.062^{a} \pm 0.005$	$0.06^{a} \pm 0.01$
5	$0.133^{a} \pm 0.002$	$0.122^{b} \pm 0.001$	$0.130^{a} \pm 0.003$
6	$3.7^{a} \pm 0.4$	$3.24^{a} \pm 0.07$	$3.34^{a} \pm 0.08$
7	$13^{a} \pm 2$	$14.1^{a} \pm 0.4$	$14^{a} \pm 3$
8	$22^{a} \pm 2$	$20^{a} \pm 2$	$21^{a} \pm 2$
9	$10.4^{a} \pm 0.6$	$10.5^{a} \pm 0.2$	$11^{a} \pm 1$
10	$1.17^{a} \pm 0.02$	$1.06^{b} \pm 0.04$	$1.3^{a,b} \pm 0.2$
11	$13.7^{a} \pm 0.5$	$12.9^{a} \pm 0.1$	$13.2^{a} \pm 0.5$
12	$4.2^{a} \pm 0.2$	$4.1^{a} \pm 0.3$	$4.3^{a} \pm 0.2$
13	$3.6^{a} \pm 0.1$	$3.29^{a} \pm 0.02$	$3.6^{a} \pm 0.2$
14	$181^{a} \pm 3$	$174^{b} \pm 2$	$175^{a,b} \pm 9$
15	$18.7^{a} \pm 0.6$	$18.3^{a} \pm 0.4$	$18^{a} \pm 1$
16	$4.63^{a} \pm 0.08$	$4.42^{b} \pm 0.01$	$4.48^{a,b} \pm 0.05$
17	$1.38^{a} \pm 0.03$	$1.40^{a} \pm 0.03$	$1.35^{a} \pm 0.05$

$^{a, b, c}$ Different letters indicate statistically significant differences ($p < 0.05$).

However, there was no significant difference in concentration of these substances between cooling times of 15 and 35 min, as well as between cooling times of 25 and 35 min. Concentrations of all other compounds did not differ significantly with any cooling time.

3.4.3 Extent of grinding

Roasted coffee was ground to three different degrees of grind. Fine grinding was carried out with a Ditting KFA1403 disk grinder (Ditting Maschinen AG, Bachenbülach, Switzerland) at level 2, medium and coarse grinding were carried out using the Bühler-Miag 4000 grinder (Bühler Ltd., Milano, Italy) with level 3 and 9, respectively. The ground coffee was then immediately subjected to aroma analysis.

The resulting concentrations of odorants are shown in Table 3.5. For some of the highly volatile compounds, concentration increased in coarser grounds (dimethyl sulfide (**2**), dimethyl disulfide (**3**), methylpropanal (**7**), 2-methylbutanal (**8**), 3-methylbutanal (**9**), *N*-methylpyrrole (**13**), and pyridine (**14**)). This is explained by a reduced evaporation of these compounds in coarser ground coffee and is in agreement with the results presented in chapter 3.4.1. 3-mercapto-3-methylbutyl formate (**5**), 2,3-butanedione (**11**) and 2,3-pentanedione (**12**) were not affected by the extent of grinding. 2-furfurylthiol (**6**), hexanal (**10**), 2,3,5-trimethylpyrazine (**16**), and 2-ethyl-3,5-dimethylpyrazine (17), for which no decrease by elongated resting time between grinding and extraction was observed, were also unaffected by the extent of grinding. 4-vinylguaiacol (**15**) and dimethyl trisulfide (**4**) were the only compounds with slightly decreasing concentration in coarsely ground coffee, which was most probably due to a less efficient extraction caused by larger particles.

It is concluded that the extent of grinding influences mostly compounds which are highly volatile. In order to reduce losses, ground coffee should be coarse for aroma analysis. However, too coarse grinding can reduce extraction yield and recovery of less volatile compounds.

Table 3.5 Effect of the extent of grinding on aroma analysis.

Odorant	Concentration of odorants [mg/ kg dm] depending on the degree of grinding (n = 3)		
	Fine	*Medium*	*Coarse*
1	n.a.	n.a.	n.a.
2	$0.9^{a} \pm 0.1$	$1.21^{a,b} \pm 0.08$	$1.6^{b} \pm 0.2$
3	$0.50^{a} \pm 0.02$	$0.52^{a} \pm 0.01$	$0.65^{b} \pm 0.04$
4	$0.083^{a} \pm 0.004$	$0.046^{b} \pm 0.003$	$0.044^{b} \pm 0.002$
5	$0.12^{a} \pm 0.01$	$0.12^{a} \pm 0.01$	$0.11^{a} \pm 0.01$
6	$3.5^{a} \pm 0.2$	$3.41^{a} \pm 0.04$	$3.5^{a} \pm 0.3$
7	$10^{a} \pm 1$	$11.7^{a} \pm 0.4$	$15.1^{b} \pm 0.4$
8	$26^{a} \pm 1$	$29^{a,b} \pm 2$	$33^{b} \pm 2$
9	$11.6^{a} \pm 0.6$	$13^{a,b} \pm 1$	$14.4^{b} \pm 0.9$
10	$1.1^{a} \pm 0.1$	$1.1^{a} \pm 0.1$	$1.0^{a} \pm 0.1$
11	$13.1^{a} \pm 0.8$	$14.0^{a} \pm 0.8$	$13.37^{a} \pm 0.07$
12	$4.6^{a} \pm 0.2$	$4.9^{a} \pm 0.4$	$4.8^{a} \pm 0.1$
13	$3.4^{a} \pm 0.1$	$3.5^{a} \pm 0.1$	$4.1^{b} \pm 0.2$
14	$171^{a} \pm 4$	$178^{a} \pm 3$	$184^{b} \pm 1$
15	$17.3^{a} \pm 0.3$	$16.8^{a,b} \pm 0.4$	$16.2^{b} \pm 0.2$
16	$4.6^{a} \pm 0.2$	$4.5^{a} \pm 0.4$	$4.8^{a} \pm 0.2$
17	$1.36^{a} \pm 0.06$	$1.3^{a} \pm 0.1$	$1.40^{a} \pm 0.09$

$^{a, b, c}$ Different letters indicate statistically significant differences ($p < 0.05$).

4 Coffee roasting and aroma formation: Application of different time–temperature conditions

The impact of time–temperature combinations of roasting processes on the kinetics of aroma formation in coffee were investigated. The development of 16 aroma compounds and the physical properties of coffee beans was followed in a commercial horizontal drum roasting process and in laboratory scale fluidizing-bed roasting processes at high temperature–short time and low temperature–long time conditions. All trials were run to an equal roast end point as defined by the lightness of coffee beans. In addition, the effect of excessive roasting on the aroma composition was studied. Compared to low temperature–long time roasting, high temperature–short time roasting resulted in considerable differences in the physical properties and kinetics of aroma formation. Excessive roasting generally led to decreasing or stable amounts of volatile substances, except for hexanal, pyridine and dimethyl trisulfide, whose concentrations continued to increase during over-roasting. When the drum roaster and the fluidizing bed roaster were operated in the so-called temperature profile mode, that is, along the identical development of coffee bean temperature over roasting time, the kinetics of aroma generation were similar in both processes.

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4.1 Introduction

In the processing chain from the ripe coffee cherry to roasted coffee, roasting presents the most important step, whose main objective is to produce the desired aroma and taste. Furthermore bean color turns to brown or even black, and brittleness is greatly increased so that grinding and extraction become possible. High temperatures of beyond 200 °C are required for the roasting process. Green coffee beans exhibit exceptional hardness due to unusually thick cell walls and a lack of intracellular spaces. Consequently they may be regarded as an aggregation of microreactor units that support a considerable pressure build-up during roasting. Theoretical values of internal pressure of up to 16 bars after roasting have been calculated [5, 8, 58, 59]. Despite the high pressure conditions during roasting, no evidence of cell wall disruption was observed in scanning electron microscopy [5], which is probably due to the fact that at high temperature coffee cell walls change from a glassy state to the more elastic rubbery state, which also allows the considerable volume increase during roasting [5, 6]. Fundamental changes in the microfibril network of cell walls and the formation of an intracellular pore structure were described [5, 7].

Physical and chemical properties of roasted coffee are highly influenced by process conditions during roasting, in particular by the time–temperature conditions within the coffee bean as a function of heat transfer. Heat transfers by contact, conduction, radiation, and convection. Although all types of heat transfer take place during roasting, convection is most effective and most appropriate for uniform roasting. Almost exclusive convective heat transfer is achieved by fluidizing-bed roasting, which allows fast roasting and results in low density, high yield coffee [16]. Traditional horizontal drum roasting involves more conductive heat transfer and is slower. Fast roasting is reported to yield more soluble solids, less degradation of chlorogenic acids, less burnt flavor, and lower loss of volatiles [15]. Fast roasted coffee is generally suspected to be more affected by lipid oxidation due to higher oil migration from the bean core to the surface [5] and there are concerns about organoleptical properties of fast roasted coffee [9]. Sivetz [10], however, reported increased flavor and aroma in fast roasted coffee.

The state of a roasted coffee bean as influenced by the roasting conditions is described in terms of the degree of roast. There are various possibilities to define the degree of roast, i.e., color development, roast loss, organic roast loss, and water content. Indirect determination methods for the degree of roast by ratios of free amino acids [11], alkylpyrazines [12], and content of chlorogenic acids [9] have also been proposed. Of these methods, color of coffee beans or ground coffee is the most frequently used indicator. As bean color intensity is correlated to the final roasting temperature [9, 10], temperature measurements also are applied. However, Schenker [5] carried out a series of roasting trials on a production scale with various temperature profiles, which did not result in a direct relationship between degree of roast and final product temperature. He concluded that data on final bean temperature are of limited value as they differ in the function of raw material and process conditions. Recently, new approaches for online determination of roast degree during the roasting process have been investigated. Dorfner and coworkers [13] analyzed roaster gases directly by laser mass spectrometry, reported evolution of several aroma components during roasting, and postulated a multivariate statistics model to monitor the degree of roast. An approach using a chemosensor array was chosen by Hofmann and coworkers [14]. They identified 2-furfurylalcohol and hydroxy-2-propanone as possible marker substances to monitor the course of roasting. Though literature frequently refers to an optimum degree of roast, a concise definition of it is usually not given because of its complexity, and to date, no clear and universally accepted definition exists. It is obvious that an optimum degree of roast is in particular a function of green coffee origin, intended coffee brewing method and personal taste preferences.

From the several hundred volatile compounds identified in coffee, around 30 have been identified as aroma impact compounds [40, 60-62]. Various authors described the formation of aroma compounds during roasting. Holscher and Steinhart [63] compared *Arabica* and *Robusta* coffees and provided data on the evolution of methanethiol, dimethyl sulfide, 2,3-butanedione, 2,3-pentanedione, methylpropanal, 2- and 3-methylbutanal, methylacetate, and 2-methylfuran as a function of the degree of roast. The development upon roasting was similar, but concentration differences between the two coffee varieties were found. Grosch [64] investigated the formation

of 2-furfurylthiol. He concluded that it is formed by reactions of cysteine with arabinose and reported on substantial amounts of 2-furfurylthiol being linked by disulfide bonds to other components of roasted coffee. A masking effect by odorants formed in the later stages of roasting, covering the sweet and earthy notes, was found by Gretsch and coworkers [65]. The authors correlated global sensory attributes with relative composition of aroma compounds at various degrees of roast. Mayer and coworkers [51] investigated the influence of the degree of roast on concentrations of aroma impact compounds in three coffee varieties. However, detailed specifications on the applied roasting process and determination of color values were not given. Several different roasting processes were assessed in terms of flavor formation by Schenker and coworkers [66]. He found that most aroma compounds exhibited the highest increase in concentration at the medium stage of dehydration and pleaded for the precise control of roasting time and temperature in order to reach specific flavor profiles.

Numerous publications appeared on the nature of reactions leading to roasted coffee flavor (for an overview, see Flament [20], Reineccius [21] and Shibamoto [17]). Despite the high value of insights into possible reaction mechanisms resulting from model systems, it must be taken into account that such model systems simulate reaction conditions within a coffee bean only to a limited extent. Model systems are usually heated mixtures of precursor substances in solution, which are in contrast to the low moisture content within coffee beans. It was shown that, depending on water content of the reaction mixtures, fundamentally different reaction pathways might be followed, for example, in the reaction of glucose with L-proline [23]. For these reasons, new approaches for model reactions involving extracted coffee bean shells were developed for in-bean roasting experiments [26]. However, in view of the complexity of coffee roasting, experiments with real green coffee beans on standard roasting equipment under well controlled conditions are still the most efficient way to gain insight into the kinetics of coffee flavor generation.

The aim of this chapter was to investigate the evolution of aroma compounds during roasting with different time–temperature conditions and to compare experimental results from a laboratory scale fluidizing-bed process to those from a traditional production scale horizontal drum roasting process. For this purpose, a commercial single origin coffee traditionally roasted in a drum roaster was chosen as a model, and time–temperature conditions were established on the laboratory roaster to achieve the same color of roasted coffee. Furthermore the question whether these time–temperature conditions lead to equivalent coffees in terms of aroma and physical properties was investigated.

4.2 Materials and methods

4.2.1 Roasting process and process characterization

Raw material

Washed green *Coffea arabica Tip.* variety from Sumatra (Mandheling, S-795, Kartika 1) was supplied by Rast Ltd. (Ebikon, Switzerland). The moisture content of green coffee was 10.04 g/ 100 g wb.

Roasting trials

At the production scale, coffee was roasted using a G-45 drum roaster (Probat Ltd., Emmerich, Germany) with a batch size of 20 kg. At the laboratory scale, batches of 100 g of green beans were roasted using a fluidizing-bed hot-air laboratory roaster (G. W. Barth AG, Freiberg/Neckar, Germany), which was described in detail by Schenker [5] and Geiger and coworkers [67]. Two isothermal programs, i.e., high temperature–short time (HTST) and low temperature–long time (LTLT), and one temperature profile program (Profile) were carried out. Coffees were roasted to a target roast degree with lightness L* = 21, where 100 means white and 0 means black.

Process parameters and roasted coffee properties are described in Table 4.2. For aroma analysis, samples were taken at different roasting times during drum roasting (Table 4.1). At the laboratory scale, batches were roasted during different roasting

times according to Table 4.1. Bean core temperature in the laboratory roaster was recorded during roasting by placing thermocouples (Type K, 0.5 mm, Thermocoax Ltd., Surèsnes, France) into drilled holes in the green coffee beans, as described in Geiger and coworkers [67].

Moisture content and color measurement

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

The degree of roast was determined from the lightness value (L*) of the CIE L*a*b* color space. Coffee was ground and gently pressed to form an even surface, and color was measured using a colorimeter CR-310 (Minolta, Japan).

Density

For the determination of coffee bean density, a displacement method was used, as described by Schenker [7]. A stainless steel wire basket with and without 30 g of coffee beans was immersed into peanut oil, and the weight difference corresponded to the weight of oil displaced by coffee beans. Using a density of 910 kg m^{-3} for peanut oil at 25 °C, coffee bean density could be determined. Air bubbles between coffee beans had to be removed by moving the basket up and down, but care had to be taken not to overextend weight measuring time, in order to prevent oil from penetrating into the pores of coffee beans.

Table 4.1 Roasting times for intermittent sampling of coffee beans for aroma analysis.

Roasting process	Roasting time [s]							
HTST	30	70	100	130	145	160[a]	200	
LTLT	120	240	420	600	660[a]	720	840	1140
Profile	375	510	630	780	900[a]	1200		
Drum Roasting	180	360	540	660	780	900	1170[a]	

[a] Corresponds to the targeted roasting end point with lightness L* = 21

Table 4.2 Process parameters of roasting trials and product properties.

	Laboratory scale (fluidizing-bed roaster)					Production scale
			Profile			
	HTST	LTLT	Step 1	Step 2	Step 3	Drum Roasting
	Process parameters					
Hot air temperature [° C]	260	228	180	180→232 (linear)	232	n. a.
Roasting time [s]	160	660	180	360	360	1170
Hot air velocity [m/s]	3	3	3	3	3	
	Product properties (n = 3)					
Lightness [L*]	21.05±0.15	21.00±0.16		20.78±0.16		21.00±0.16
Roast loss [g/100 g wb]	16.64±0.02	17.05±0.05		17.66±0.03		n. a.
Organic roast loss [g/100 g wb]	8.54±0.13	9.24±0.04		10.10±0.12		n. a.
Density [g/cm^3]	0.548±0.001	0.588±0.002		0.584±0.005		0.592±0.002
Water content [g/100 g wb]	1.30±0.02	1.57±0.01		1.73±0.02		1.79±0.40

n.a.: not available

4.2.2 Aroma analysis

Methanethiol, dimethyl sulfide, dimethyl trisulfide, 3-mercapto-3-methylbutyl formate, 2-furfurylthiol, methylpropanal, 2-methylbutanal, 3-methylbutanal, hexanal, 2,3-butanedione, 2,3-pentanedione, *N*-methylpyrrole, pyridine, 4-vinylguaiacol, 2,3,5-trimethylpyrazine, and 2-ethyl-3,5-dimethylpyrazine were sampled, separated and quantified with the method described in chapter 3.2.

4.2.3 Statistical analysis

Student's *t*-test was applied to the results with a level of significance of 95%.

4.3 Results and discussion

4.3.1 Evolution of physical properties during roasting

Bulk and bean core temperatures during roasting with the laboratory scale roaster are displayed in Figure 4.1. Although bean core temperature rapidly converged to bulk temperature, a small difference between the two remained, and the temperature of incoming hot air was never attained. Bean temperature measurement in the commercial drum roaster was not possible, but it is supposed that bean core temperature evolution took place in a way similar to that as in the profile roasting process, although temperature increase was probably slower. The development of the physical properties of coffee during roasting strongly depended on the applied temperature and roasting time (Figures 4.2-4.4). High temperature roasting led to lower density, higher bean volume, less roast loss, and lower moisture content compared to roasting processes at lower temperature. These results are in agreement with findings from other authors [5, 68]. However, Geiger and coworkers [67] established mass balance during similar HTST and LTLT processes and found higher water content after HTST roasting than after LTLT. In those tests, initial water content of green coffee was considerably lower, which may have led to different water evaporation kinetics. Compared to the classical drum roasting process, the laboratory scale fluidizing-bed processes were faster with regard to moisture loss, color development, and evolution of coffee bean density. Evolution of these properties

during profile and drum roasting was similar, but because of the obviously faster temperature increase in profile roasting, the development of roasting parameters was slightly faster. Use in the profile roast of an initially lower air temperature that subsequently rose more slowly probably would have produced bean temperature behavior more similar to that for the drum roast and thus would have provided an even better basis for comparing these two roasts.

4.3.2 Evolution of aroma compounds during roasting with different time-temperature conditions

The following graphic presentations show the development of aroma compounds over roasting time. The development of aroma compounds was also plotted as a function of L*-values. In order to increase the clarity of these latter presentations, an inverse and logarithmic scale was selected. This change of scale does not stipulate any physical meaning.

Sulfur compounds

Sulfur compounds are among the most important aroma compounds in coffee. Methanethiol, dimethyl trisulfide, 3-mercapto-3-methylbutyl formate, and especially 2-furfurylthiol were cited as being impact compounds of coffee aroma [40, 60]. It is generally thought that sulfur-containing amino acids act as the sulfur source for aroma compounds during roasting [69-71]. Methanethiol is believed to result from the pyrolysis of methionine [70], and it is likely that dimethyl sulfide and dimethyl trisulfide are further oxidation and disproportionation products of the same reaction sequence [72]. It could also be that *S*-methylmethionine, which is known to occur in flowering plants as an intermediate, could serve as a precursor for dimethyl sulfide. For these reasons, formation kinetics of these compounds should be at least partly related to each other.

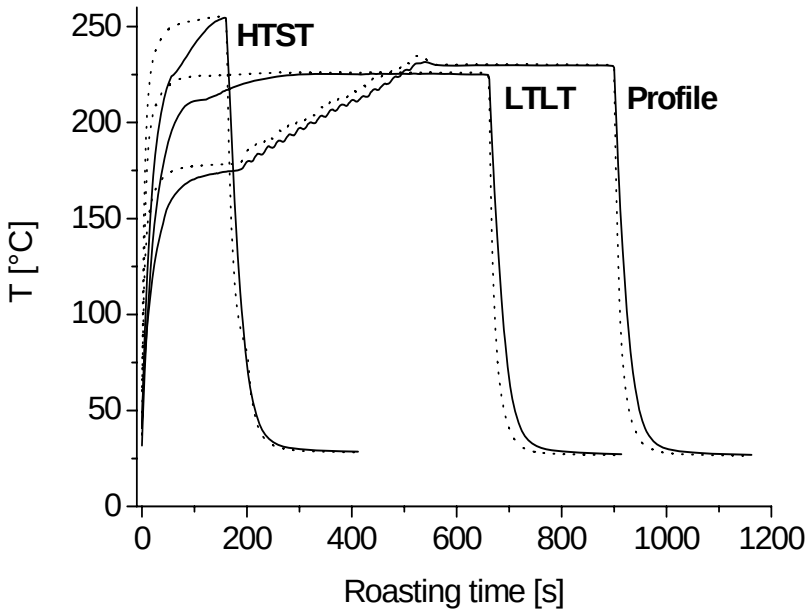

Figure 4.1 Evolution of bean core (—) and bulk (····) temperature during roasting with the fluidizing-bed hot-air laboratory roaster.

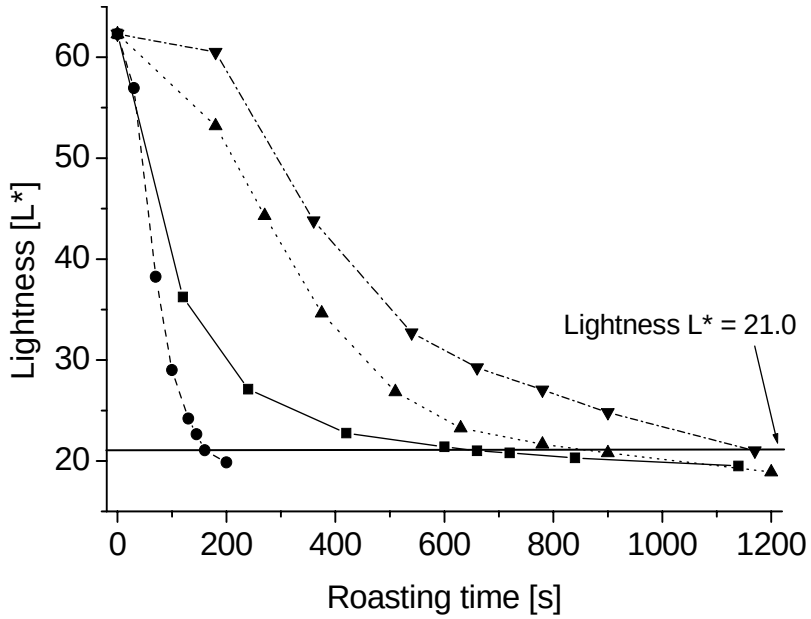

Figure 4.2 Evolution of the lightness of coffee beans during different roasting processes (LTLT: ■, HTST: ●, Profile: ▲, Drum roasting: ▼).

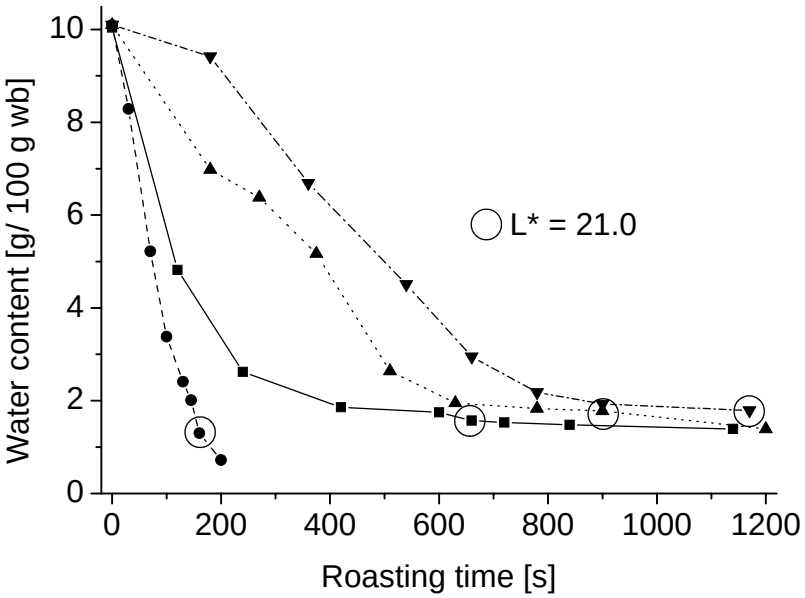

Figure 4.3 Evolution of the water content of coffee beans during different roasting processes (LTLT: ■, HTST: ●, Profile: ▲, Drum roasting: ▼).

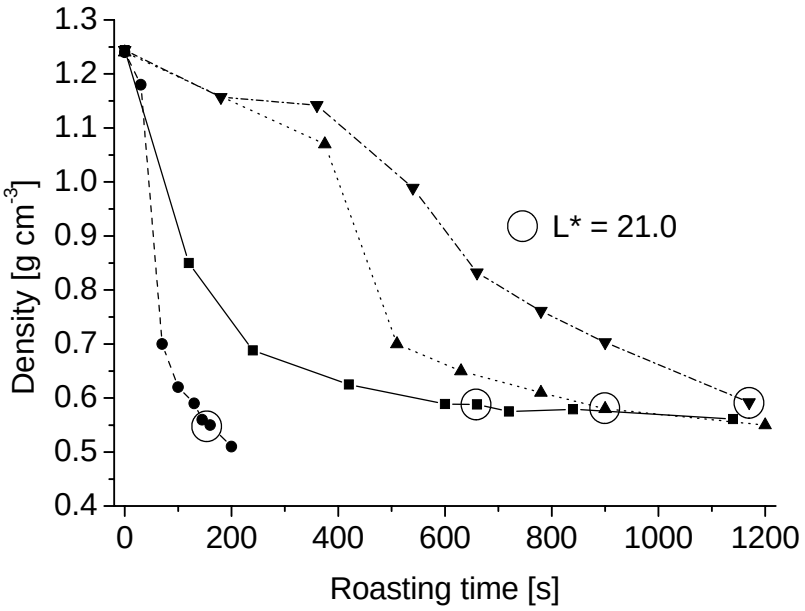

Figure 4.4 Evolution of the density of coffee beans during different roasting processes (LTLT: ■, HTST: ●, Profile: ▲, Drum roasting: ▼).

The development of sulfur compounds during roasting is presented in Figure 4.5. Concentrations at L* = 21 are shown in Table 4.3. The sulfides and methanethiol exhibited a large increase during the first stages of roasting. Methanethiol formation seemed to be favored by higher temperatures since the HTST process resulted in highest methanethiol concentration. Degradation took place at the end of HTST roasting, while during the other roasting processes, decrease of methanethiol concentration was not observed. In contrast, formation of dimethyl sulfide was faster with regard to the evolution of lightness, and maximum concentration was higher when low temperature was applied. The fact that in drum roasting, where temperature increase within coffee beans was slow, dimethyl sulfide formation started also very early, suggests that the required activation energy is low, and hence, reaction mechanisms involving radical species are probably predominant. Decrease of dimethyl sulfide concentration was observed toward the end of the roasting process.

Dimethyl trisulfide exhibited biphasic behavior. During all four roasting processes, a relatively fast increase was observed during the first stages, followed by decrease through medium roast degree. Two additional measuring points were determined in the case of profile roasting (after 180 and 270 s roasting time) in order to make the early increase visible. Toward the end of the roasting process, distinct reincrease was observed.

Formation of 3-mercapto-3-methylbutyl formate obviously required high activation energy since formation started late in the roasting process. The onset of formation was observed at L* values between 40 and 30, which corresponded to roasting times of around 30 s at 260 °C (LTLT) and 120 s at 228 °C (LTLT), and to bean core temperatures of 212 °C (LTLT) and 194 °C (HTST). A maximum value was then quickly achieved followed by a fast degradation. During HTST roasting, at the roasting end point, 3-mercapto-3-methylbutyl formate concentration was around twice as high as that in the other roasting processes. 2-Furfurylthiol concentration increased continuously during the roasting process depending on temperature, and no decrease was observed, which is in agreement with results from other authors [5, 51, 65, 71]. The constant increase of 2-furfurylthiol during roasting suggests the existence of a

large pool of precursor compounds. As in the case of 3-mercapto-3-methylbutyl formate, a certain onset temperature was necessary in order to initiate formation. At L* = 21, significantly higher amounts of 2-furfurylthiol were found in the low temperature–long time roasting processes (LTLT, profile, and drum roasting) compared to the HTST roast.

Aldehydes and α-diketones

Strecker aldehydes such as methylpropanal, 2-methylbutanal, and 3-methylbutanal are regarded to be products of decarboxylative transamination of amino acids with subsequent addition of water and breakdown into aminoacetone and the corresponding Strecker aldehyde [22].

The development of aldehydes and α-diketones during roasting is shown in Figure 4.5 (methylpropanal and 2-methylbutanal are not shown). Concentrations at L* = 21 are displayed in Table 4.3. Their behavior upon roasting is similar. A fast increase during the first stages of roasting is followed by decreasing concentration toward higher degrees of roast. This is in agreement with other studies [19, 51, 63]. Formation of the three Strecker aldehydes in the beginning of the roasting process seemed to be slightly favored by high temperature, and at lightness L* = 21, 2- and 3-methylbutanal concentration in HTST roasted coffee was significantly higher than in the long-time roasts, with the exception of 2-methylbutanal in profile roasting, where its concentration was lower than that for HTST roasting but not significantly so at the $p<0.05$ level. Hexanal is not formed by the Maillard reaction but results from oxidation of lipids [20]. Considerable amounts of hexanal were found in green coffee (around 1.5 mg/ kg dm). Temperatures of nearly 220 °C were necessary to further increase its concentration. The extent of formation and maximum concentration depended on roasting temperature (HTST and LTLT: 3.5–4.0 mg/ kg dm; profile and drum roasting, which exhibited lower product temperature before hexanal peak concentration was attained, ca. 2.5 mg/ kg dm). Peak concentration of hexanal was attained at L* values between 40 and 30, then degradation of hexanal was observed. At L* = 21, hexanal concentration was significantly higher in HTST roasted coffee

than in LTLT roasted coffee. Profile and drum roasting both resulted in significantly lower hexanal concentrations than those in the two isothermal roasting processes.

Various possible formation pathways for the α-diketones 2,3-butanedione, and 2,3-pentanedione have been suggested. From model systems of glucose with alanine, Yaylayan and Keyhani [73] concluded that 2,3-butanedione is formed by a single pathway involving glucose carbon atoms only, while in model systems with glucose and glycine, formation via C_3/C_3 and C_2/C_4 cleavage was possible. Formation of 2,3-pentanedione was observed involving glucose carbons only (10%) and via the incorporation of C2'–C3' atoms of alanine to a C_3 carbon unit from glucose. In a model experiment under roasting conditions and using the carbohydrate module labeling approach, Schieberle and coworkers [74] showed that in the reaction of glucose with proline, 87% of the resulting 2,3-butanedione emerged from a C_3/C_1 recombination of glucose, 13% from a C_2/C_2 recombination, while none of the 2,3-butanedione was formed from the intact carbohydrate. This was in accordance with a proposed reaction mechanism involving aldol condensation of acetaldehyde with hydroxyacetaldehyde and hydroxyacetone [75]. A second model with formaldehyde and hydroxypropanone also led to the formation of 2,3-butanedione [74]. Other reaction pathways were proposed, involving the 1-deoxyglycosone [76] and sugar fragmentation followed by intramolecular condensation [75]. In addition, 2,3-pentanedione was cited to be the main volatile thermal degradation product of 4-hydroxy-2,5-dimethyl-3(2H)-furanone [20]. Formation of 2,3-butanedione required a certain activation energy and was clearly accelerated by high roasting temperature. During HTST roasting, a maximum concentration of almost 40 mg/ kg dm was attained and remained constant during a period of 45 s. Then fast degradation was observed. With lower temperature roasting processes, the evolution of 2,3-butanedione was similar, but less rapid with lower maximum concentrations. 2,3-Pentanedione formation and elimination followed a similar pattern as in the case of 2,3-butanedione, but differences in maximum concentration were low, and evolution as a function of lightness was similar for all time–temperature profiles applied. This is an indication that, in contrast to 2,3-butanedione, the formation of 2,3-pentanedione seems to be substrate limited and less dependent on roasting time and temperature. It

is therefore assumed that 2,3-pentanedione does not result from the same sugar fragments as 2,3-butanedione and that the formation and degradation pathways are different. Formation of 2,3-pentanedione from the reaction of 2,3-butanedione with formaldehyde with subsequent loss of water, proposed by Weenen and Apeldoorn [76] as linked to formation of 2,3-butanedione, is therefore not corroborated in the case of coffee roasting.

At roasting end point with lightness L* = 21, HTST roasted coffee exhibited double the amount of 2,3-butanedione and 2,3-pentanedione as for all other roasts. However, degradation of both diketones was very fast at the end of HTST roasting, and concentrations similar to those resulting from the long time processes would have been obtained by extending the HTST process by 30 to 40 s, with only minor change in roasted coffee lightness (Figure 4.2).

Heterocyclic and phenolic compounds

Heterocycles and phenolic compounds are typical roasting products, resulting from the Maillard reaction (pyrazines), thermal decomposition of ferulic acid (guaiacols), and trigonelline degradation (pyridine, *N*-methylpyrrole). In model reaction systems, pyridine and *N*-methylpyrrole also resulted from classical Maillard reaction mixtures consisting of amino acids and glucose/sucrose [20]. Among the examined heterocyclic and phenolic compounds, 2-ethyl-3,5-dimethylpyrazine and 4-vinylguaiacol are of key importance for coffee aroma.

Figure 4.5 shows the development of heterocyclic compounds during roasting, and concentrations at L* = 21 are presented in Table 4.3. Formation kinetics of pyridine were found to be very similar to those of 2-furfurylthiol. High temperature was needed to initiate reactions leading to pyridine, and once formation began, pyridine concentration continuously rose during roasting. Impact of roasting time was higher than the effect of temperature, and at L* = 21, the highest pyridine concentrations were found in profile and drum roasting. Formation of *N*-methylpyrrole was observed at roasting temperatures of around 170 °C, and the rate of formation increased with increasing temperature. For better comparison between profile and drum roasting, *N*-methylpyrrole concentration was measured at two additional points during the first

stage of profile roasting (180 and 270 s roasting time). In contrast to pyridine, the reactions seemed to be much more temperature-dependent, and consequently, the highest amount at L* = 21 was found after HTST roasting.

2,3,5-Trimethylpyrazine and 2-ethyl-3,5-dimethylpyrazine both exhibited relatively fast increase in the beginning of the roasting process. At darker degrees of roast, a slight decrease was observed for HTST roasting, while in the other processes, the concentration increase leveled off. In the case of LTLT roasting, degradation was observed when coffees were over-roasted. Similar observations were made by Gretsch and coworkers [65], however, for relatively light roasts only (roasting temperature of 230 °C during max. 9 min). At roasting end point with L* = 21, the amount of 2,3,5-trimethylpyrazine was significantly higher in LTLT and HTST roasted coffees compared to that in the drum and profile roastings, while no significant differences were observed in concentrations of 2-ethyl-3,5-dimethylpyrazine.

Formation of 4-vinylguaiacol immediately started in the beginning of the roasting process, which suggests low activation energy and hence the involvement of a radical reaction pathway. The evolution of 4-vinylguaiacol during roasting was highly dependent on temperature. The isothermal processes with very fast increase of bean core temperature both resulted in high formation rates during the first stage of roasting, while profile and drum roasting processes led to slower increase of 4-vinylguaiacol. After attaining maximum concentration, which was higher with increasing roasting temperature, elimination occurred. At the end of the roasting process (L* = 21), HTST roasting yielded by far the highest concentration of 4-vinylguaiacol. Dorfner and coworkers [77] found the same evolution of 4-vinylguaiacol during roasting and established a two-channel model for the degradation of 5-feruloylquinic acid during coffee roasting. In the first, endothermic roasting stage, formation of 4-vinylguaiacol is predominant because of low activation energy. Once exothermic roasting conditions are attained, 4-vinylguaiacol degrades yielding guaiacol, which then degrades to phenol.

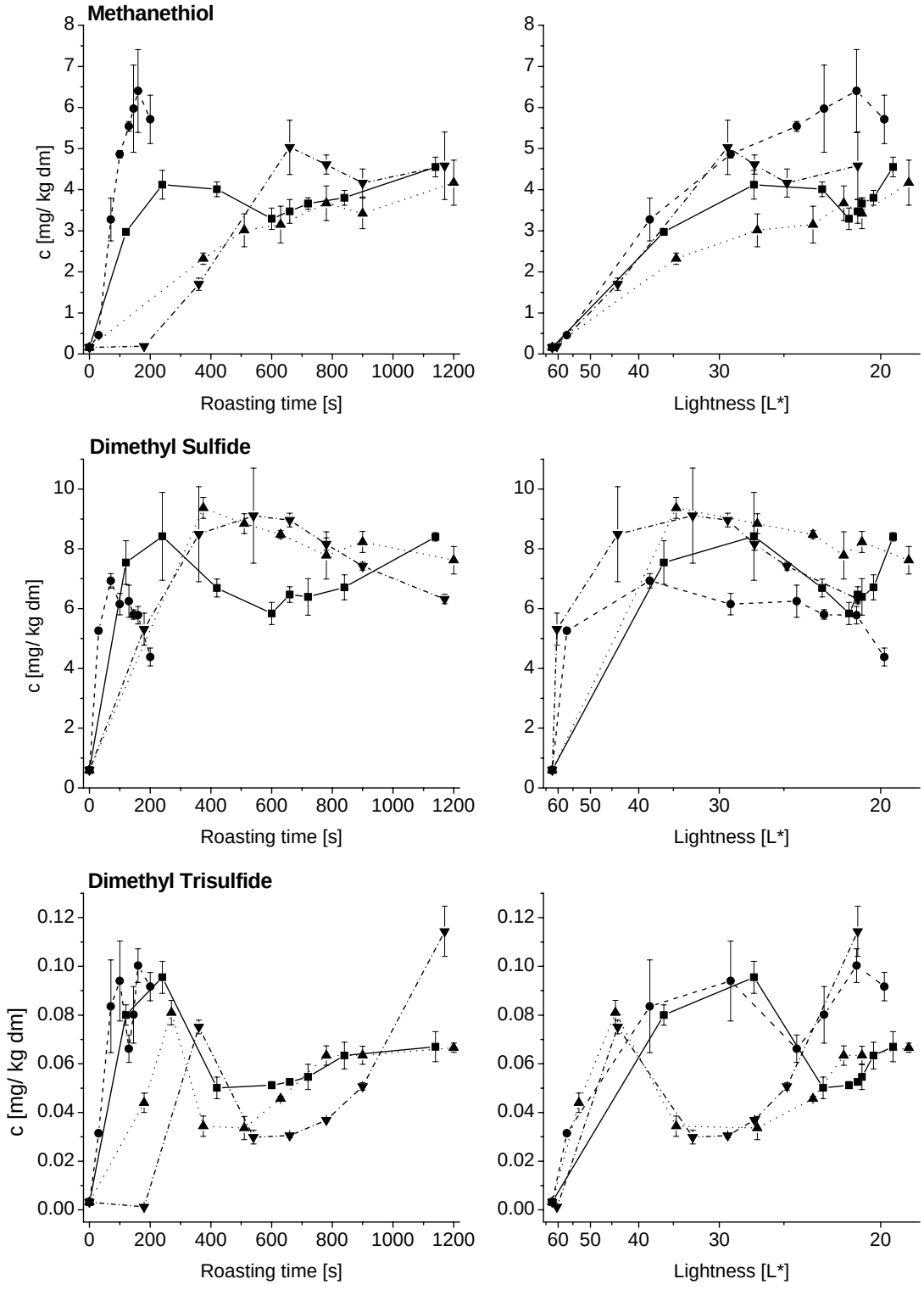

Figure 4.5a Evolution of selected coffee aroma compounds during roasting as a function of time and lightness (LTLT: ■, HTST: ●, Profile: ▲, Drum roasting: ▼).

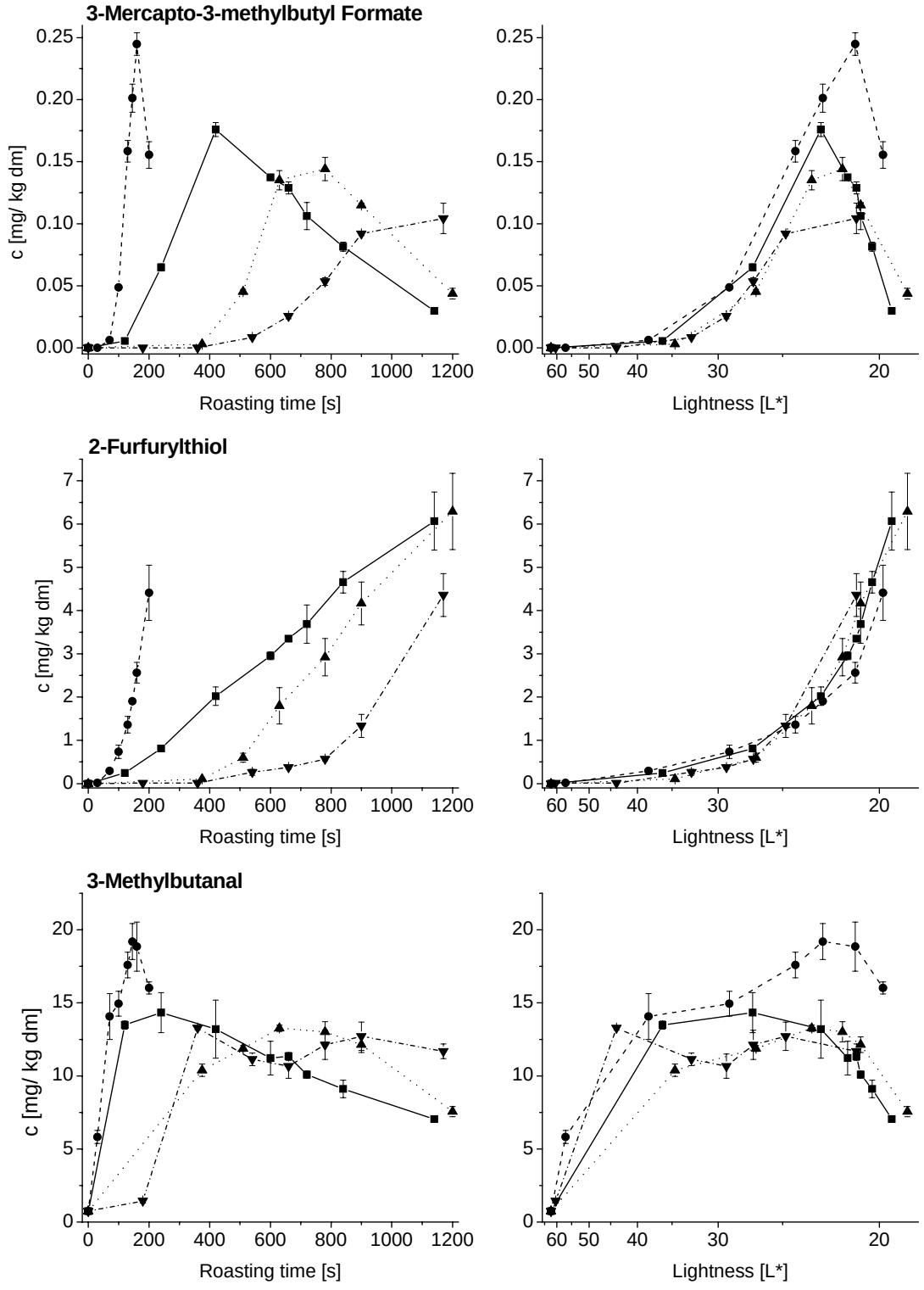

Figure 4.5b Evolution of selected coffee aroma compounds during roasting as a function of time and lightness (LTLT: ■, HTST: ●, Profile: ▲, Drum roasting: ▼).

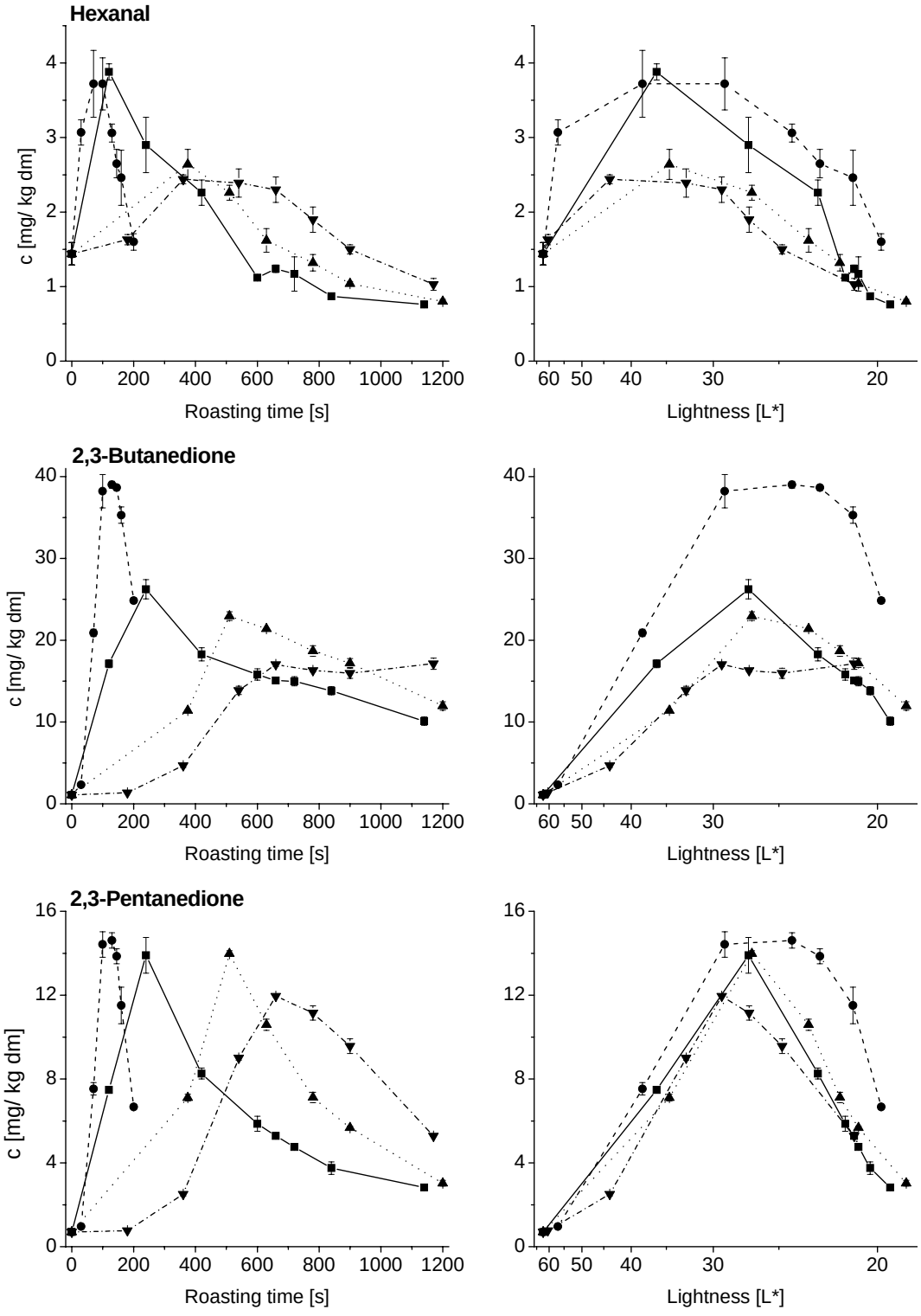

Figure 4.5c Evolution of selected coffee aroma compounds during roasting as a function of time and lightness (LTLT: ■, HTST: ●, Profile: ▲, Drum roasting: ▼).

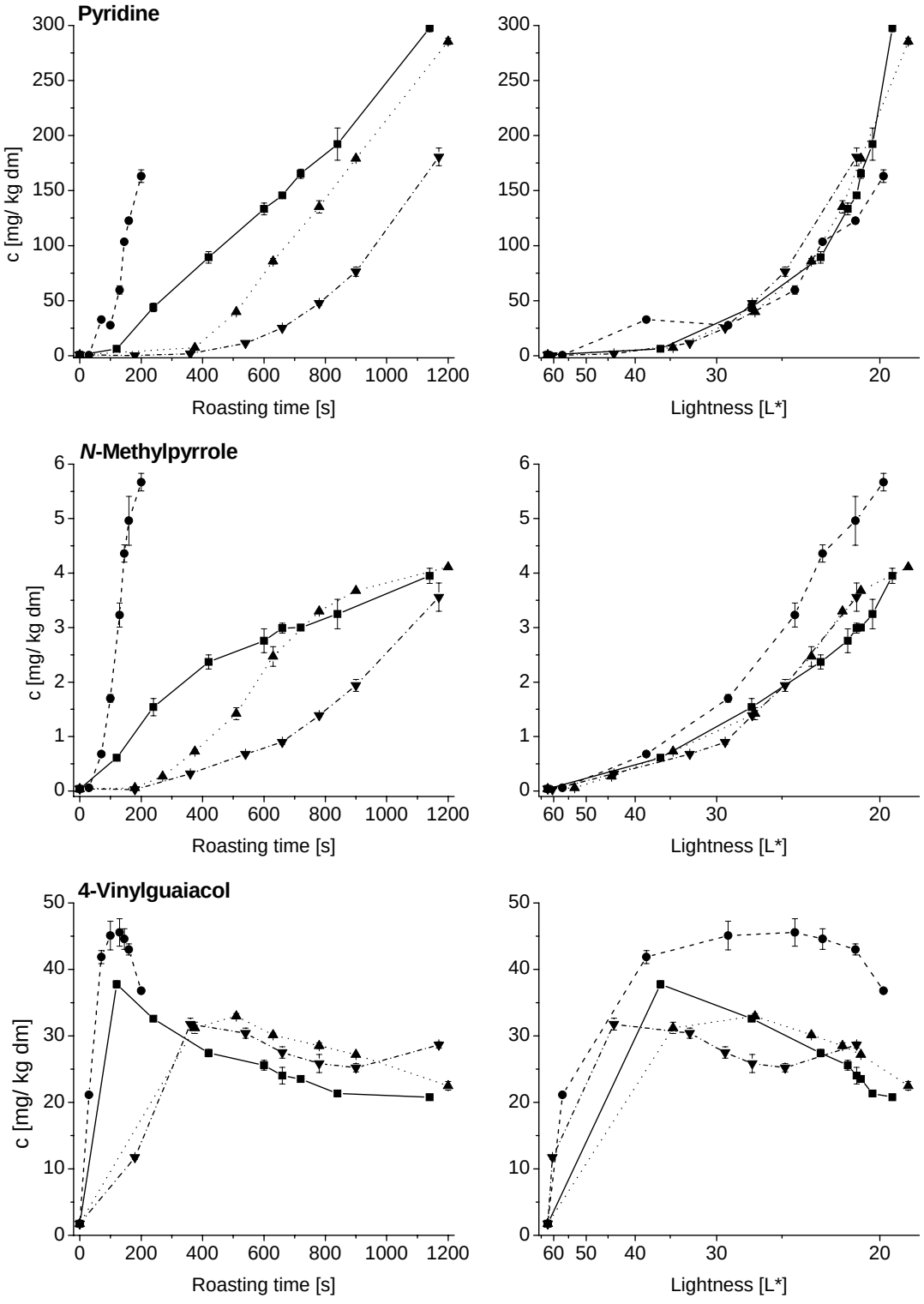

Figure 4.5d Evolution of selected coffee aroma compounds during roasting as a function of time and lightness (LTLT: ■, HTST: ●, Profile: ▲, Drum roasting: ▼).

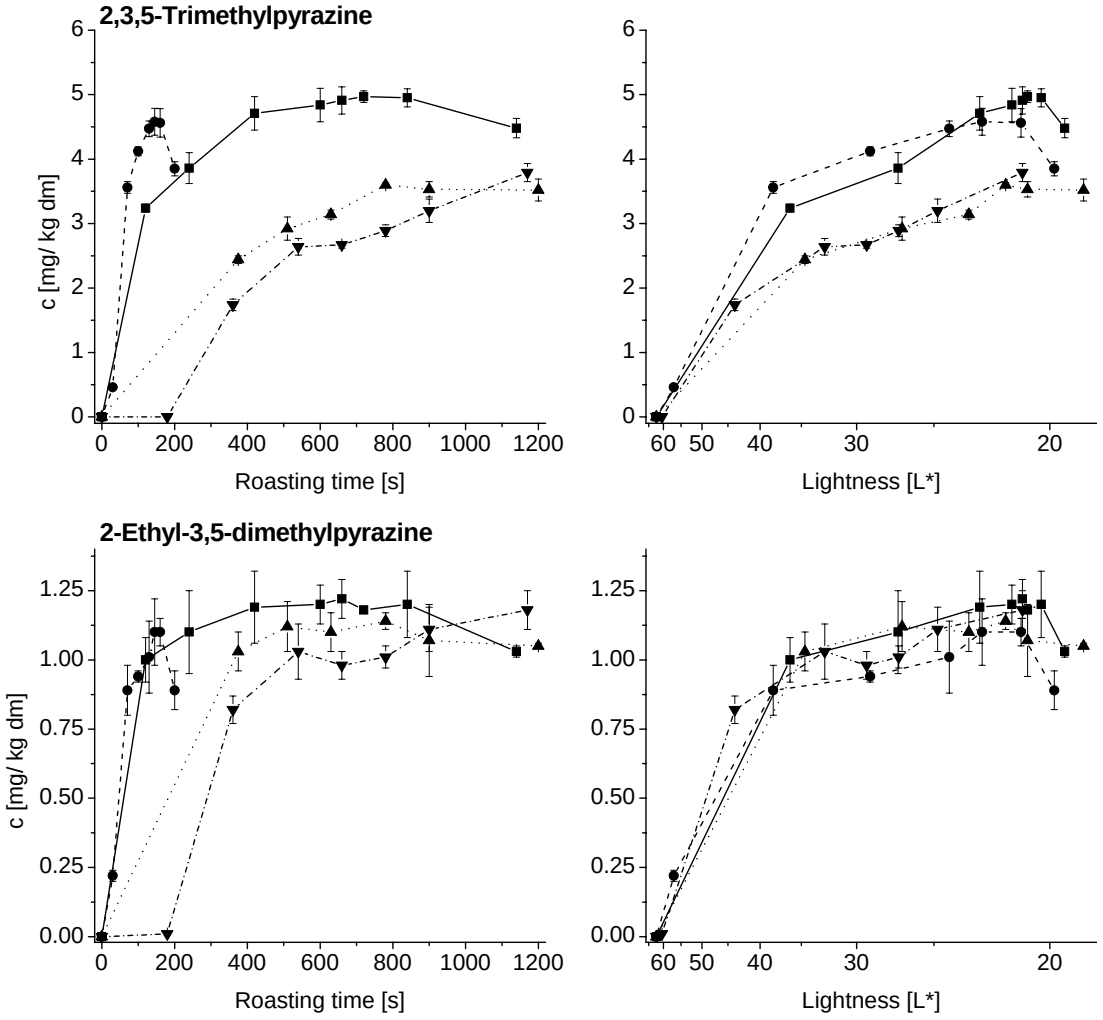

Figure 4.5e Evolution of selected coffee aroma compounds during roasting as a function of time and lightness (LTLT: ■, HTST: ●, Profile: ▲, Drum roasting: ▼).

Table 4.3 Influence of time-temperature conditions on concentration of aroma compounds after roasting (L* = 21).

	Roasting process			
	LTLT	HTST	Profile	Drum Roasting
Aroma compound	[mg/ kg dm]	[mg/ kg dm]	[mg/ kg dm]	[mg/ kg dm]
Methanethiol	$3.5^{a} \pm 0.3$	$6.4^{b} \pm 1.0$	$3.4^{a} \pm 0.4$	$4.6^{a, b} \pm 0.8$
Dimethyl sulfide	$6.5^{a} \pm 0.3$	$5.8^{b} \pm 0.3$	$8.2^{c} \pm 0.4$	$6.3^{a, b} \pm 0.2$
Dimethyl trisulfide	$0.053^{a} \pm 0.001$	$0.10^{b} \pm 0.01$	$0.064^{c} \pm 0.004$	$0.11^{b} \pm 0.01$
3-MMBF [e]	$0.129^{a} \pm 0.005$	$0.24^{b} \pm 0.01$	$0.115^{c} \pm 0.002$	$0.10^{a, c} \pm 0.01$
2-Furfurylthiol	$3.35^{a} \pm 0.03$	$2.6^{b} \pm 0.2$	$4.2^{a} \pm 0.5$	$4.4^{a} \pm 0.5$
Methylpropanal	$20.2^{a} \pm 0.9$	$23.1^{a} \pm 2.2$	n.a.	$14.0^{b} \pm 1.1$
2-Methylbutanal	$18.7^{a} \pm 0.2$	$24.4^{b} \pm 2.0$	$21.7^{b} \pm 0.7$	$19.2^{a} \pm 1.1$
3-Methylbutanal	$11.3^{a} \pm 0.3$	$18.9^{b} \pm 1.7$	$12.1^{a} \pm 0.5$	$11.7^{a} \pm 0.5$
Hexanal	$1.24^{a} \pm 0.05$	$2.5^{b} \pm 0.4$	$1.04^{c} \pm 0.03$	$1.03^{c} \pm 0.08$
2,3-Butanedione	$15.1^{a} \pm 0.1$	$35.3^{b} \pm 1.0$	$17.2^{c} \pm 0.5$	$17.1^{c} \pm 0.7$
2,3-Pentanedione	$5.29^{a} \pm 0.08$	$11.5^{b} \pm 0.9$	$5.67^{c} \pm 0.08$	$5.28^{a} \pm 0.01$
N-Methylpyrrole	$2.99^{a} \pm 0.09$	$5.0^{b} \pm 0.4$	$3.7^{c} \pm 0.2$	$3.6^{a, c} \pm 0.3^{c}$
Pyridine	$145.7^{a} \pm 0.7$	$122.6^{b} \pm 2.5$	$179.3^{c} \pm 1.1$	$180.6^{c} \pm 8.1$
4-Vinylguaiacol	$24.0^{a} \pm 1.2$	$43.0^{b} \pm 0.8$	$27.18^{c} \pm 0.06$	$28.7^{d} \pm 0.5$
2,3,5-TMP [f]	$4.9^{a} \pm 0.2$	$4.6^{a} \pm 0.2$	$3.5^{b} \pm 0.1$	$3.8^{b} \pm 0.1$
EDMP [g]	$1.22^{a} \pm 0.07$	$1.10^{a} \pm 0.05$	$1.1^{a} \pm 0.1$	$1.18^{a} \pm 0.07$

[a, b, c, d] Different letters indicate statistically significant differences ($p < 0.05$).

[e] 3-Mercapto-3-methylbutyl formate

[f] 2,3,5-Trimethylpyrazine

[g] 2-Ethyl-3,5-dimethylpyrazine

n.a. = data not available

4.3.3 Effect of over-roasting on aroma compounds

To determine the effect of excessive roasting beyond usual degrees of roast on the formation and degradation of aroma compounds, the profile roasting process was extended to 20, 25, 30, 35, and 40 min, i.e. after completing the temperature step, coffee beans were kept during 11, 16, 21, 26, and 34 min respectively at 232 °C. Lightness L* of the resulting coffee beans was 18.9, 18.5, 18.2, 17.7, and 17.6, respectively. Trends and final concentration after 40 min of roasting time are shown in Table 4.4. For many of the investigated aroma compounds, degradation exceeded formation, and decreasing amounts were found in coffee roasted for excessive periods. 3-Mercapto-3-methylbutyl formate, as the most extreme example degraded to zero concentration after 40 min of roasting time. Other compounds, such as the Strecker aldehydes (methylpropanal, 2-methylbutanal, and 3-methylbutanal) and the α-diketones (2,3-butanedione and 2,3-pentanedione) were also degraded, but decrease seemed to level off at a certain concentration, whereas 4-vinylguaiacol exhibited a steady decrease throughout excessive roasting. 2-Furfurylthiol concentration increased until 25 min of roasting time, but then the concentration decreased. Dimethyl sulfide concentration also decreased, albeit slowly. Concentration of pyridine increased throughout 40 min of roasting, whereas the increase of *N*-methylpyrrole decelerated and leveled off after 35 min of roasting. Dimethyl trisulfide, which already exhibited increasing concentration toward the end of roasting to normal degrees of roast, increased further at excessive conditions. Hexanal revealed minimum concentration after 20 min of roasting time, then increased steadily during the next 20 min. 2,3,5-Trimethylpyrazine and 2-ethyl-3,5-dimethylpyrazine remained at stable concentration during 35 min of roasting and then slowly decreased.

Table 4.4 Effect of over-roasting in profile roasting on aroma compounds.

Compound	Behavior upon excessive roasting	Concentration after 40 min of roasting (n=1) [mg/ kg dm]
Methanethiol	n. a.	n.a.
Dimethyl sulfide	slightly decreasing	7.0
Dimethyl trisulfide	steadily increasing	0.14
3-MMBF [a]	decreasing to 0 mg/ kg dm	n.d.
2-Furfurylthiol	increasing until 25 min, then decreasing	4.6
Methylpropanal	decreasing, leveling off after 35 min	8.5
2-Methylbutanal	decreasing, leveling off after 35 min	4.6
3-Methylbutanal	decreasing, leveling off after 35 min	3.3
Hexanal	decreasing until 20 min, then increasing	1.8
2,3-Butanedione	decreasing, leveling off after 35 min	6.5
2,3-Pentanedione	decreasing, leveling off after 35 min	1.2
N-Methylpyrrole	increasing, leveling off after 35 min	5.0
Pyridine	increasing	586
4-Vinylguaiacol	decreasing	9.4
2,3,5-TMP [b]	stable, decreasing after 35 min	3.2
EDMP [c]	stable, decreasing after 35 min	0.9

n.a.: results not available

n.d.: not detected

[a] 3-Mercapto-3-methylbutyl formate

[b] 2,3,5-Trimethylpyrazine

[c] 2-Ethyl-3,5-dimethylpyrazine

4.3.4 Relationship between color development, physical changes, and aroma formation

The results obtained from this study showed that attaining the same coffee bean color (which is most frequently referred to as the degree of roast) using different time–temperature conditions during roasting does not necessarily mean that coffees are equivalent in terms of aroma and physical properties. High speed roasting with high hot air temperature led to different formation and elimination kinetics and in many cases to different concentrations of aroma compounds at roast color L* = 21 (Table 4.3). The same observations applied for the evolution of physical properties such as density, roast loss, and water content (Table 4.2). Similar results were obtained by Schenker [5]. Aroma compounds whose concentrations peaked and then decreased at medium degrees of roast, degraded rapidly near the end of HTST roasts. Thus for HTST roasts, small increases in roasting time would have reduced their concentration to levels similar to or lower than those attained in the longer roasts and would have reduced L* only slightly. However, small increases in HTST roasting time would not have produced pyridine and 2-furfurylthiol levels equal to those produced by the longer roasts. It is highly probable that the different time–temperature profiles applied do not only result in differences with regard to aroma compounds but also to flavor in general.

Using a time–temperature profile on the laboratory scale fluidizing-bed roaster, which approximated the temperature profile in a traditional drum roaster, similar results were obtained for physical properties and aroma formation in the resulting coffees. Temperature increase in the first stage of roasting was still faster in profile roasting than in drum roasting. Even better accord would be expected if a lower rate of temperature rise had been used during the profile roast. It is therefore possible to transfer roasting conditions of a traditional horizontal drum roaster to a fluidizing-bed system, but roasting time would not be reduced, if the roaster wants to produce a coffee with identical flavor properties.

The degree of roast is ultimately a question of definition, and the definition should depend on the specific requirements. In industrial practice, where constant quality of green coffee is roasted on the same roasting equipment, color measurement is surely an adequate, fast, and simple method for determining of the degree of roast. However, if coffee of equal sensory quality is intended to be produced with different roasting processes, more details about the roasting processes are needed. An exhaustive list of important physical values for reports on coffee roasting was proposed by Eggers and Pietsch [16]. The more physical and chemical parameters taken into account for the definition of a degree of roast, the more precise its determination and the better the transferability from one roasting process to another. In addition, an ideal definition of a degree of roast should also be independent from variations in raw material. Concentrations and ratios of different reaction products and remaining amounts of green coffee precursors (amino acids, chlorogenic acids, etc.) are potentially well suited indicators; however, their analysis is usually too complex for industrial practice.

5 Coffee roasting and aroma formation: Effect of initial moisture content and steam treatment

Initial moisture of green coffee may vary as a function of green coffee processing and storage conditions. The impact of initial moisture and steam treatment on roasting behavior and aroma formation was investigated. Steam treated coffees as well as coffees with initial moisture content of 5.10, 10.04, and 14.70 g water per 100 g wb were roasted. Light and dark roasting trials were carried out using a fluidizing-bed roaster with a batch size of 100 g of green beans. Differences in roast coffee attributes, that is, color, density, organic roast loss, and odorant concentrations were more marked in light roasted than in dark roasted coffees. The results of roasting steam treated coffee suggest that this step affects roasting behavior primarily by extracting some aroma precursor compounds.

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5.1 Introduction

For the development of the characteristic flavor of coffee, roasting is the key step that converts the nearly odorless, slightly pea smelling green coffee beans into roasted coffee. The water content of green coffee is usually around 10 g/ 100 g wb, but varies depending on the processing and drying methods, as well as on storage conditions. Clarke and Macrae [8] state that moisture content in excess of 13 g/ 100 g wb should be avoided in order to prevent mould growth.

It is known that roasting behavior of green coffee beans depends on water content. Schenker [5] showed that high initial water content leads to higher dehydration rate and faster increase of roast loss. Organic roast loss, however, remained practically unaffected by initial water content. Increase in bean temperature was delayed in coffee beans with high initial water content. Because of these differences in roasting behavior, predrying of green coffee to a moisture content of 5 g/ 100 g wb was proposed in order to obtain more uniform roast color and reduced density of fast roasted coffee [5].

Roasting of a series of Robusta coffees with moisture contents of 6, 11, and 14 g/ 100 g wb, respectively, resulted in higher end water content, higher percentage of soluble solids, and less titratable acidity at the highest initial moisture content compared to the lowest one [78]. Little and coworkers [79] roasted unwashed Arabica (Santos) and Robusta coffees with different initial moisture content and found that for partially dehydrated beans and beans stored at normal atmosphere, roast loss was a linear function of initial water content. The authors stated that the increase of roast loss is not only due to a higher loss of water but also to a higher loss of organic matter. Weight loss in hydrated beans (18 g/ 100 g wb) was proportionally less severe, and the authors drew the conclusion that conditions for roasting beans with high initial water content would be different from those with low water content.

Steam treating coffee is claimed to diminish undesired substances (e. g. catechol, pyrogallol, and hydroquinone) and to improve flavor quality [80, 81]. Contrary to steam roasting, green coffee steam treatment involves pressures of a few bars at most.

The effects of steam treatment on green coffee was investigated by several authors. Maier [82, 83] showed that steam treated coffee exhibited lower amounts of volatile saturated acids and mentioned that during steaming of green beans, contents of chlorogenic acids changed: 3-caffeoylquinic acid (3-CQA) and 3,4-dicaffeoylquinic acid (3,4-DCQA) increased, while others decreased. Milo and coworkers [52] extracted green coffee with hot water and found decreasing concentrations of caffeine (10% of the initial value) and chlorogenic acids (40% of the initial value). Luger and Steinhart [84] analyzed the carbohydrate fraction in steam treated coffee. They found increased amounts of monosaccharides, especially fructose and glucose, and notably decreased amounts of saccharaose, while the content of polysaccharides remained unchanged. Similar experiments were carried out in order to determine the impact of steam treatment on the amino acid pattern [85]. Free amino acids were reduced to around 50% of the initial value, whereas protein bound amino acids only decreased slightly to about 90% of the initial amount. Theurillat and coworkers [86] found that upon roasting, steam treated coffee reached target color faster, and hence, roasting time for the same degree of roast was shorter. The resulting coffee was sweeter, more acidic, less bitter, and exhibited higher acrylamide content than untreated coffee due to shorter roasting time.

The present investigation aimed at studying the impact of green coffee moisture content on roasting behavior and aroma development. For this purpose, light and dark roasting was carried out. In addition, the effect of steam treatment on roasting was investigated.

5.2 Materials and methods

5.2.1 Roasting process and process characterization

Raw material

Washed green *Coffea arabica Tip.* variety from Sumatra (Mandheling, S-795, Kartika 1) was supplied by Rast Ltd. (Ebikon, Switzerland).

Green coffee treatment

Water content of raw coffee was 10.05 g/ 100 g wb. To obtain a moisture content of 5.10 g/ 100 g wb, raw coffee was dried at 50 °C during 24 h and at 40 °C for another 26 h. Moistening of coffee was carried out by storing raw coffee over pure water for 20 days, which resulted in a water content of 14.70 g/ 100 g wb. A 5 L steel pressure chamber (maximum pressure 50 bar) was used for steam treatment of raw coffee beans. Batches of 400 g of green coffee beans were treated with steam for 6 min using a steam pressure of 2 bars. After steam treatment, green coffee was cooled passively for 4 min and green coffee was dried at 50 °C to 9.32 g/ 100 g wb moisture content.

Roasting trials

Coffee was roasted in batches of 100 g of green beans using a fluidizing-bed hot-air laboratory roaster (G. W. Barth AG, Freiberg/Neckar, Germany), which was described in detail by Schenker [5] and Geiger and coworkers [67]. An isothermal low-temperature process was applied, with hot air temperature of 227 °C. Roasting time was 210 s for light and 660 s for dark roasts. All roasting trials were carried out in triplicate. Color was measured and moisture content determined using the methods described in chapter 4.2. Bean core temperature was recorded during roasting by placing thermocouples (Type K, 0.5 mm, Thermocoax Ltd., Surèsnes, France) into drilled holes in the green coffee beans.

Density

Density of green and roasted coffee was determined using the method described in chapter 4.2.

5.2.2 Aroma analysis

Dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, 3-mercapto-3-methylbutyl formate, 2-furfurylthiol, methylpropanal, 2-methylbutanal, 3-methylbutanal, hexanal, 2,3-butanedione, 2,3-pentanedione, *N*-methylpyrrole, pyridine, 4-vinylguaiacol, 2,3,5-trimethylpyrazine, and 2-ethyl-3,5-dimethylpyrazine were sampled, separated and quantified with the method described in chapter 3.2.

5.2.3 Statistical analysis

Student's *t*-test was applied to the results with a level of significance of 95%.

Table 5.1 Basic properties of light and dark roasted coffees.

Green coffee	Water content [g/ 100g wb]	Roast loss [g/ 100g wb]	Organic roast loss [g/ 100g wb]	Color [L*]	Bean density [g/ cm^{-3}]
	Light roasts				
dried [a]	2.65 ± 0.10	8.14 ± 0.03	5.76 ± 0.10	27.52 ± 0.11	0.671 ± 0.002
untreated [b]	2.82 ± 0.04	12.38 ± 0.03	5.34 ± 0.05	28.62 ± 0.16	0.707 ± 0.002
moistened [c]	3.19 ± 0.06	16.04 ± 0.10	4.70 ± 0.12	29.60 ± 0.12	0.751 ± 0.005
steam treated [d]	2.67 ± 0.03	12.00 ± 0.02	5.54 ± 0.09	27.64 ± 0.13	0.716 ± 0.004
	Dark roasts				
dried [a]	1.70 ± 0.02	12.37 ± 0.01	9.23 ± 0.02	21.35 ± 0.06	0.608 ± 0.003
untreated [b]	1.71 ± 0.01	17.08 ± 0.02	9.39 ± 0.03	21.13 ± 0.16	0.606 ± 0.004
moistened [c]	1.70 ± 0.05	21.15 ± 0.10	9.14 ± 0.12	21.29 ± 0.07	0.608 ± 0.001
steam treated [d]	1.65 ± 0.02	16.84 ± 0.01	9.80 ± 0.08	20.74 ± 0.15	0.616 ± 0.003

[a] initial moisture content 5.10 ± 0.01 g/ 100 g wb
[b] initial moisture content 10.04 ± 0.02 g/ 100 g wb
[c] initial moisture content 14.70 ± 0.03 g/ 100 g wb
[d] initial moisture content 9.32 ± 0.08 g/ 100 g wb

5.3 Results and discussion

5.3.1 Influence of initial water content on the basic properties of roasted coffee

Table 5.1 shows water content, roast loss, organic roast loss, color, and density of the roasted coffees. The results are in agreement with those obtained by Schenker [5]. In general terms, differences were more marked in light roasts than in dark roasted coffees. Water content, lightness L*, and density were higher in light roasted coffees with higher initial water content. It is obvious that high initial moisture content implied the need for more energy for water evaporation and therefore retarded the temperature increase and hence development of a degree of roast during the first stage of roasting (Figure 5.1). Organic roast loss was correspondingly smaller in moist coffees. Roast loss, however, was higher in coffees with high initial water content due to higher quantity of evaporated water. However, with the exception of roast loss, these differences disappeared in dark roasted coffees.

5.3.2 Aroma development in coffees with different initial water contents

Concentrations of aroma compounds after light and dark roasting are displayed in Tables 5.3 and 5.4. As seen in the preceding section, the desired degrees of roast were faster attained in coffees with low water content. This fact helps to explain most of the concentration differences of the individual aroma components. *N*-methylpyrrole, pyridine, 3-mercapto-3-methylbutyl formate, 2,3,5-trimethylpyrazine and 2-ethyl-3,5-dimethylpyrazine are typical roast products with increasing concentration during the roasting process [chapter 4]. After light roasting, their concentrations were significantly higher with decreasing initial moisture content. In dark roasts, significant differences were still observable for 2-ethyl-3,5-dimethylpyrazine and 2,3,5-trimethylpyrazine, while for the other compounds, concentration differences leveled off. Similar observations were made in the case of 2-furfurylthiol, but the differences were not significant, due to the relatively high standard deviations caused by the analysis method that was not perfectly suited for compounds exhibiting a strong matrix effect, such as 2-furfurylthiol.

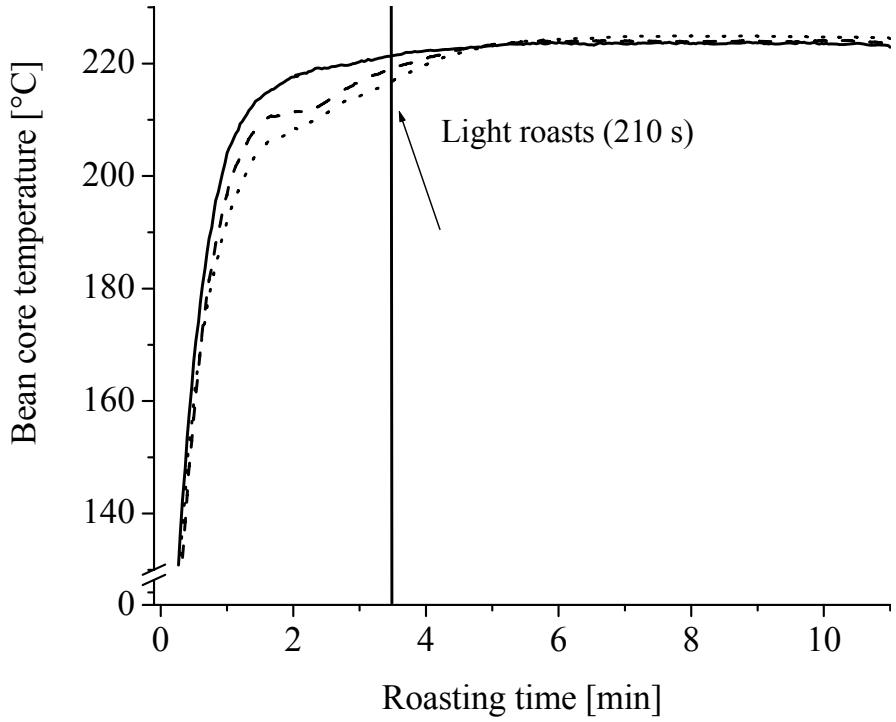

Figure 5.1 Bean core temperature during roasting of coffee beans with different initial water contents (—— dried [5.10 g H_2O/ 100 g wb], – – – untreated 10.04 g H_2O/ 100 g wb], ... moistened [14.70 g H_2O/ 100 g wb]).

Strecker aldehydes and α-diketones generally exhibit maximum concentration at medium degree of roast, but at higher temperature formation is counterbalanced by degradation reactions [51, 65, 66, 87]. Therefore, depending on the onset temperature where degradation of the compounds starts, a coffee with low initial moisture content may exhibit higher (before degradation) or lower (during degradation) concentration than a coffee with high initial water content at same roasting time. After light roasting, the dried coffee exhibited lowest amount of methylpropanal and 3-methylbutanal, and highest amount of 2,3-butanedione and 2,3-pentanedione. There was no significant difference in 2-methylbutanal concentration. In dark roasts, differences in Strecker aldehydes or α-diketones concentration were small and, in most cases, not significant. Formation of 4-vinylguaiacol did not seem to be affected much by initial water content neither.

A particular behavior was observed in the case of the three investigated sulfides. Dimethyl sulfide and dimethyl disulfide both were at maximum concentration in the coffee with original moisture (10 g/ 100 g wb) at both roast degrees. In the case of dimethyl disulfide, all moisture contents had a significant influence on concentration, and in the case of dimethyl sulfide, the amount in the moistened coffee was significantly lower than in the others at both roast degrees. A similar, but less pronounced behavior was observed with dimethyl trisulfide. As seen in chapter 4, dimethyl trisulfide exhibits biphasic behavior during roasting: after a sharp increase during the first stage of roasting, degradation takes place, followed by further concentration increase at the end of the roasting process. This specific conduct may be the reason for the fact, that medium initial moisture content resulted in highest concentration.

In conclusion, it may be stated that initial moisture content had an influence particularly on light roasted coffee, while in dark roasted coffees, most differences in odorants concentration leveled off.

Table 5.2 Influence of initial moisture content and steam treatment on concentration of selected aroma compounds after light roasting.

	Aroma concentration [mg/ kg dm] at initial moisture content of green coffee beans [g/ 100 g wb] of			
Aroma compound	5.1	10.0	14.7	9.3[e]
Dimethyl sulfide	6.2[a] ± 0.3	7.4[a] ± 0.7	5.0[b] ± 0.3	4.9[b] ± 0.4
Dimethyl disulfide	0.93[a] ± 0.04	1.04[b] ± 0.04	0.61[c] ± 0.01	1.46[d] ± 0.08
Dimethyl trisulfide	0.034[a] ± 0.002	0.036[a] ± 0.001	0.027[b] ± 0.003	0.037[a] ± 0.001
3-MMBF [f]	0.057[a] ± 0.004	0.038[b] ± 0.004	0.023[c] ± 0.002	0.035[b] ± 0.001
2-Furfurylthiol	0.46[a] ± 0.11	0.39[a] ± 0.03	0.27[a] ± 0.11	0.91[b] ± 0.15
Methylpropanal	25.8[a] ± 1.4	30.3[b] ± 0.4	29.7[a,b] ± 2.0	25.5[a,b] ± 2.2
2-Methylbutanal	21.6[a,b] ± 0.6	21.9[a] ± 0.5	22.2[a] ± 0.8	20.2[b] ± 0.7
3-Methylbutanal	11.9[a] ± 0.3	13.0[b] ± 0.3	13.3[b] ± 0.5	12.7[a,b] ± 0.6
Hexanal	3.57[a] ± 0.03	3.9[a,b] ± 0.5	3.3[a,b] ± 0.2	2.97[b] ± 0.06
2,3-Butanedione	23.7[a] ± 0.3	22.1[b] ± 0.6	22.1[b] ± 0.6	23.2[a,b] ± 0.2
2,3-Pentanedione	14.9[a] ± 0.3	13.2[b] ± 0.3	12.8[b] ± 0.2	13.3[b] ± 0.4
N-Methylpyrrole	1.78[a] ± 0.06	1.22[b] ± 0.06	0.85[c] ± 0.01	0.88[c] ± 0.04
Pyridine	49.0[a] ± 1.5	30.1[b] ± 1.5	19.7[c] ± 0.7	24.8[d] ± 0.3
4-Vinylguaiacol	29.2[a] ± 1.2	27.8[a] ± 1.1	29.1[a] ± 0.8	23.7[b] ± 0.4
2,3,5-TMP [g]	4.9[a] ± 0.4	4.7[a] ± 0.3	3.7[b] ± 0.1	4.4[a,b] ± 0.4
EDMP [h]	1.5[a] ± 0.1	1.0[b] ± 0.1	0.69[c] ± 0.04	1.0[b] ± 0.1

[a, b, c, d] Different letters indicate statistically significant differences ($p < 0.05$).

[e] Steam treated coffee

[f] 3-Mercapto-3-methylbutyl formate

[g] 2,3,5-Trimethylpyrazine

[h] 2-Ethyl-3,5-dimethylpyrazine

Table 5.3 Influence of initial moisture content and steam treatment on concentration of selected aroma compounds after dark roasting.

	Aroma concentration [mg/ kg dm] at initial moisture content of green coffee beans [g/ 100 g wb] of			
Aroma compound	5.1	10.0	14.7	9.3[e]
Dimethyl sulfide	6.0[a] ± 0.4	6.3[a] ± 0.6	4.1[b] ± 0.3	4.5[b] ± 0.4
Dimethyl disulfide	0.98[a] ± 0.03	1.20[b] ± 0.06	0.78[c] ± 0.05	1.86[d] ± 0.04
Dimethyl trisulfide	0.053[a,b] ± 0.001	0.047[c] ± 0.002	0.044[a,c] ± 0.005	0.059[b] ± 0.004
3-MMBF [f]	0.104[a] ± 0.002	0.10[a] ± 0.01	0.104[a] ± 0.005	0.100[a] ± 0.003
2-Furfurylthiol	4.5[a] ± 0.9	4.3[a] ± 1.1	3.6[a] ± 0.6	3.4[a] ± 0.3
Methylpropanal	24.8[a] ± 1.0	29.6[a,b] ± 2.4	28.7[b] ± 0.4	27.1[b] ± 0.8
2-Methylbutanal	19.5[a,b] ± 0.4	20.2[a] ± 0.2	21.3[a,b] ± 1.3	19.6[b] ± 0.3
3-Methylbutanal	10.5[a] ± 0.1	11.1[b] ± 0.3	11.3[a,b] ± 0.4	11.6[b] ± 0.1
Hexanal	1.2[a] ± 0.2	1.5[a] ± 0.2	1.31[a] ± 0.09	1.2[a] ± 0.1
2,3-Butanedione	13.7[a] ± 0.8	13.2[a] ± 0.3	13.9[a] ± 0.5	13.5[a] ± 0.1
2,3-Pentanedione	5.3[a,b] ± 0.2	5.0[a] ± 0.2	5.61[b] ± 0.02	5.3[a,b] ± 0.3
N-Methylpyrrole	3.1[a] ± 0.1	3.05[a] ± 0.03	2.95[a] ± 0.09	2.2[b] ± 0.1
Pyridine	154[a] ± 7	148[a] ± 3	144[a] ± 2	113[b] ± 2
4-Vinylguaiacol	21.1[a,b] ± 0.1	20.8[a] ± 0.2	22.4[b] ± 0.6	18.1[c] ± 0.3
2,3,5-TMP [g]	5.5[a] ± 0.3	4.8[a] ± 0.2	4.1[b] ± 0.1	4.34[c] ± 0.03
EDMP [h]	1.5[a] ± 0.2	1.11[b] ± 0.03	0.93[c] ± 0.06	0.97[c] ± 0.04

[a, b, c, d] Different letters indicate statistically significant differences ($p < 0.05$).

[e] Steam treated coffee

[f] 3-Mercapto-3-methylbutyl formate

[g] 2,3,5-Trimethylpyrazine

[h] 2-Ethyl-3,5-dimethylpyrazine

5.3.3 Impact of steam treatment on coffee roasting behavior

Steam treated raw coffee was dried to a moisture content of 9.32 g water per 100 g wb. Its behavior upon roasting was similar compared to the untreated coffee. Color development was faster, and dark roasting of steam treated coffee resulted in the lowest L*-value of all roasting trials (Table 5.1). However, evolution of several aroma compounds during the roasting of steam treated coffee was different compared to that in untreated coffee (Table 5.2 and Table 5.3). After light roasting of untreated and steam treated coffees, significant differences in concentration were found for dimethyl sulfide, dimethyl disulfide, 2-furfurylthiol, 2-methylbutanal, *N*-methylpyrrole, pyridine, and 4-vinylguaiacol. Dark roasting led to significant concentration differences in dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, 2-methylbutanal, *N*-methylpyrrole, pyridine, 4-vinylguaiacol, 2,3,5-trimethylpyrazine, and 2-ethyl-3,5-dimethylpyrazine. Concentration of 2-furfurylthiol also was considerably lower in dark roasted steam treated coffee, but because of high standard deviation during analysis, the difference was not significant. Most of the concentration differences of individual aroma components may be explained by the fact that steam treatment partly extracted precursor compounds. According to Milo and coworkers [52], a decreased amount of feruloylquinic acid is most probably responsible for the lower amount of 4-vinylguaiacol. The same authors attributed low amounts of Strecker aldehydes in roasted coffee to strong reduction of free amino acids due to hot water extraction of green coffee. Steam treatment is not expected to result in the same degree of amino acid reduction, but still a significantly lower concentration of 2-methylbutanal was found in steam treated coffee compared to that in the untreated coffee.

Formation pathways of pyridine and *N*-methylpyrrole include degradation of trigonelline [88] or pyrolysis of amino acids [70, 89]. It was found, however, that steaming of green coffee beans reduces trigonelline content by less than 1% [90]; therefore lower amounts of pyridine and *N*-methylpyrrole may be explained by partial extraction of free amino acids during steam treatment. For 2,3,5-trimethylpyrazine and 2-ethyl-3,5-dimethylpyrazine, formation pathways using hexose and glycine or alanine, respectively, were proposed [91]. Their significantly lower amounts in dark

roasted steam treated coffee may therefore be explained by a restricted quantity of free amino acids available for the respective reaction. Considerable differences in dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide concentrations were found between untreated and steamed coffee. While the amount of dimethyl sulfide was significantly lower in steamed coffee, dimethyl disulfide and dimethyl trisulfide concentrations were significantly higher. One possible reaction pathway of sulfides during roasting is the oxidation and subsequent disproportionation of methanethiol, which is the product of Strecker degradation and β-elimination of methionine [20, 92]; however, at high temperatures, other reaction pathways involving methionine and cysteine are also possible. As dimethyl disulfide and dimethyl trisulfide both exhibit biphasic behavior upon roasting, the higher amounts in steam treated coffee may be explained by the faster development of the degree of roast.

The effect of steam treatment on 2-furfurylthiol formation seemed to be complex. Light roasted steam treated coffee exhibited more than 2-fold higher amount of 2-furfurylthiol than untreated coffee, while after dark roasting, 2-furfurylthiol concentration was higher in untreated coffee. Milo and coworkers [52] found that 2-furfurylthiol concentration doubled upon roasting hot water extracted beans and supposed that this is due to the absence of competing reactions. The results from this study suggest indeed that in the first stages of roasting, a rapid 2-furfurylthiol formation pathway is preferred because of the absence of competing reactions. However, at higher degrees of roast, and hence higher product temperature, different formation pathways involving mostly precursors not extracted by water are favored.

Steam treatment mostly influences the roasting behavior of coffee by extracting some precursor compounds. Consequently, concentrations of several odorants were different compared to those in untreated coffee, both in light and dark roasts. The sensory impact of these concentration differences is unclear and needs to be elucidated by sensory tests.

6 Influence of water quench cooling on degassing and aroma stability of roasted 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 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.

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6.1 Introduction

Once the desired degree of roast is achieved, fast quenching of coffee beans is necessary in order to avoid over-roasting 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 [9] and is relatively slow. Therefore, exothermic reactions within coffee beans may continue during the first 15 s of the cooling process [93]. Water quenching cools down coffee faster and temperature drops from 230 °C to 100 °C in less than 1 second are reported [93]. When bean temperature falls below 100 °C, exothermic moisture condensation occurs and coffee beans can take up moisture. Eggers [93] 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 the 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 [93].

Water quenching is generally associated with loss of coffee quality, although explicit experimental data are lacking. Illy and Viani [9] 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 and coworkers [67] 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 [8, 94].

In studies on degassing of roasted coffee, Radtke [59] 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 on the amount of entrapped CO_2 in coffee beans, values up to 8-16 bar are found [8, 59]. Shimoni and Labuza [95] suggested that the major part of carbon dioxide in coffee powder is in a sorption/desorption equilibrium and only a minor part entrapped in collapsed structure. However neither the mechanisms of CO_2 entrapping and sorption nor the driving forces and mechanisms of degassing within coffee beans are fully understood.

Spadone and Liardon [4] 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 ageing were independent of water content in roasted coffee. Clinton [29] 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 [30] showed that the reaction of roast and ground coffee can be considerably accelerated by effect of temperature, moisture, and coffee density.

Nicoli and coworkers [96] 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.

Table 6.1 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
Dimethyl sulfide (**2**)	62	[$^{2}H_6$]-**2**	68
Dimethyl trisulfide (**4**)	126	[$^{2}H_6$]-**4**	132
2-Methylbutanal (**8**)	86	[$^{2}H_2$]-**9**	88
3-Methylbutanal (**9**)	71	[$^{2}H_2$]-**9**	73
Hexanal (**10**)	56	[$^{2}H_2$]-**10**	58
2,3-Butanedione (**11**)	43	[$^{13}C_4$]-**11**	45
2,3-Pentanedione (**12**)	100	[$^{13}C_2$]-**12**	102
Pyridine (**14**)	79	[$^{2}H_5$]-**14**	84
4-Vinylguaiacol (**15**)	150	[$^{2}H_3$]-**15**	153
2,3,5-Trimethylpyrazine (**16**)	122	[$^{2}H_6$]-**17**	141
2-Ethyl-3,5-dimethylpyrazine (**17**)	135	[$^{2}H_6$]-**17**	141
2-Ethyl-3,6-dimethylpyrazine (**18**)	135	[$^{2}H_6$]-**17**	141
2-Ethyl-3-methylpyrazine (**19**)	121	[$^{2}H_6$]-**17**	141
2-Ethyl-5-methylpyrazine (**20**)	121	[$^{2}H_6$]-**17**	141
2-Ethyl-6-methylpyrazine (**21**)	121	[$^{2}H_6$]-**17**	141

6.2 Materials and methods

6.2.1 Roasting process and process characterization

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.

Moisture content and color measurement

Color of the roasted coffee and moisture content were determined as described in chapter 4.2.

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) using a low-temperature long-time process (LTLT, 228 °C, 12 min, [67]). The roaster has been described in detail by Schenker [5] and Geiger and coworkers [67].). 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 [5], 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 in pouring of 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).

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.

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.

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.

Mercury intrusion porosimetry

Porosimetry was carried out using mercury porosimeters Pascal 140 and 440 (Thermo Electron Corporation, Waltham, MA) as described by Schenker and coworkers [7].

6.2.2 Aroma analysis

Chemicals

Isotopically labeled standards were obtained from Dr. Ehrenstorfer GmbH, Augsburg, Germany ([$^2H_6$]-dimethyl sulfide, [$^2H_5$]-pyridine, [$^2H_2$]-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 [55], [$^2H_6$]-dimethyl trisulfide [54], [$^{13}C_4$]-2,3-butanedione and [$^{13}C_2$]-2,3-pentanedione [56].

SPME-GC-MS analysis and quantification of coffee aroma compounds

Samples of coffees roasted in 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 hours 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, 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 6.1).

Ground coffee (5 g for the first group of compounds **2**, **10**, and **16**-**21**; 1 g for the second group of compounds **4**, **8**, **9**, **11**, **12**, **14**, and **15**) was weighed in a 100 mL flask and extracted with 100 mL boiling water during 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 isotope labeled internal standards [$^2H_6$]-**2**, [$^2H_2$]-**10**, [$^2H_6$]-**17** for the first group, and [$^2H_6$]-**4**, [$^2H_2$]-**9**, [$^{13}C_4$]-**11,** [$^{13}C_2$]-**12**, [$^2H_5$]-**14**, [$^2H_3$]-**15** for the second group,

respectively. 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 during 10 min using a 50/30 µm StableFlex divinylbenzene/carboxen/poly-dimethylsiloxane (DVB/CAR/PDMS) fibre (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) using a Fisons 8000 Series gas chromatograph (Thermo Electron, Allschwil, Switzerland) using the following temperature programs: 40 °C (6 min), 4 °C/min, 135 °C (0 min), 40 °C/min, 240 °C (5 min) for compounds **2**, **10**, and **16-21**; and 40 °C (4 min), 4 °C/min, 140 °C (0 min), 40 °C/min, 240 °C (5 min) for compounds **4**, **8**, **9**, **11**, **12**, **14**, 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 SSQ710 (Finnigan MAT, San Jose, California) 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.

6.3 Results and discussion

6.3.1 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 6.1). However, after one week of storage, no marked difference in degassing rate is found anymore. In addition, Figure 6.1 shows that coffees with same roast degree and comparable water content exhibit similar degassing rates throughout storage, unaffected from 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 wb immediately after cooling. The second part was left untreated. Degassing of the remoistened coffee was very similar to degassing of film cooled coffee (Figure 6.2), which gives rise to the assumption that fast degassing of coffees with high water content is due to remaining moisture only and 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 6.3). 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 [95, 97] 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.

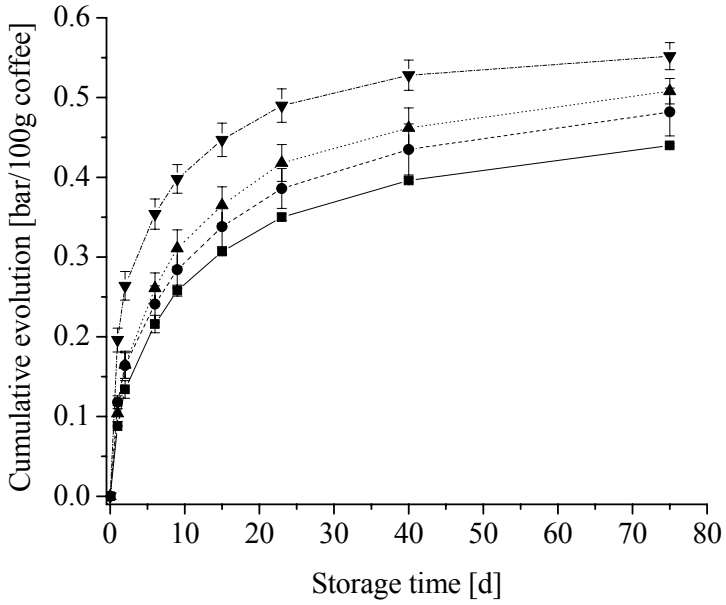

Figure 6.1 Degassing of coffee beans: passively cooled (■, 1.7 g H2O/ 100 g wb), air cooled (●, 1.9 g H2O/ 100 g wb), spray cooled (▲, 2.1 g H2O/ 100 g wb), and film cooled (▼, 4.2 g H2O/ 100 g wb) [bar/100 g dm].

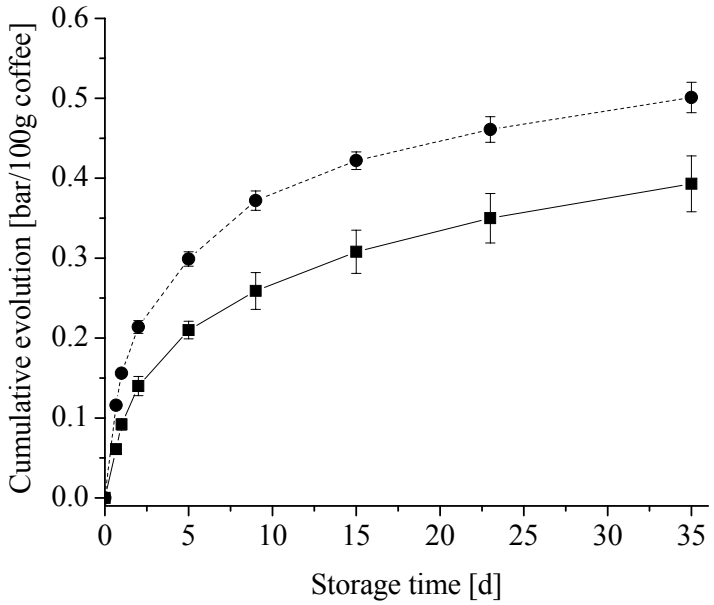

Figure 6.2 Degassing of air cooled coffee (■) and remoistened air cooled coffee (●) [bar/100 g dm].

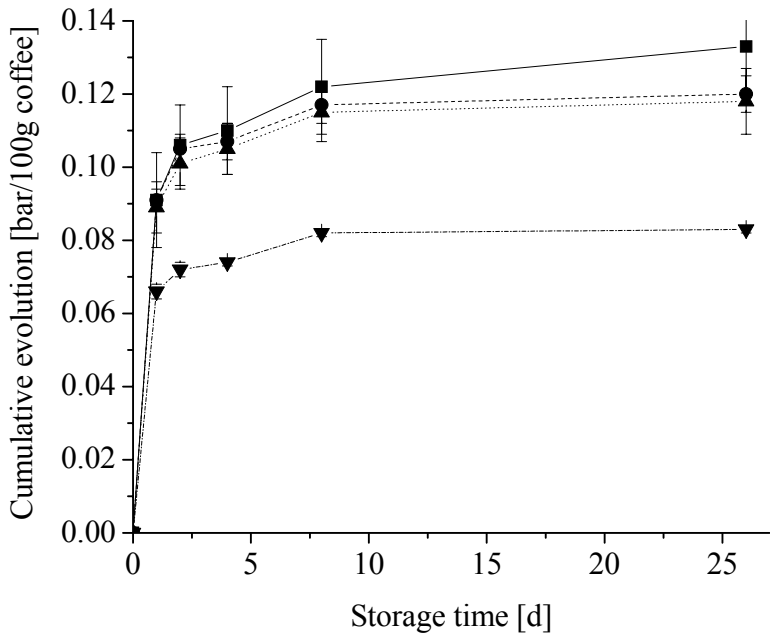

Figure 6.3 Degassing of ground coffee: passively cooled (■, 1.7 g H2O/ 100 g wb), air cooled (●, 1.9 g H2O/ 100 g wb), spray cooled (▲, 2.1 g H2O/ 100 g wb), and film cooled (▼, 4.2 g H2O/ 100 g wb) [bar/100 g dm].

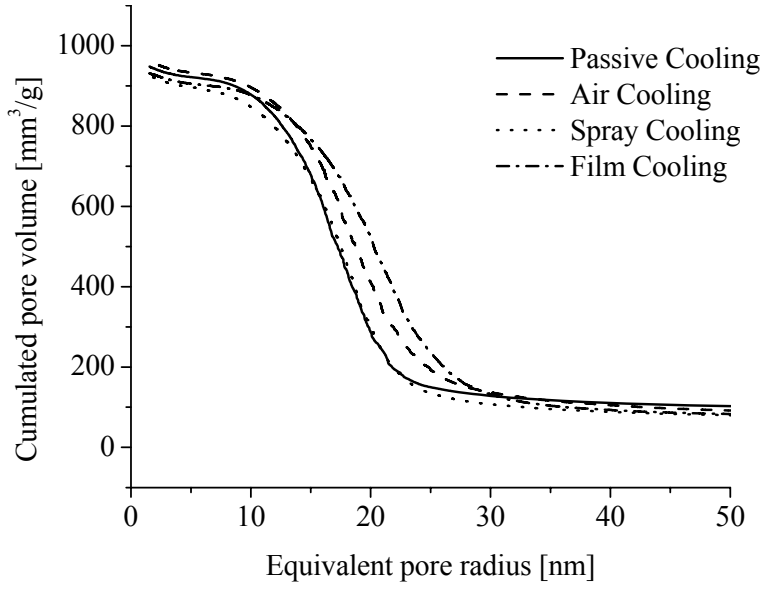

Figure 6.4 Cumulated intruded mercury volume in coffees from laboratory roasting trials.

For water quenched coffee beans, the assumption was made that fast degassing is linked to opening of pores during the cooling step [9]. Schenker and coworkers [5] 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 slowly-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 6.4). It must be noted, though, that mercury intrusion porosimetry gives insight into the intracellular pore system but does not provide information about surface porosity [5]. The origin and structure of the micropore system within coffee cell walls still remains unclear, and the question of how gas and oil is 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 (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 6.5). 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.

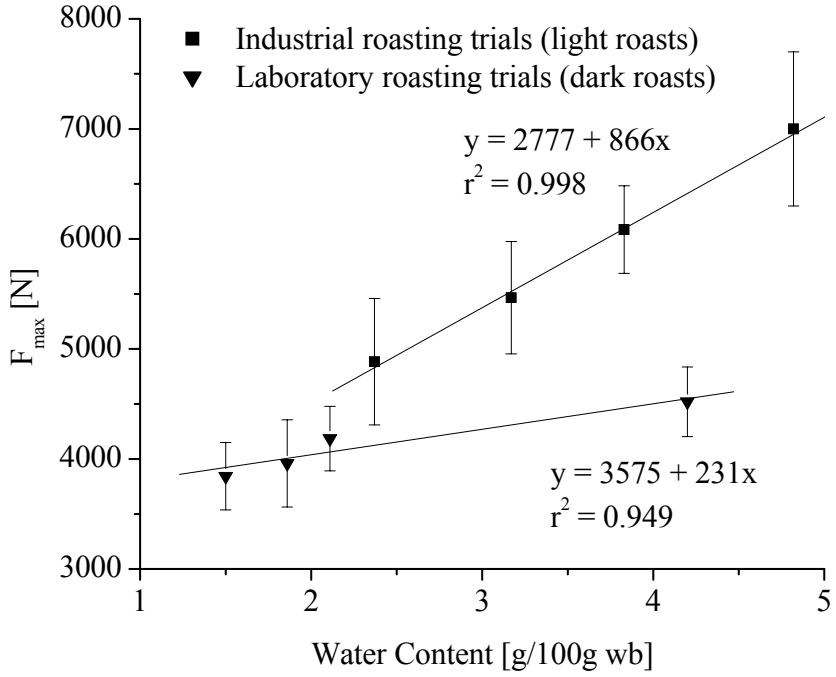

Figure 6.5 Firmness of coffee beans roasted in laboratory and industrial trials.

6.3.2 Aroma stability

Odorants for the assessment of coffee shelf-life were chosen on the basis of studies that linked analytical to sensory data [40, 98]. 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 as a relatively stable marker substance.

Storage trials with roasted coffee beans obtained from laboratory trials revealed substantial changes in aroma profile (Figure 6.6 and Table 6.2). After 133 days of storage, concentrations of volatile substances like 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, and 2,3-pentanedione decreased to 40 to 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 6.2 shows retention of aroma compounds after 56 days of storage, while Figure 6.6 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 were 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 the 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 [1] 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 6.6). 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 [72, 92]. 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 [63], water quenched coffee with increased moisture content probably exhibits an accelerated loss of freshness attributes.

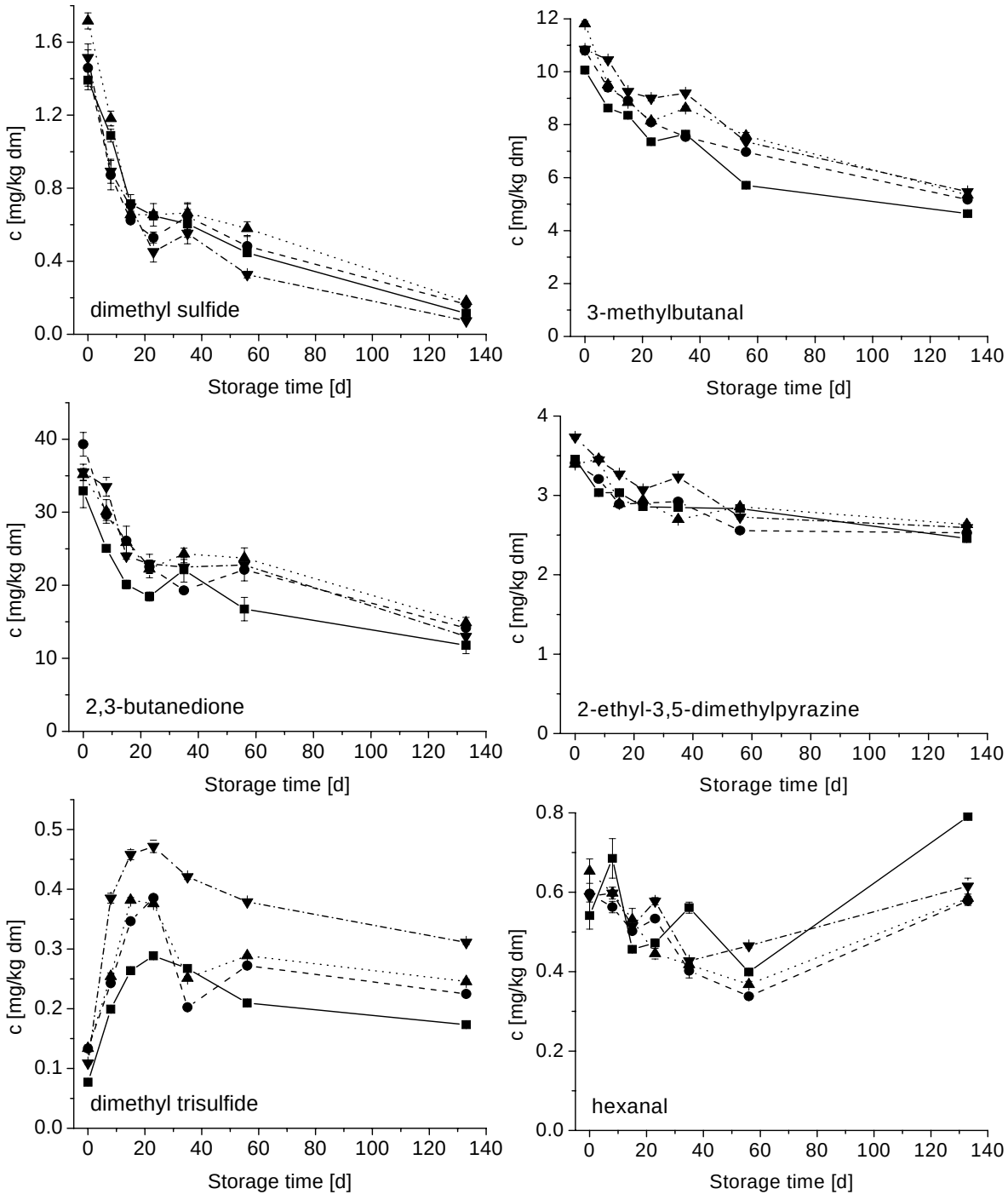

Figure 6.6 Alteration of selected coffee aroma compounds in passively cooled coffee (■, 1.7 g H_2O/ 100 g wb), air-cooled coffee (●, 1.9 g H_2O/ 100 g wb), spray-cooled coffee (▲, 2.1 g H_2O/ 100 g wb), and film-cooled coffee (▼, 4.2 g H_2O/ 100 g wb).

Table 6.2 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.

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 in 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 6.7 and Table 6.3), 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 a faster decay of freshness attributes.

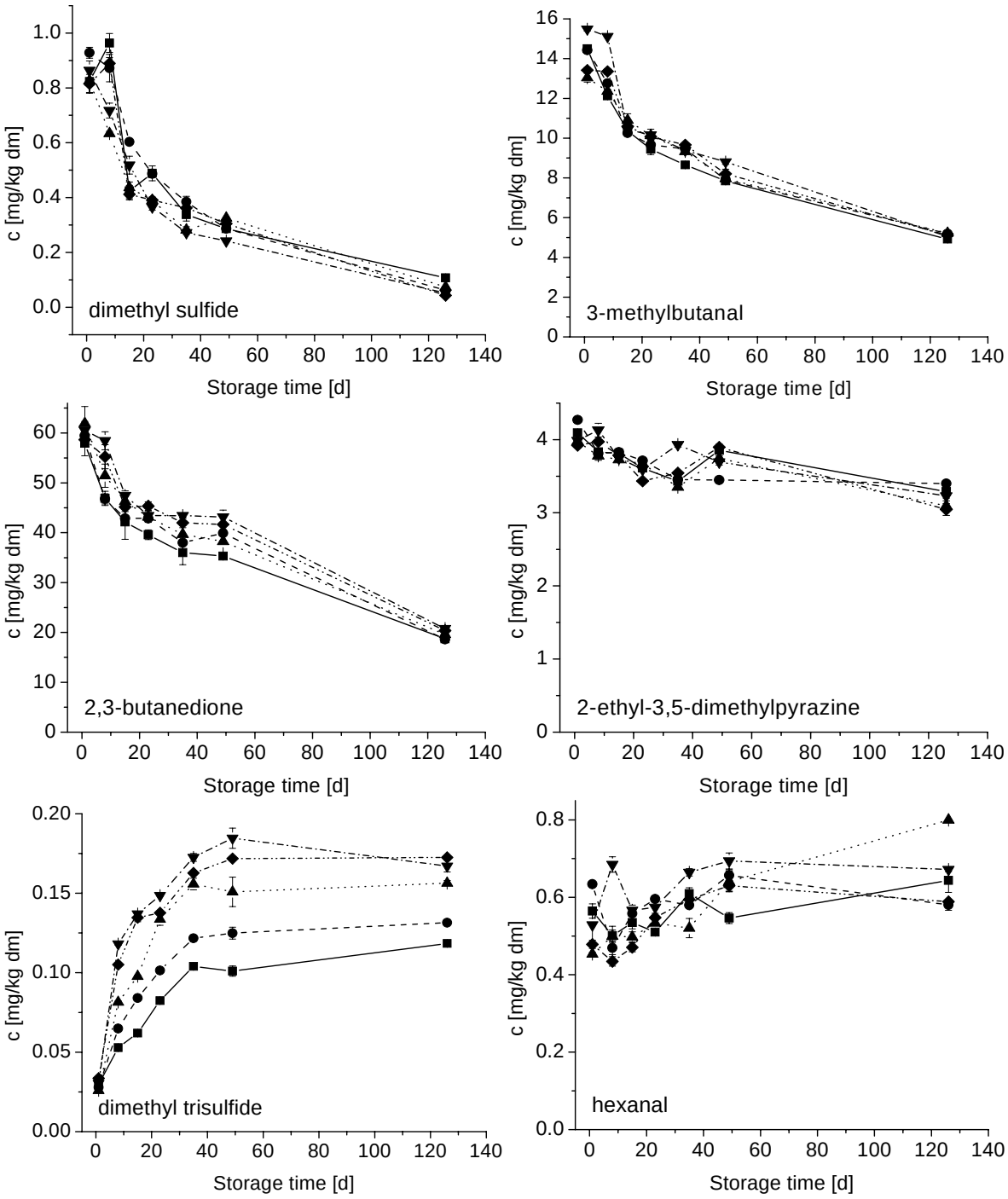

Figure 6.7 Alteration of selected coffee aroma compounds in coffees from industrial roasting trials with 2.4 g H_2O/ 100 g wb (■), 3.2 g H_2O/ 100 g wb (●), 3.8 g H_2O/ 100 g wb (▲), 4.8 g H_2O/ 100 g wb (▼), and 5.3 g H_2O/ 100 g wb (◆).

Table 6.3 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.

7 Moisture content and aroma stability of roast and ground coffee

Roasted coffee beans with different moisture content were ground and packaged under nitrogen and under normal atmosphere. The evolution of characteristic odorants was followed by means of headspace solid-phase microextraction–gas chromatography–mass spectrometry. Upon open storage under atmospheric conditions, decrease of dimethyl sulfide, 3-mercapto-3-methylbutyl formate, and *N*-methylpyrrole was fastest in the coffee with highest water content. Storage under nitrogen atmosphere during 83 days at 37 °C resulted in considerable faster degradation of dimethyl sulfide, 3-mercapto-3-methylbutyl formate, *N*-methylpyrrole, 2-furfurylthiol, 2- and 3-methyl-butanal, 2,3-butanedione, and 2,3-pentanedione. With both storage conditions, a large increase of dimethyl trisulfide concentration was observed; the increase being more pronounced in coffees with higher moisture content. Since dimethyl trisulfide is a product of methanethiol degradation, faster thiol oxidation is assumed. The decrease in aroma stability of coffees with increased moisture content is mainly attributed to a plasticizing effect of water, which decreases glass transition temperature of ground coffee and by this increases mobility of reactants.

7.1 Introduction

Aroma stability during storage of roasted coffee is very limited. It is supposed that aroma staling of coffee is mainly a result of stripping and degradation of important odorants such as methanethiol and 2-furfurylthiol, rather than an effect of newly formed off-odorants [28, 63]. The loss of aroma compounds is particularly fast if storage takes place under normal atmospheric conditions. Roast and ground coffee is especially susceptible to oxidation because of the increased surface and the shorter diffusion distance for the action of oxygen. However, even if roast and ground coffee is stored under nitrogen at -20 °C, deterioration of the sensory quality is observed only after some months of storage [99]. In chapter 6, it was shown that during the open storage of whole coffee beans with differing moisture content, degradation of many odorants (2-methylbutanal, 3-methylbutanal, 2,3-butanedione, 2,3-pentanedione, several di- and trialkylpyrazines, dimethyl sulfide, pyridine, and 4-vinylguaiacol) took place in a similar manner, while the evolution of dimethyl trisulfide was highly influenced by the moisture content. A relationship to methanethiol oxidation and hence loss of freshness attributes was supposed [100].

Recently, single sealed portions of roast and ground coffee have become popular and have gained a high market share. High storage stability is expected, since grinding, degassing, and packaging usually take place under protective atmosphere. However, manufacturers tend to increase the moisture content to the maximum allowed (5g / 100 g wb), although there is still little knowledge about the influence of water content on aroma deterioration in roast and ground coffee under protective atmosphere.

The aim of this part of the research project was to gain a deeper insight into the influence of moisture content on aroma staling in roast and ground coffee. The list of odorants investigated in chapter 6 was extended by *N*-methylpyrrole and several sulfur compounds (methanethiol, 2-furfurylthiol, and 3-mercapto-3-methylbutyl formate), since sulfur compounds were supposed to be most affected by water content of roasted coffee. Storage stability was studied under normal atmospheric conditions and under nitrogen atmosphere.

7.2 Materials and methods

7.2.1 Raw material and roasting trials

Batches (45 kg) of Colombian *Coffea arabica* with initial water content of 10 g/ 100 g wb were roasted with a semi-fluidizing bed roaster CR-1250 from G. W. Barth Ltd. (Freiberg/Neckar, Germany).

The roaster layout with separate roasting and cooling zones (Figure 7.1) allowed the application of different quenching methods, i.e., air quenching, water quenching in the roasting zone, and water quenching in the cooling zone. If water quenching is applied, coffee beans can take up water as soon as their temperature falls below 100 °C. It was therefore possible to water quench coffee in the roasting zone without increasing the water content, by stopping the operation at a bulk temperature of 120 °C, and then continuing quenching in the cooling zone with cold air. The application of water in the cooling zone, however, resulted in increased moisture content in the final product.

Using the quenching methods mentioned above, four batches of coffee with identical degree of roast and differing water contents were produced (Table 7.1). Typical progressions of inlet air temperature, exhaust air temperature, and roasting and cooling zone bulk temperatures are displayed in Figure 7.2. The roasting times and bulk temperatures of the roasting endpoints and the evolution of temperature during quenching is illustrated in Figure 7.3.

Roasted coffees were packaged under nitrogen in polyethylene valve bags in portions of 1 kg as soon as the quenching process was completed.

Color and moisture content were determined as described in chapter 4.2.

7.2.2 Grinding, packaging, and storage conditions

After 24 hours of equilibration time under nitrogen atmosphere at room temperature, the roasted coffee beans were ground and packaged. To prevent the contact of coffee with oxygen, the full operation was carried out under nitrogen. For this purpose, a disk mill (Bühler-Miag 4000, Bühler Ltd., Milano, Italy) was placed in a glove box with controlled nitrogen atmosphere (<1% O_2). Coffee beans were ground at level 3, then

transferred to 100 g polyethylene valve bags, which were then heat sealed. The packaged coffee was stored at 37 °C during 83 days. In addition, open storage at normal atmosphere and 25 °C in the absence of light during 40 days was carried out.

7.2.3 Aroma analysis

Methanethiol, dimethyl sulfide, dimethyl trisulfide, 3-mercapto-3-methylbutyl formate, 2-furfurylthiol, 2-methylbutanal, 3-methylbutanal, hexanal, 2,3-butanedione, 2,3-pentanedione, *N*-methylpyrrole, and 2,3,5-trimethylpyrazine were sampled, analyzed, and quantified as described in chapter 3.2.

Table 7.1 Roasting trials with different quenching methods and resulting water contents.

Batch	Quenching method	Water used in RZ[a] [L]	Water used in CZ[b] [L]	Moisture content of roasted coffee [g/ 100 g wb]	Color [L*]
Q1	air	0	0	1.3	21.2
Q2	water (RZ) & air	5	0	1.4	21.2
Q3	air & water (CZ)	0	6	3.2	21.2
Q4	air & water (CZ)	0	8	6.5	21.5

[a] roasting zone

[b] cooling zone

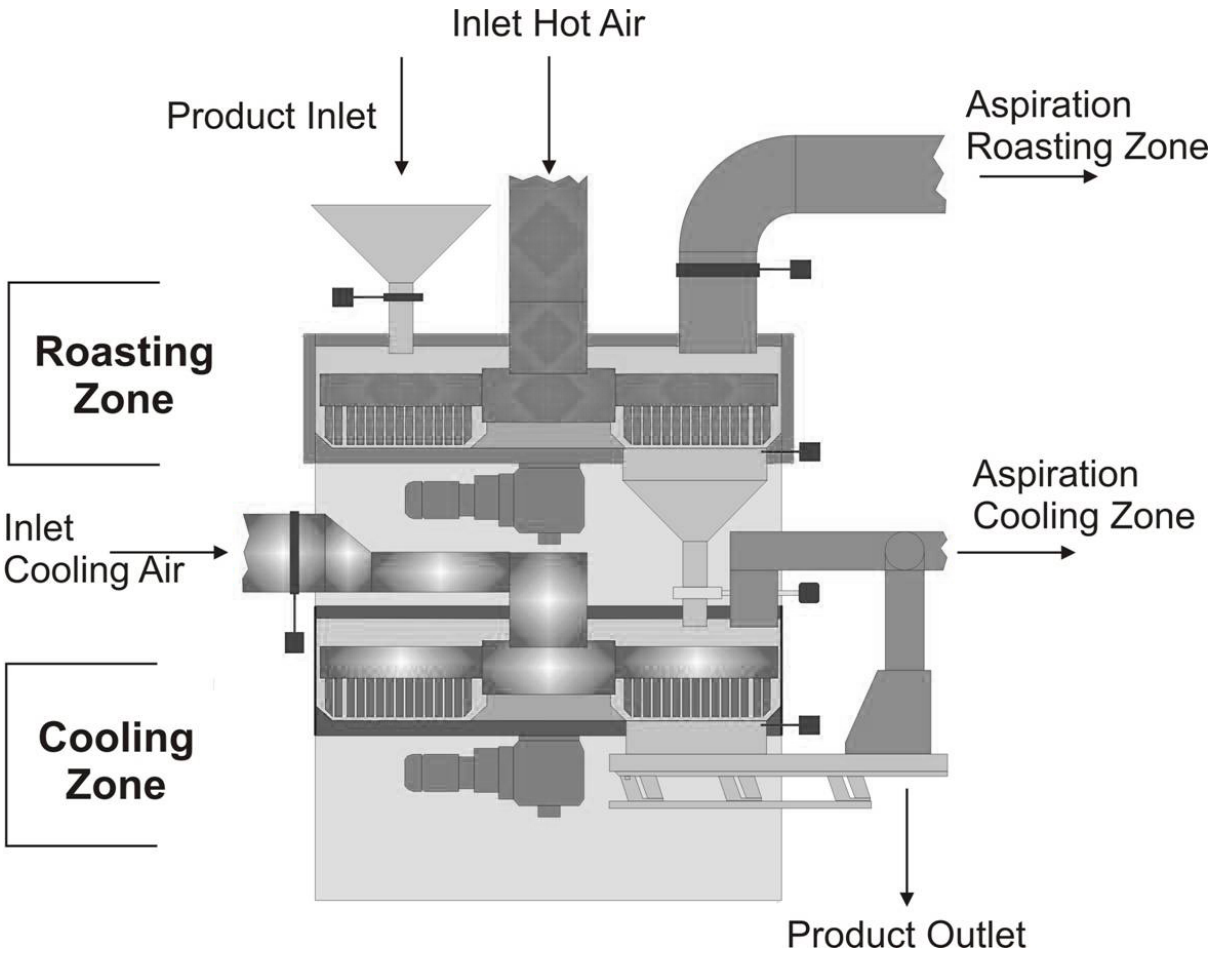

Figure 7.1 Schematic representation of the G. W. Barth CR1250 semi-fluidizing bed coffee roaster (courtesy of G. W. Barth AG, Germany).

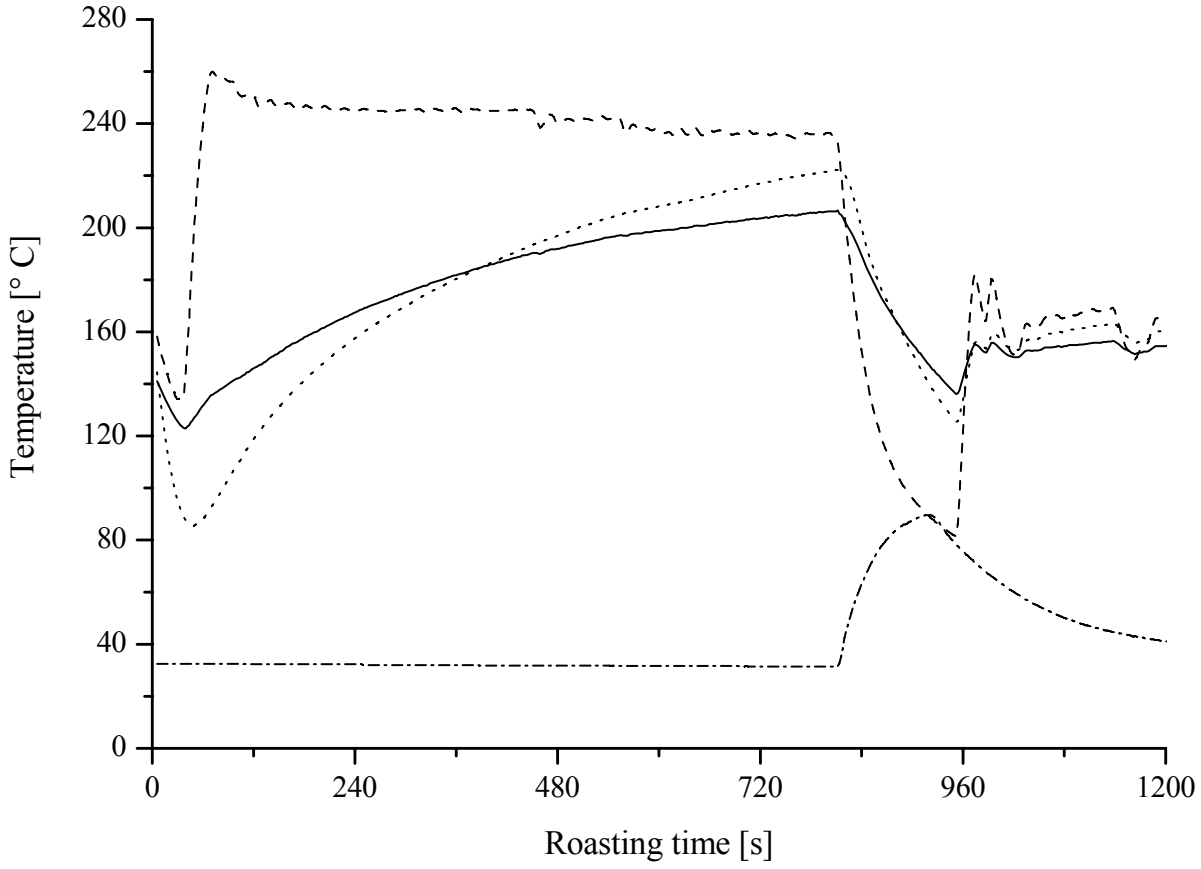

Figure 7.2 Roasting of coffee with the G. W. Barth CR1250 roaster (roasting trial Q1): Evolution of bulk temperature in roasting zone (——), inlet hot air temperature (– – – –), exhaust air temperature (.....), and bulk temperature in cooling zone (–.–.–).

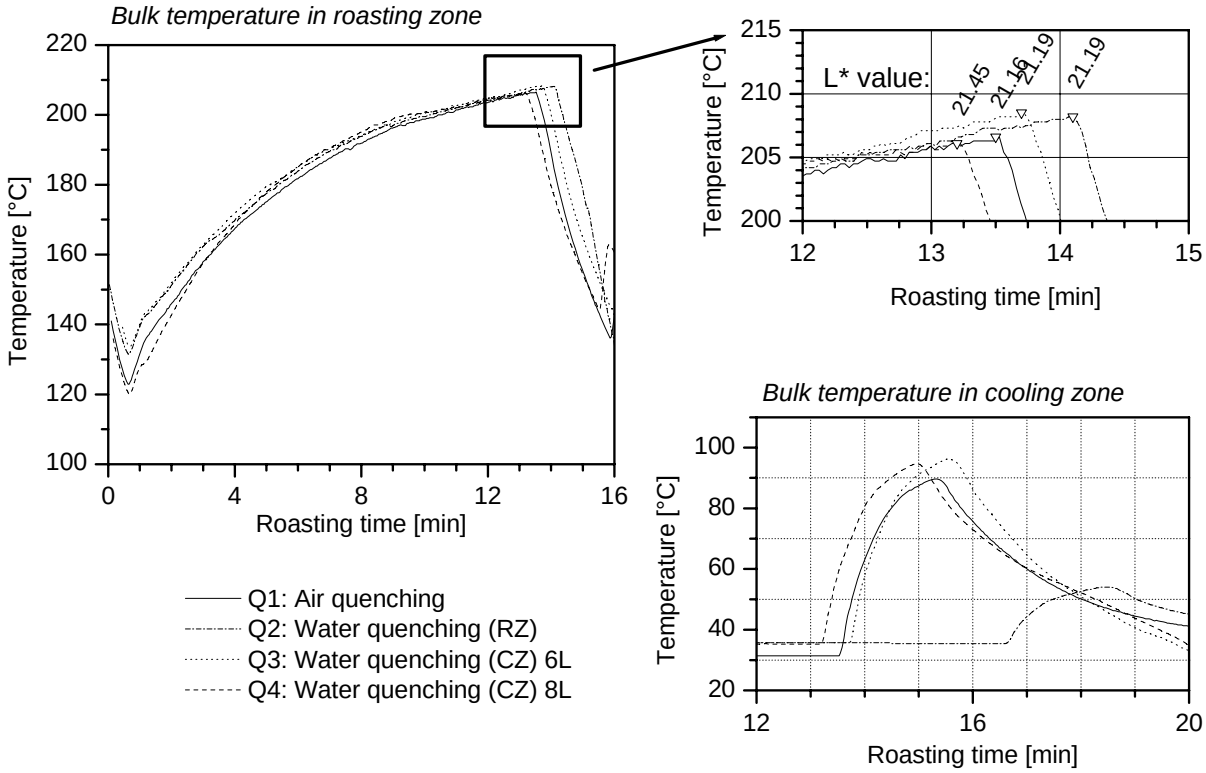

Figure 7.3 Roasting end points and evolution of bulk temperature in the roasting and cooling zones.

7.3 Results and discussion

7.3.1 Open storage of roast and ground coffee

Open storage of roast and ground coffee implies fast loss and/or degradation of aroma compounds [28]. Similar to the study on storage stability involving storage of whole roasted coffee beans [chapter 6], no differences in the behavior during open storage of roast and ground coffees with different moisture contents were observed for 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, 2,3-pentanedione, and 2,3,5-trimethylpyrazine (Figure 7.4). In addition, no differences in hexanal evolution were found. This was not surprising, because during short storage time in the absence of light, lipid oxidation is not expected to take place at a large extent. However, the moisture content of roast and ground coffee influenced other aroma compounds (Figure 7.5). Decrease of dimethyl sulfide, 3-mercapto-3-methylbutyl formate, and *N*-methylpyrrole was accelerated in the coffee with the highest water content. The increase of dimethyl trisulfide during the first days of storage was largely enhanced with increasing water content, corroborating the results presented in chapter 6. Due to a probable relationship between the increase of dimethyl trisulfide during storage and the degradation of dimethyl sulfide and methanethiol [72, 92, 100], it was assumed that methanethiol degradation should also be governed by the water content. The assumption was not corroborated by the results; a clear trend in methanethiol degradation could not be observed.

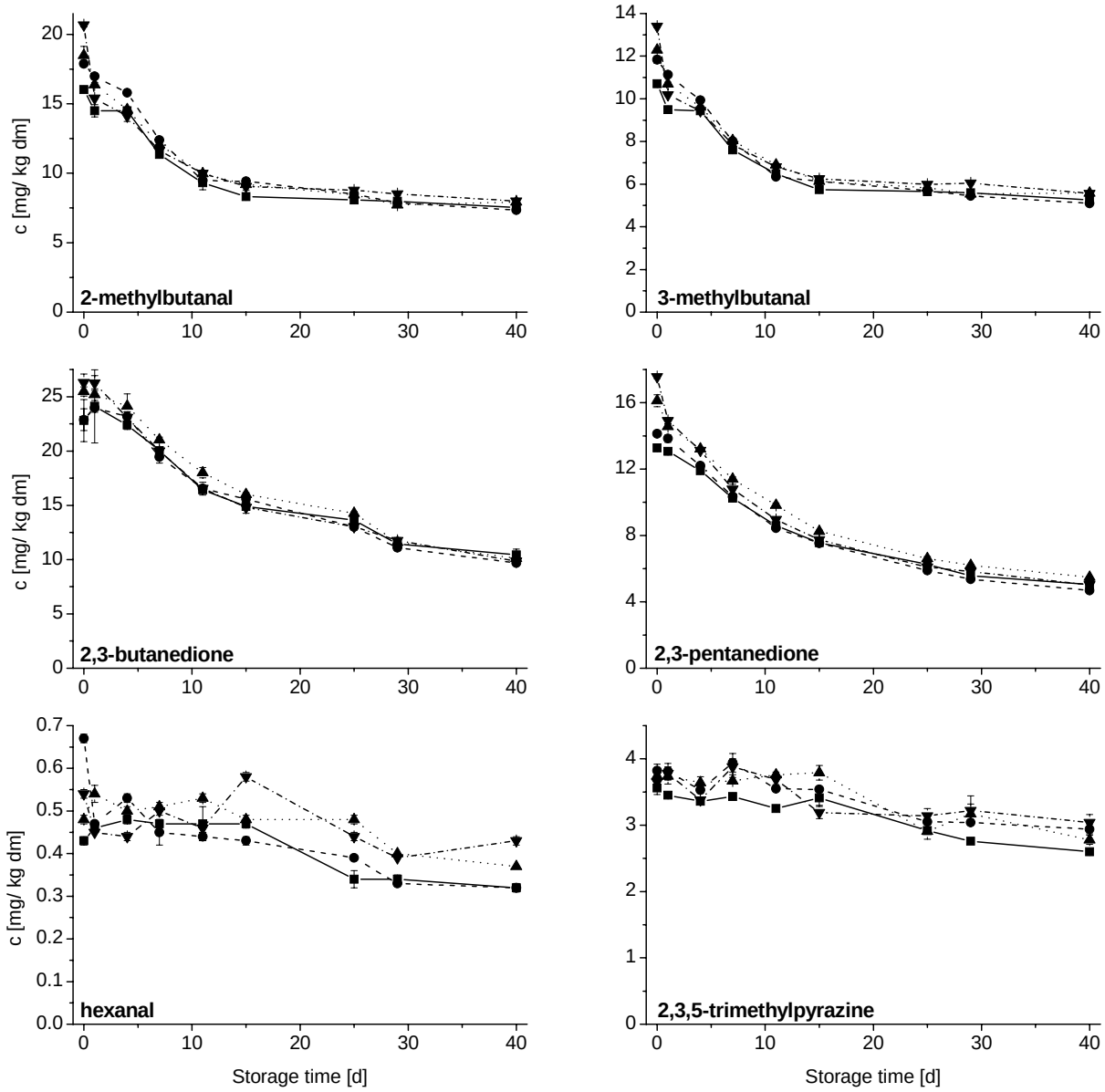

Figure 7.4 Alteration of selected aroma compounds during open storage of roast and ground coffee: air quenched (Q1, 1.3 g H_2O/ 100 g wb, ■), water quenched in roasting zone (Q2, 1.4 g H_2O/ 100 g wb, ●), water quenched in cooling zone (Q3, 3.2 g H_2O/ 100 g wb, ▲), water quenched in cooling zone (Q4, 6.5 g H_2O/ 100 g wb ▼).

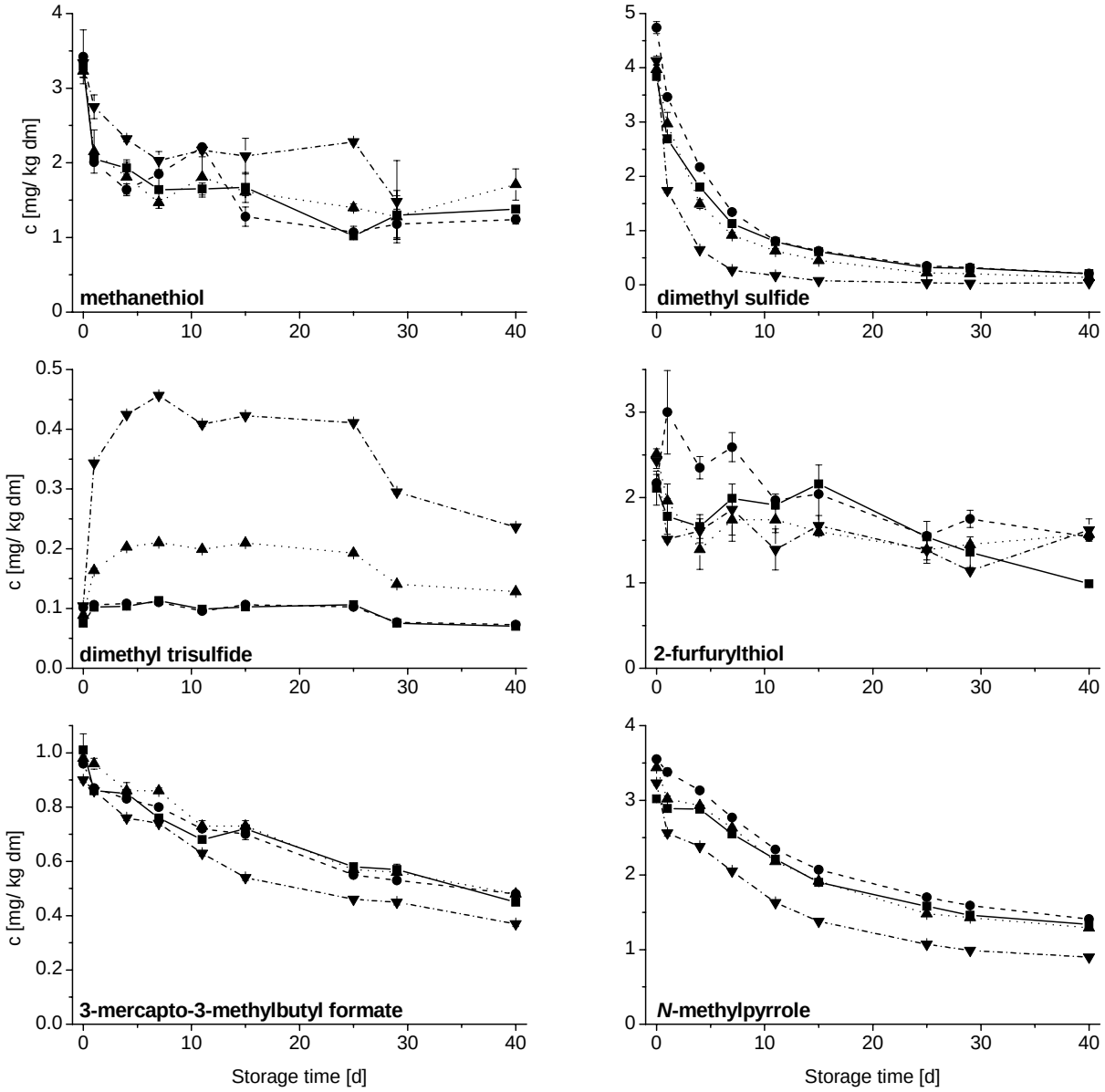

Figure 7.5 Alteration of selected aroma compounds during open storage of roast and ground coffee: air quenched (Q1, 1.3 g H2O/ 100 g wb, ■), water quenched in roasting zone (Q2, 1.4 g H2O/ 100 g wb, ●), water quenched in cooling zone (Q3, 3.2 g H2O/ 100 g wb, ▲), water quenched in cooling zone (Q4, 6.5 g H2O/ 100 g wb ▼).

7.3.2 Storage of roast and ground coffee under nitrogen atmosphere

Roast and ground coffee sealed in valve bags with an oxygen concentration lower than 1% was stored at 37 °C during 83 days. The increased storage temperature was chosen in order to shorten storage time. The impact of temperature on roast and ground coffee shelf-life was investigated by Cardelli and Labuza [2]. The authors found a decrease of shelf-life of about 20% by increasing the storage temperature by 10 °C. The remaining fractions of aroma compounds after storage are displayed in Figure 7.6. As in the case of open storage, dimethyl sulfide, 3-mercapto-3-methylbutyl formate, and *N*-methylpyrrole were more rapidly degraded in coffees with high moisture content. 2,3,5-Trimethylpyrazine was hardly degraded and its final concentration was more than 90% of the initial value in all examined coffees. The evolution of dimethyl trisulfide was similar as in storage under normal atmosphere. A large concentration increase was observed, with highest values for coffees with higher moisture content. The concentration of hexanal was more than doubled after 83 days of storage, and no differences with differing moisture content were observed. The effects of moisture content on lipid oxidation of low-moisture and intermediate-moisture foods are well investigated and it is known that too dry food products are susceptible to oxidation. The optimal moisture level to prevent rancidity development corresponds to the monolayer coverage of water on the food at a water activity of approximately 0.3 to 0.35. At a high water activity (0.55 to 0.85), the susceptibility for oxidation increases again [101, 102]. For roast and ground coffee, a monolayer moisture value of 3.7 g H_2O/ 100 g wb was reported [103]. The water activities of roast and ground coffee with 2 and 5 g water per 100 g wb were estimated as being approximately 0.1 and 0.5, respectively [104, 105]. According to Labuza [101], lipid oxidation is only slightly enhanced at these two water activity values. Therefore only minor differences between coffees with moisture contents between 1.3 and 6.5 g/ 100 g wb are expected with regard to the generation of the secondary lipid oxidation product hexanal.

2-Furfurylthiol, the Strecker aldehydes 2- and 3-methylbutanal, and the α-diketones 2,3-butanedione and 2,3-pentanedione were highly influenced by the moisture content. Considerable higher losses of these important odorants were observed in the coffees with increased water content. Faster degradation reactions in coffees with high

moisture content may be explained by the plasticizing effect of water, which reduces the glass transition temperature in amorphous solid systems [106]. It was shown that reduced glass transition temperature led to increased reaction rates in low moisture systems [106-108]. In addition, Karmas and coworkers [109] demonstrated that structural changes, i.e., glass transition and collapse, induced changes in diffusion constants of the reactands, and therefore effected the kinetics of non-enzymatic browning in model systems. Poisson and coworkers [53] showed that the degradation of 3-methylbutanal was at least partially not oxygen-related, and assumed that odorants containing high electrophilic groups, such as carbonyls, were susceptible to other chemical reactions. These reactions might also exhibit increased rates in higher moisture systems.

Apparently, favorable storage conditions, i.e., a protective atmosphere, are a pre-requisite to observe moisture-induced differences in the degradation of 2-furfurylthiol, the Strecker aldehydes and α-diketones, and it is assumed that, upon storage at normal atmosphere, the differences are superimposed by fast oxidative reactions with external oxygen. The results are in good agreement with information on sensory shelf-life of roast and ground coffee given by Cardelli and Labuza [2]. The authors showed that roast and ground coffee stored at increased water activity exhibited a shorter sensory shelf-life. The shelf-life differences between coffees stored at different water activities were large at low partial oxygen pressure, while at normal atmosphere, the differences were considerably smaller.

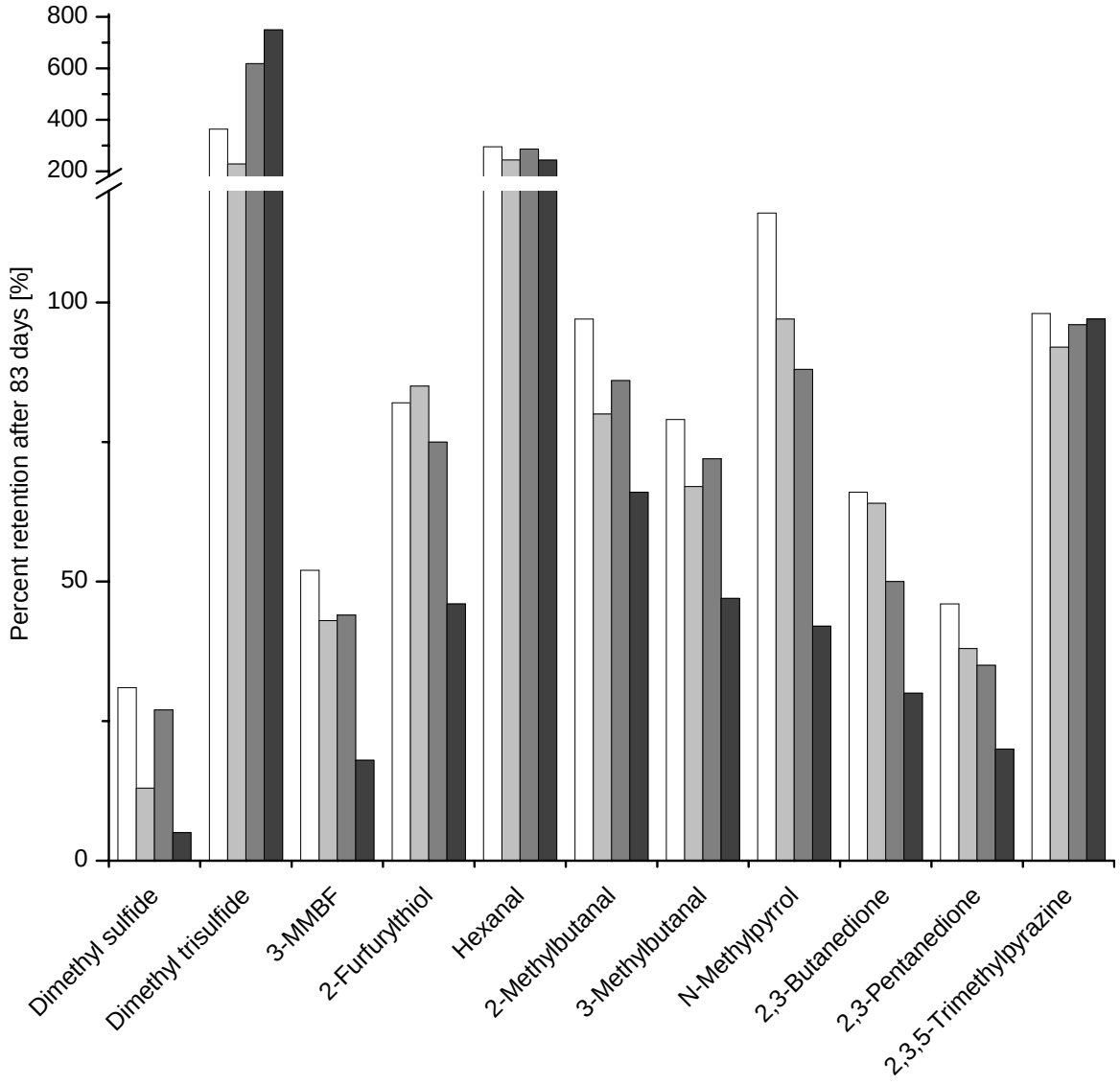

Figure 7.6 Percent retention (relative to t = 0 days) of aroma compounds during storage under nitrogen atmosphere at 37 °C. Air quenched (Q1, 1.3 g H_2O/ 100 g wb, □), water quenched in roasting zone (Q2, 1.4 g H_2O/ 100 g wb, ▭), water quenched in cooling zone (Q3, 3.2 g H_2O/ 100 g wb, ▬), water quenched in cooling zone (Q4, 6.5 g H_2O/ 100 g wb, ■). 3-MMBF: 3-mercapto-3-methylbutyl formate.

8 Water content of roasted coffee: Impact on grinding behavior, extraction, and aroma retention

Normal and long time roasting trials were carried out on industrial scale. Different amounts of water were applied during quenching, resulting in water contents in the range of 2.3–8.8 g/ 100 g wb. Coffees were ground immediately after cooling, and after equilibration times of 6 and 24 h. Particle size distribution of ground coffees, percolation time, and extraction properties were investigated on an espresso coffee machine. Coffees ground after 24 h resting time were subjected to storage trials to determine aroma stability as influenced by water content. Coffees with high moisture content exhibited coarser particles upon grinding, and equilibration time prior to grinding was needed for coffees with high water content to improve grinding results. Coffees with low water content did not exhibit this time dependency prior to grinding. Coffees with low water content were extracted more effectively than high moisture coffees, and percolation was slower. During open and closed storage, evolution of hexanal and sulfides was highly sensitive to water content. However, differences in evolution of other aroma compounds were found during closed storage only, where moisture content had a negative impact on aroma stability of the coffees subjected to investigation.

This chapter has been published in an adapted form as:

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8.1 Introduction

Coffee beverages are prepared by extracting and dispersing the desired types and amount of components from roasted coffee beans into water. Thereby, size reduction of the roasted beans by grinding is a prerequisite for controlled extraction and dispersion. The formation of small particles and large particle surface are essential for rapid liberation of carbon dioxide, reduction of diffusion distance for soluble substances during extraction, and improved transfer of colloidal substances to the liquid phase [110]. Coffee is usually comminuted by gap grinding using roller, conical, or flat cutters. In industrial practice roller cutters are the most frequently used grinders. Due to specific structural properties of roasted coffee beans, a crushing phase for reducing the coffee bean into coarse pieces is necessary prior to fine grinding. In grinding devices this is achieved by using cutters with unequal teeth (flat and conical cutters) or by using series of grinding stages with decreasing gap width in roller grinding systems [9].

Not much information is available on coffee grinding dynamics. Using computer simulation of the action of a disk grinder on a particle composed of several cells, it was shown that the exerted stress was not uniform and resulted in formation of one large and several very small particles [111]. As expected, grinding behavior of coffee beans depends on water content after roasting. According to grinding tests of beans with different water contents, the proportion of fine particles and the particle-specific surface increased when the water content was low [112, 113].

The efficiency of extraction is controlled by the particle size distribution of ground coffee. Basically, extraction rate and extent depend on the percolation properties of the bed of ground coffee, the wettability of the individual particles in the aqueous system, and the overall particle surface for diffusion. Computer simulation showed that coarsely ground coffee leads to the build-up of large channels in which the extraction water flows at high velocities so that extraction yields are low [114]. On the other hand, if the particle size becomes too small, filters are clogged, particles may even flow through the filters, and over-extraction occurs due to extended contact time. Also, a balance between wettability, for which particles must not be too small, and

diffusion, which increases with decreasing particle size, must be attained. Therefore, in order to optimize extraction one tries to obtain a bimodal particle size distribution with medium particle size of about 0.5 mm and a small amount of fine particles [9, 24]. For espresso type beverages, for which careful adjustment of grinding parameters is particularly important with regard to final cup quality, the bimodal particle size distribution ensures a proper percolation due to the coarse fraction and, at the same time, high diffusion rates from small particles [9].

The influence of grinding on extraction was also studied for specific compounds. It was shown that extraction of caffeine was more efficient from finely ground than from coarsely ground coffee [115, 116]. Overall flavor profile of espresso coffee made from a blend with 80 % Arabica and 20 % Robusta coffee was judged as a function of grinding fineness. It was found that finely ground coffee exhibited better aroma and flavor characteristics than coarsely ground coffee [112].

Final water content of coffee beans after roasting does not only influence grinding behavior as stated above. There is also evidence that water content controls aroma retention and stability during storage of roasted coffee [chapter 6], which means that there exists a dual dependence of cup quality for water content, one direct and one indirect via grinding behavior. The present investigation aims at elucidating the influence of water content on grinding, percolation, and extraction properties of ground coffee, as well as on aroma stability during storage of ground coffee in an open and a closed packed system.

8.2 Materials and methods

8.2.1 Roasting process and process characterization

Roasting

Green *arabica* coffee from Colombia (Excelso) was roasted at industrial scale using a RT1000 tangential roaster (Probat Ltd., Emmerich, Germany). A normal and a long time process were used. Normal time roasting was carried out with a batch size of 120 kg and roasting time of approximately 340 s. Inlet air temperature was 350 °C in the first stage of roasting, and was reduced to 330 °C when bulk temperature reached 160 °C. Long time roasting was carried out with a batch size of 170 kg and roasting time was around 650 s. Roasting temperature in the long time process was lower. Initial inlet air temperature was 310 °C, and was reduced to 300 °C when bulk temperature attained 175°C. All batches were roasted to the same degree of roast, but different amounts of water were applied during the cooling step resulting in different water contents. Roasting parameters are illustrated in Table 8.1.

Water content and color measurement

Water content and color of roasted coffee were determined as described in chapter 4.2.

Table 8.1 Roasting parameters and roasted coffees properties.

	Normal time roasts			Long time roasts		
Batch	NT 1	NT 2	NT 3	LT 1	LT 2	LT 3
Batch size [kg]	100	100	100	170	170	170
Roasting time [s]	343.7	340	340.5	651.5	637.7	641.4
Final bulk temperature [° C]	225.0	222.2	222.2	222.1	222.1	222.1
Color [L*]	22.6	23.3	22.6	23.5	23.4	23.1
Water used for quenching [L]	12	20	30	16	25	32
Water content [g/ 100 g wb]	2.3	5.1	8.8	2.9	3.6	5.9
Bulk density [g/ L]	335	347	344	353	358	358

8.2.2 Grinding and packaging

Grinding

Roasted coffees were ground with a UW246 roll grinder (Probat Ltd., Emmerich, Germany). The grinder consisted of three serial anvil rollers in which the first one served as a pre-crusher and the following two as fine grinders. The gap between the rollers was set to 1.4 and 0.22 (arbitrary units) for the first and the second fine grinding unit, respectively. To determine the impact of resting time upon grinding, roasted coffees were ground immediately, 6, and 24 h after roasting.

Particle size distribution of ground coffee

Analysis of particle size distribution was carried out using the image analysis sensor QICPIC (Sympatec Ltd., Clausthal-Zellerfeld, Germany). The sensor worked with a pulsed light source and sub-nanosecond illumination. Results were obtained as sum of distribution and distribution density.

Packaging

For experiments concerning extraction yield, percolation time, and evolution of aroma compounds, portions of 6.3 g ground coffee were packaged into small synthetic containers and sealed under normal atmosphere.

8.2.3 Extraction yield and percolation time

Extraction yield and percolation time of ground coffees were determined with a commercial espresso machine (Gaggia S.p.a, Robecco Sul Naviglio, Italy). Coffee was extracted for 20 s, then the extract was dried during 70 h at 103 °C, and extraction yield was determined gravimetrically. To determine percolation time, the time necessary for percolation of 60 mL water was measured.

8.2.4 Evolution of aroma compounds during storage of roast and ground coffee

The evolution of aroma compounds (dimethyl sulfide, dimethyl trisulfide, 2-methylbutanal, 3-methylbutanal, hexanal, 2,3-butanedione, 2,3-pentanedione, pyridine, and 4-vinylguaiacol) was followed with the method described in chapter 6.2.

Storage trials were carried out with all long time roasted and one normal time roasted coffee, ground after 24 h resting time (NT 3, LT 1, LT 2, LT 3). Ground coffee was stored under open conditions (25 °C, normal atmosphere) and in portions of 6.3 g in tightly sealed small containers with normal atmosphere at 25 °C. Samples of open stored coffee were taken after 1, 3, 8, 15, 22, 37, and 56 days, whereas one sample of each coffee was packaged under nitrogen directly after grinding and analyzed as a reference with a period of 24 h between packing and analysis. In the case of packaged coffee, aroma was analyzed after 8, 23, 41, 56, and 224 days.

8.3 Results and discussion

8.3.1 Particle size distribution of ground coffee

A typical particle distribution of a ground roasted coffee is shown in Figure 8.1. The distribution in particle size is bimodal with a relative maximum at average particle size of around 70 µm and an absolute maximum at average particle size of around 425 µm. To characterize particle distribution of ground coffees, 3 parameters were found to be sufficient for differentiation: distribution density at 70.71 µm, average particle size at the absolute maximum, and distribution density at the absolute maximum (Table 8.2). High water content in roasted coffee leads to less brittleness of coffee beans [chapter 6], and, therefore more energy is needed to comminute them. The resulting ground coffee is coarser with increasing water content. The importance of the application of equilibration time before grinding is shown in Figure 8.2. While for coffees exhibiting low water content, differences in particle size distributions were rather small with different equilibration time, medium moist roasted coffees required a certain resting time before grinding in order to obtain satisfactory fineness. However excessive moisture contents (> 6 g/ 100 g wb) lead to unacceptable grinding results with regard to particle size distribution even after 24 hours of equilibration. It has to be noted at this point that the legal limit for moisture content is usually 5 g/ 100 g wb.

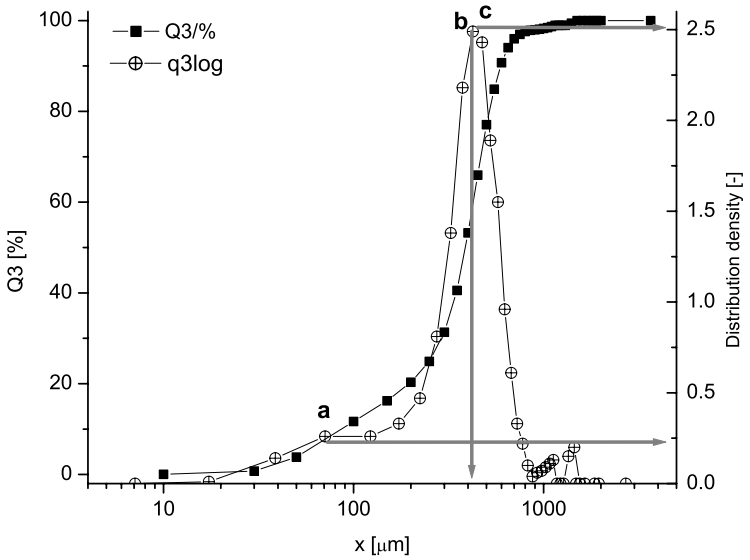

Figure 8.1 Particle size distribution and distribution density of LT 1 roasted coffee ground after equilibration time of 24 hours (**a**: distribution density at 70.71 µm, **b**: particle size at absolute maximum, **c**: distribution density at absolute maximum).

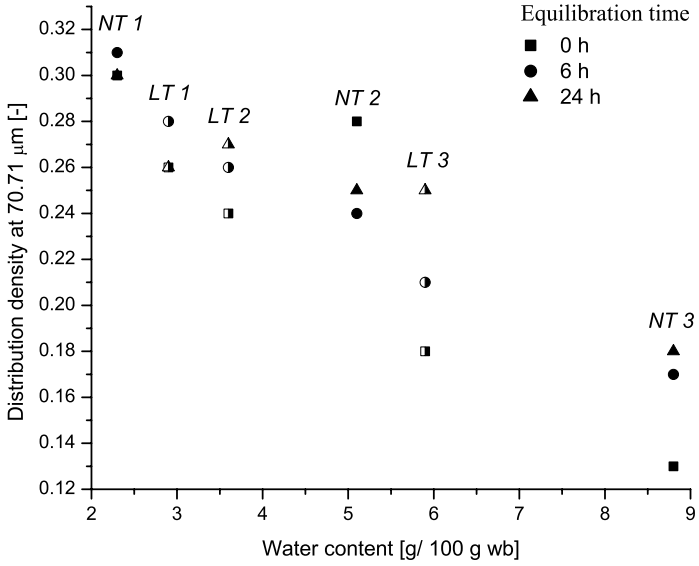

Figure 8.2 Influence of water content and equilibration time prior to grinding on distribution density at average particle size of 70.71 µm. Abbreviations of roasting trials according to Table 8.1.

Table 8.2 Distribution density at 70.71 µm, average particle size at the absolute maximum, and distribution density at the absolute maximum for coffees ground after different equilibration times prior to grinding.

Equilibration time before grinding [h]	Batch [a]	Water content [g/ 100 g wb]	Distribution density at x = 70.71 µm	Average particle size at absolute maximum [µm]	Distribution density at absolute maximum
0	NT 1	2.3	0.30	424.26	2.52
0	NT 2	5.1	0.28	424.26	2.17
0	NT 3	8.8	0.13	1949.36	2.94
0	LT 1	2.9	0.26	424.26	2.50
0	LT 2	3.6	0.24	424.26	2.10
0	LT 3	5.9	0.18	524.40	2.06
6	NT 1	2.3	0.31	424.26	2.36
6	NT 2	5.1	0.24	474.34	2.50
6	NT 3	8.8	0.17	874.64	3.42
6	LT 1	2.9	0.28	424.26	2.55
6	LT 2	3.6	0.26	474.34	2.44
6	LT 3	5.9	0.21	524.40	2.49
24	NT 1	2.3	0.30	424.26	2.50
24	NT 2	5.1	0.25	424.26	2.65
24	NT 3	8.8	0.18	574.46	2.58
24	LT 1	2.9	0.26	424.26	2.49
24	LT 2	3.6	0.27	424.26	2.57
24	LT 3	5.9	0.25	474.34	2.54

[a] Batch designation according to Table 8.1

8.3.2 Extraction yield and percolation time

Extraction yields depended on roasting time and water content (Figure 8.3). The longer roasted coffees exhibited lower extraction yields than the normal time roasted coffees, which confirms results found in earlier studies [5]. Within same roasting times, coffees with higher water content were less efficiently extracted than low moisture coffees. As seen in the preceding paragraph, higher water content lead to larger particles and, therefore, to less surface after grinding, which was probably the main reason for diminished extraction yield.

The differences in particle size distribution of ground coffees with different water contents influenced percolation in a similar manner as extraction yield. Grinding of coffees with higher water content resulted in less fine particles, and hence, faster percolation times (Figure 8.4). These results are in agreement with those of other researchers [114]. Although particles were very coarse, percolation time of NT 3 ground directly after roasting was high. This is probably an effect of the relatively large ground coffee volume, which leads to excessive filling volume and inefficient percolation in the espresso machine.

Impact of resting time prior to grinding was different for extraction and percolation. Extraction yield seemed not to be affected much by the resting time. Only extraction yield of NT 3 was increasing with increasing resting time – but as described above, the low extraction in the case where no resting time was applied might also be due to technical difficulties. In contrast, percolation times were generally decreased with increasing resting times.

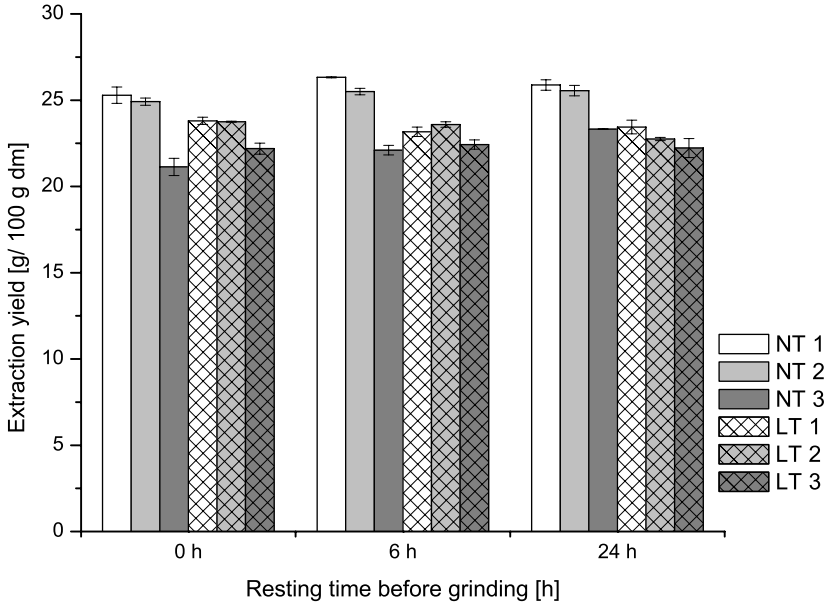

Figure 8.3 Extraction yields of roast and ground coffees. Resting times of 0, 6, and 24 h were applied prior to grinding. Abbreviations of roasting trials according to Table 8.1.

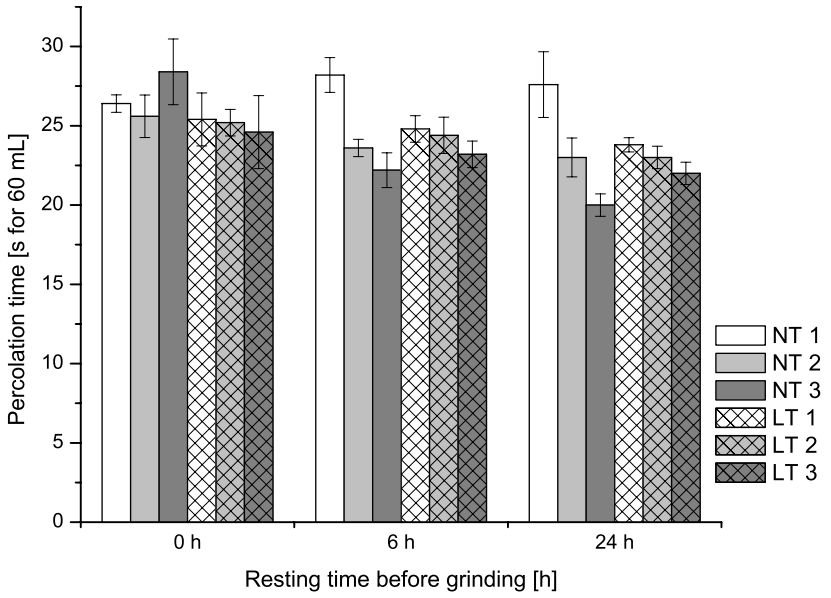

Figure 8.4 Percolation times of 60 mL water through roast and ground coffees packaged in capsules (6.3 g). Resting times of 0, 6, and 24 h were applied prior to grinding. Abbreviations of roasting trials according to Table 8.1.

8.3.3 Evolution of aroma compounds during storage of roast and ground coffee

Changes of coffee aroma were assessed using the evolution of several typical aroma compounds. The examined substances were aroma impact compounds [40], with the exception of dimethyl sulfide (freshness marker [98]), hexanal (secondary product of lipid oxidation), and pyridine (relatively stable component of coffee volatiles).

Open storage of roast and ground coffee

Volatile compounds in roast and ground coffee were very rapidly lost by stripping and degradation (Figure 8.5 and Table 8.3). Loss of dimethyl sulfide, for example, was more than 80 % within one single day of storage. Alteration of 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, 2,3-pentanedione, 4-vinylguaiacol, and pyridine seemed to be independent from water content. Similar results for the storage of whole coffee beans were already presented in chapter 6. In contrast, decrease of dimethyl sulfide was faster with increasing water content. Concentration of dimethyl trisulfide increased in the first days of storage and then slightly decreased during the following weeks. The coffee with highest water content (NT 3) seemed to behave in a very different manner than the other coffees, since at time zero, concentration was considerably higher than in the other coffees, and a fast decrease was observed (Figure 8.5). It is assumed that the accumulation of dimethyl trisulfide starts immediately after roasting, even under protective conditions. As mentioned in the "Materials and methods" section, the point of origin of aroma changes was determined using coffee that was ground, packaged under nitrogen, and analyzed after 24 hours. Therefore, the results of aroma analysis at time zero assumingly do not reflect the real concentration directly after grinding due to fast accumulation of this compound. Indeed, as shown in chapter 6, the increase of dimethyl trisulfide in whole roasted coffee beans during the first period of storage is directly related to the water content of coffee beans. Therefore an over-estimation of dimethyl trisulfide concentration at $t = 0$ is assumed and increasing water content would lead to more severe over-estimation. Interestingly, a relatively stable concentration of dimethyl trisulfide was attained after about 7 days of storage. This equilibrium concentration was dependent on water content (Figure 8.5). As dimethyl trisulfide is an end product of thiol oxidation, these findings indicate faster oxidation of thiols due to increasing water content in roast and ground coffee.

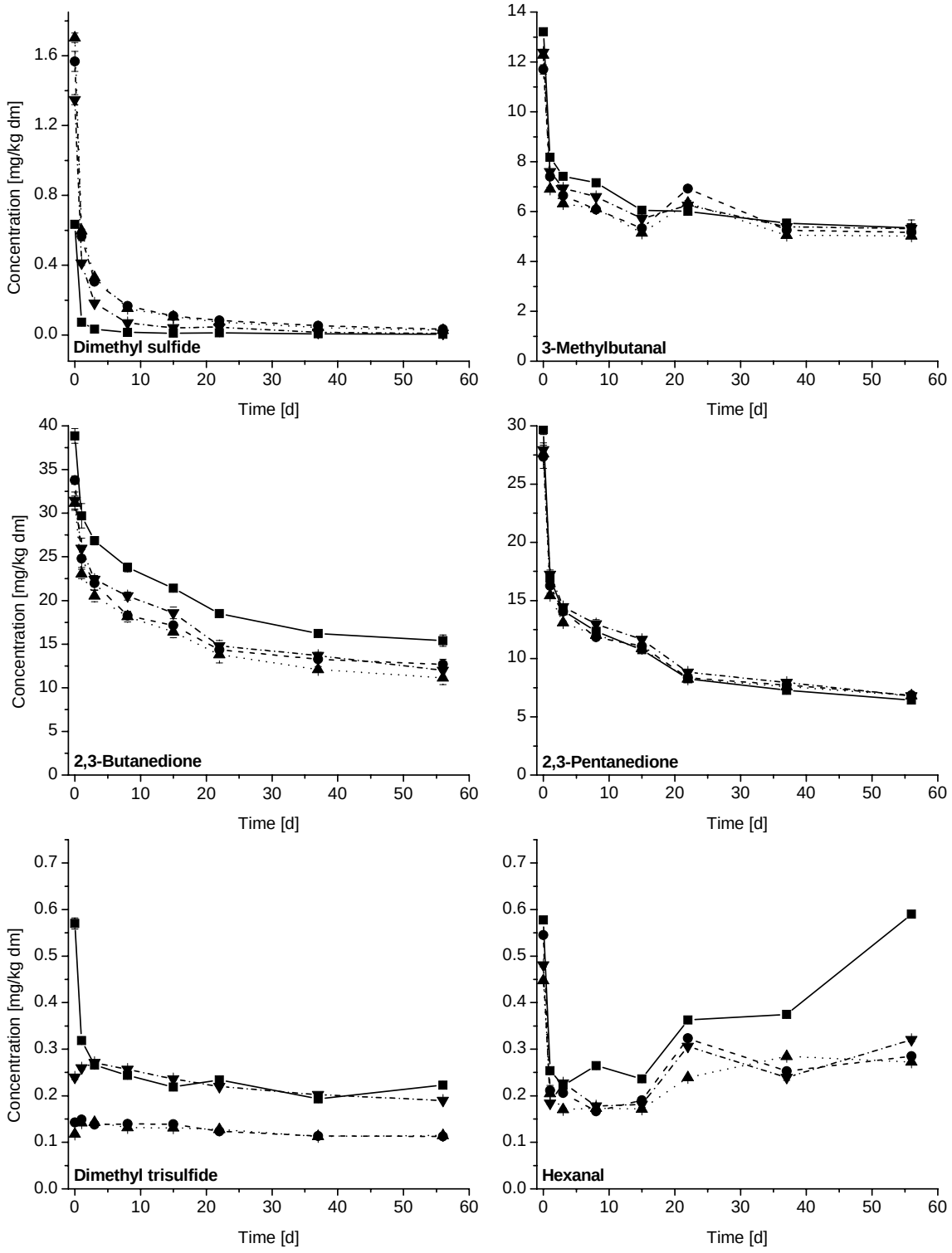

Figure 8.5 Evolution of selected aroma compounds during open storage of roast and ground coffee: NT 3 (■, 8.8 g H_2O/ 100 g wb), LT 1 (●, 2.9 g H_2O/ 100 g wb), LT 2 (▲, 3.6 g H_2O/ 100 g wb), LT 3 (▼, 5.9 g H_2O/ 100 g wb).

Hexanal concentrations decreased in all coffees during the first few days and increased afterwards. Re-increase of hexanal was fastest in the normal time roasted coffee with highest moisture content (NT 3), while no difference was found between the long time roasted coffees. Hence, the fast hexanal increase might be an effect of shorter roasting time leading to larger oil migration due to higher roasting temperature [5], and/or an effect of the excessive moisture content of NT 3.

Table 8.3 Percent retention of aroma compounds after 56 days of open storage of roast and ground coffee.

	Retention [%] in batch [a]			
	LT 4 2.9 g H_2O [b]	LT 5 3.6 g H_2O [b]	LT 6 5.9 g H_2O [b]	NT 3 8.8 g H_2O [b]
Dimethyl sulfide	2.1	1.6	0.7	0.7
Dimethyl trisulfide	79.2	97.4	79.2	39.1
Hexanal	52.3	60.9	66.6	102.2
2-Methylbutanal	41.7	39.7	39.7	33.9
3-Methylbutanal	44.1	40.9	43.0	40.5
4-Vinylguaiacol	61.4	56.6	66.6	62.5
Pyridine	56.5	58.6	62.5	60.6
2,3-Butanedione	37.5	35.7	38.1	39.6
2,3-Pentanedione	25.1	24.7	24.3	21.7

[a] Batch designation according to Table 8.1.

[b] Water content is expressed as grams of H_2O/ 100 g wb.

Closed storage of roast and ground coffee

Evolution of volatile compounds of roast and ground coffee stored in single sealed small containers was similar to changes of volatiles in open stored coffee (Figure 8.6 and Table 8.4). Compared to the long time roasted coffees (LT1, LT2, LT3) with water contents of 2.9, 3.6, and 5.9 g/ 100 g wb, the normal time roasted coffee with highest moisture content (8.8 g/ 100 g wb) exhibited considerably faster decrease of 3-methylbutanal, 2,3-butanedione, 2,3-pentanedione, and 4-vinylguaiacol (Table 8.4). Loss of dimethyl sulfide was faster in both high moisture coffees LT3 and NT3. Concentration of dimethyl trisulfide increased during the first days of storage to attain a stable amount depending on water content. The value of the equilibrium concentration of dimethyl trisulfide was 2–3 times higher in closed storage than in open storage. Lower overall losses and a shift of equilibrium between matrix and headspace to the matrix could be reasons for the higher accumulation of dimethyl trisulfide in the closed system.

Loss of aroma compounds was decelerated compared to open storage, but still fast, since capsules were packaged under normal atmosphere. After 56 d of storage, concentrations of 2-methylbutanal, 3-methylbutanal, 4-vinylguaiacol, pyridine, and 2,3-butanedione were about 1.5 times higher compared to open stored coffees. The remaining amounts of dimethyl sulfide and 2,3-pentanedione were even around 5 times and 2 times higher, respectively. The amount of pyridine remained stable throughout storage. Similar results were obtained by other authors [53], who also showed that in single sealed portions of roast and ground coffee, fast decrease in levels of 2-furfurylthiol and dimethyl sulfide took place at oxygen levels equal or higher than 5 %, while at oxygen level of 2 %, these degradation reactions were significantly slowed.

Evolution of hexanal showed that lipid oxidation was slowed in closed packaged coffee. Under these conditions of restricted oxygen supply, the coffee with lowest water content exhibited fastest lipid oxidation, which is in agreement with results on oxidative stability of low-moisture foods by other authors [102].

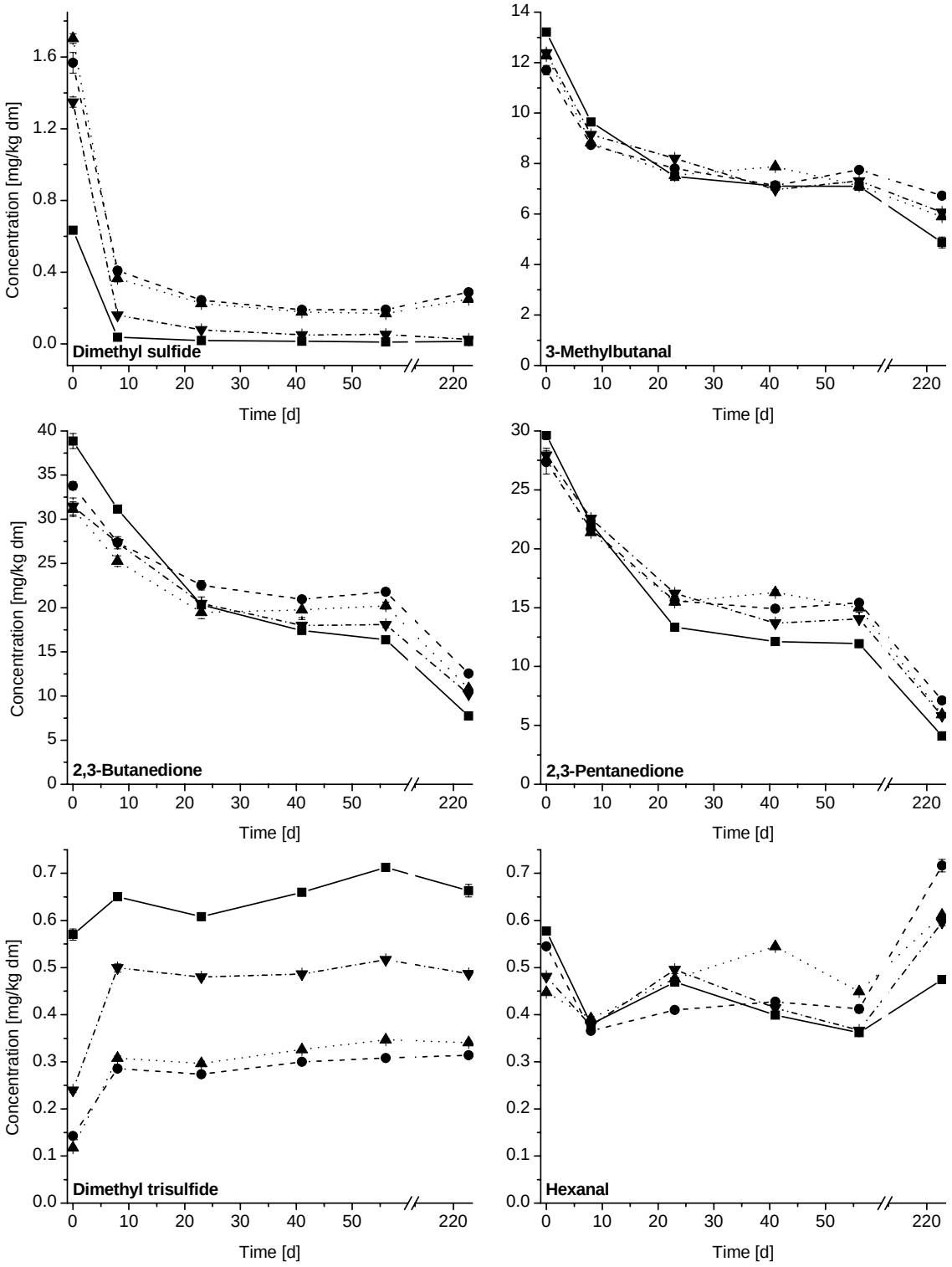

Figure 8.6 Evolution of aroma compounds during closed storage of roast and ground coffee in capsules: NT 3 (■, 8.8 g H_2O/ 100 g wb), LT 1 (●, 2.9 g H_2O/ 100 g wb), LT 2 (▲, 3.6 g H_2O/ 100 g wb), LT 3 (▼, 5.9 g H_2O/ 100 g wb).

These figures corroborate the fact that closed packaging slows loss of aroma compounds in ground coffee to a certain degree, but at the same time it is obvious that shelf-life cannot be largely extended in closed packages without protective atmosphere. In contrast to open storage, differences in storage behavior between coffees with low and high water content were visible, due to the slightly better storage conditions in closed package. Therefore, the assumption is made that increased water content leads to shorter product shelf-life due to faster degradation of aroma compounds. A possible explanation for higher rates of degradation reactions is the plasticizing effect of increased moisture content, shown by firmness measurements using a shear test in a Kramer cell [chapter 6]. Increase of moisture leads to reduction of glass transition temperature in amorphous systems [106], and, subsequently, to higher mobility of reactants [109], including faster oxygen diffusion.

Table 8.4 Percent retention of aroma compounds after 224 days of storage of roast and ground coffee in capsules.

	Retention [%] in batch [a]			
	LT 4 2.9 g H_2O [b]	LT 5 3.6 g H_2O [b]	LT 6 5.9 g H_2O [b]	NT 3 8.8 g H_2O [b]
Dimethyl sulfide	18.4	14.6	1.9	2.1
Dimethyl trisulfide	220.6	289.7	203.2	116.3
Hexanal	131.4	136.6	123.9	82.1
2-Methylbutanal	70.2	57.3	62.1	57.3
3-Methylbutanal	57.4	48.0	49.0	36.9
4-Vinylguaiacol	42.4	39.6	36.7	18.6
Pyridine	109.3	106.7	114.3	109.6
2,3-Butanedione	37.1	34.8	32.4	19.9
2,3-Pentanedione	26.0	21.5	20.9	13.9

[a] Batch designation according to Table 8.1.

[b] Water content is expressed as grams of H_2O/ 100 g wb.

9 Aroma recovery from roasted coffee by wet grinding

Aroma recovery as determined by solid-phase microextraction–gas chromatography–mass spectrometry (SPME–GC–MS) was compared in coffees resulting from conventional grinding processes, and from wet grinding with cold and hot water. Freshly roasted coffee as well as old, completely degassed coffee was ground in order to estimate the relationship of the internal carbon dioxide pressure in freshly roasted coffee with the aroma loss during grinding. The release of volatile aroma substances during grinding was found to be related to the internal carbon dioxide pressure, and wet grinding with cold water was shown to minimize the losses of aroma compounds by trapping them in water. Due to the high solubility of roasted coffee in water, the use of wet grinding is limited to processes, where grinding is followed by an extraction step. Combining grinding and extraction by the use of hot water for wet grinding resulted in considerable losses of aroma compounds because of the prolonged heat impact. Therefore, a more promising two-step process involving cold wet grinding and subsequent hot extraction in a closed system was introduced. The yield of aroma compounds in the resulting coffee was substantially higher compared to that of conventionally ground coffee.

This chapter has been prepared for publication as:
Juerg Baggenstoss, Daniela Crameri, Rainer Perren, Felix Escher. Aroma recovery from roasted coffee by wet grinding.

9.1 Introduction

For coffee brewing the whole roasted coffee beans need to be ground to increase the surface exposed to extraction. Due to the specific structural properties of roasted coffee beans, grinding is a two-step process. The brittleness of roasted coffee beans requires a crushing phase where the bean is broken down into fragments before these fragments can be finely ground using shear forces [9]. During the breakdown of cells, substantial amounts of carbon dioxide and carbon monoxide along with other volatile compounds are released. To minimize the loss of volatile substances, condensing or absorbing devices are applied, and the entrapped volatiles are used in later stages of manufacturing and packaging [8]. The volatiles released during grinding could possibly be trapped in water as proposed by some patents [117-119]. Wet grinding, for example by using a ball mill, would also have the advantage that a specific particle size distribution is relatively easy to obtain [9]. In addition, the impact of temperature during dry grinding is not negligible, and can surpass 100 °C, probably leading to undesired chemical reactions [9]. The cooling effect of water would prevent excessive temperatures during wet grinding. The fact that coffee exhibits a high solubility even in cold water, restricts the use of wet-processing equipment to applications wherein an extraction step follows immediately after grinding, as it is the case in the manufacturing of instant coffee.

The aim of this part of the project was to show whether wet grinding methods with cold or hot water can be established on a laboratory and a pilot scale, and whether these methods can reduce loss of aroma in the grinding process.

9.2 Materials and methods

9.2.1 Roasting process and process characterization

Roasting

Green washed *Coffea arabica* from Colombia was provided by Delica (Birsfelden, Switzerland) and batches of 200 g were roasted on a fluidized-bed hot air laboratory roaster (G.W. Barth AG, Freiberg/Neckar, Germany). The raw coffee was roasted under low temperature–long time process conditions [67]. Hot air temperature was 228 °C, hot air velocity was 3.5 m/s and the roasting time was 12 min. After roasting, an air stream of ambient temperature ensured fast cooling of the beans (4 min). A detailed description of the roaster can be found in Schenker [5]. Coffee was roasted to a color of L* = 22.4 ± 0.4 and to a moisture content of 1.9 g/ 100 g wb.

For experiments with completely degassed coffee, a 1:1:1 Arabica blend of Sul da Minas (Brazil, unwashed), Sidamo (Ethiopia, washed), and Tarrazu (Costa Rica, washed) provided by Rast AG (Emmen, Switzerland) was used. Roasting was carried out with a G-45 drum roaster (Probat, Emmerich, Germany) 11 months before the grinding experiments. Coffee was roasted in a batch of 6 kg to a color of L* = 22.4±0.4 and to a moisture content of 1.8 g/ 100 g wb. Coffee beans were stored in a valve bag under nitrogen atmosphere.

Water content and color measurement

Water content and color of roasted coffee were determined as described in chapter 4.2.

9.2.2 Wet grinding of roasted coffee

For the wet grinding of roasted coffee beans, two devices were investigated: a Fryma corundum stone colloid mill (MZ-80/R, Fryma-Maschinen AG, Rheinfelden, Switzerland), and a Waring laboratory blender (30BL80, Waring Products Inc., New Hartford, CT, USA). Furthermore, wet grinding was carried out with cold and hot water. The grinding processes are summarized in Table 9.1.

Wet grinding with the corundum stone mill

Grinding was carried out alternatively with cold (20±1 °C) or hot (90±1 °C) distilled water. 80 g of roasted coffee beans were first ground with 1000 mL of water at a gap width of 0.5 mm. Then the gap width was narrowed to 0.3 mm, and the coffee suspension ground again. After removing the suspension, the mill was rinsed with 400 mL of water at a gap width of 1.5 mm. A total of 1400 mL of the suspension with 57.15 g/L ground coffee resulted.

Wet grinding with the blender

Grinding of 30 g of roasted coffee was again carried out with cold (20±1 °C) or hot (90±1 °C) distilled water. Coffee was weighed in the blender, 200 mL of water were added and the coffee was ground during 2 min at the lowest speed setting. Afterwards, 280 mL of distilled water were added in order to obtain a similar concentration of the coffee suspension as in the trials with the corundum stone mill.

9.2.3 Dry grinding of roasted coffee

For dry grinding, three devices were investigated: a Bühler-Miag disc mill (4000, Bühler-Miag Ltd., Milano, Italy), a Ditting disc mill (KFA 1403, Ditting Machines Inc., Bachenbülach, Switzerland), and the Waring laboratory blender described above. The grinding processes are summarized in Table 9.1.

Dry grinding with the disc mills

Coffee was ground at level 3 (Bühler-Miag) and level 1 (Ditting). The first 30 g of ground coffee were discarded in each run.

Dry grinding with the blender

Batches of 30 g of coffee were ground for 2 min at the lowest speed setting.

9.2.4 Determination of particle size distribution of ground roasted coffee

The particle size distribution of dry ground coffees was determined by a sieve analysis on a vibrating sieve cascade (Magnetic Inc., Liestal, Switzerland) with 5 sieves of 1114, 630, 400, 200, and 125 μm mesh width, respectively.

To determine the particle size distributions of the wet ground coffees, the coffee powder had been recovered from the aqueous coffee suspension and dried. First, the coffee suspension was sieved through a 63 μm mesh sieve. The sieved off coffee particles were washed with water until the washing water was completely colorless, dried for 15 h at 103 °C, and sieved through the cascade as described above.

9.2.5 Sampling of ground coffee for aroma analysis

Each grinding run described above was carried out in triplicate and the resulting coffee suspensions were subjected to a sampling procedure and aroma analysis. Statistical analyses were performed using Student's *t*-test with a significance level of 95%.

Wet ground coffee

For retrieving samples from the suspensions of wet ground coffee, the suspensions were stirred for 2 minutes, and then samples of 20 mL and 100 mL, respectively, were removed with 20 mL and 100 mL syringes with a wide aperture of around 7 mm. The 20 mL samples were transferred to flasks, diluted to 100 mL and used for the analysis of the aroma compounds which were present in higher concentrations (compounds **4**, **8**, **9**, **11**, **12**, **14**, **15**, see Table 6.1), while the 100 mL samples were transferred to flasks and used directly for the analysis of the aroma compounds present in lower concentrations (compounds **2**, **10**, **17**, **18**, see Table 6.1). During sampling, temperatures of cold and hot ground suspensions were kept at 20±1 °C and 90±1 °C for the whole sampling procedure. The amounts of dry mass in the samples are summarized in Table 9.2.

Dry ground coffee

To maximize the comparability of the grinding methods, the sampling procedure for dry coffee was kept similar to the procedure for coffees resulting from wet grinding. The dry ground coffee powders were transferred to stainless steel buckets, suspended in cold (20±1 °C) or hot (90±1 °C) water and stirred for 2 min. Then samples were retrieved with syringes as described above. The volume of water and the amounts of dry mass in the samples are summarized in Table 9.1 and Table 9.2.

Hot extraction of cold wet and dry ground coffee

100 mL of suspensions of cold wet ground coffee, prepared as described above, were microwave heated in closed flasks at 780 W for 65 s. Then the suspensions were stirred for 10 min, cooled to room temperature under running tap water for 20 min, and used for aroma analysis.

5 g and 1 g samples of dry ground coffee were weighed into 100 mL flasks, suspended in 100 mL of cold water, microwave heated and further treated as just described. The 5 g and 1 g samples were used for the analysis of the lower and the higher concentrated aroma compounds, respectively.

Determination of the coffee mass in the suspension samples

In order to determine the amount of coffee taken up from the suspension by the syringe and to evaluate the repeatability of the sampling procedure, five samples of each grinding method were analyzed for dry matter by drying at 103 °C until weight remained constant. The respective values are summarized in Table 9.2.

9.2.6 Headspace SPME-GC-MS analysis of coffee aroma

Headspace SPME-GC-MS analysis was carried out using the method described in chapter 6.2. Three aldehydes (2-methylbutanal, 3-methylbutanal, hexanal), two ketones (2,3-butanedione, 2,3-pentanedione), two sulfides (dimethyl sulfide, dimethyl trisulfide), three heterocyclic compounds (pyridine, 2-ethyl-3,5-dimethylpyrazine, 2-ethyl-3,6-dimethylpyrazine), and one phenolic compound (4-vinylguaiacol) were analyzed. All SPME-GC-MS measurements were run in triplicate.

Table 9.1 Summary of the wet and dry grinding runs.

Grinding method		Coffee used per run [g]	Water used for grinding per run [mL]	Water added after grinding per run [mL]
Wet grinding				
W1	Corundum stone mill	80	1400	0
W2	Laboratory blender	30	200	280
Dry grinding				
D1	Ditting [a]	80	0	1400
	Ditting [b]	80	0	0 [c]
D2	Laboratory blender [a]	30	0	480
D3	Bühler-Miag 4000 [b]	80	0	0 [c]

[a] Tests for comparison of aroma recovery with that obtained from wet grinding.

[b] Tests with microwave heating (hot extraction of ground coffee).

[c] For extraction and aroma analysis, samples were directly prepared with 100 mL water and 5 g and 1 g ground coffee, respectively.

Table 9.2 Dry mass in final suspension samples for aroma analysis.

Grinding method		Dry mass for analyzing (n = 5)	
		Compounds *2, 10, 17, 18* [c] (5 g samples) [g]	Compounds *4, 8, 9, 11, 12, 14, 15* [c] (1 g samples) [g]
Wet grinding			
W1	Corundum stone mill	5.53±0.03	1.06±0.01
W2	Laboratory blender	5.5±0.3	0.99±0.07
Dry grinding			
D1	Ditting [a]	5.45±0.08	1.02±0.04
	Ditting [b]	4.905±0.005	0.981±0.005
D2	Laboratory blender [a]	5.1±0.3	1.03±0.04
D3	Bühler-Miag 4000 [b]	4.905±0.005	0.981±0.005

[a] Tests for comparison of aroma recovery with that obtained from wet grinding.

[b] Tests with microwave heating (hot extraction of ground coffee).

[c] According to Table 6.1.

9.3 Results and discussion

9.3.1 Particle size distribution of ground coffee

Figure 9.1 shows the particle size distributions in ground coffees. It is clearly visible that wet ground coffee contained a high fraction of very fine particles (< 100 µm) that was nearly absent in the dry ground coffee. The coffee ground with the Ditting coffee mill exhibited a relatively small peak at an average particle size of around 300 µm. Grinding with the Bühler-Miag mill resulted in particles of average size of around 900 µm. Among the dry grinding methods, the laboratory blender produced the largest particles and the broadest distribution, because of the rather inadequate comminution technique using a rotating knife only. Wet grinding methods led to a high fraction of very small particles of around 100 µm, which was the major part in ground coffees from the corundum stone mill. The blender produced very small particles as well, but the main fraction was relatively coarse (around 1000 µm) as seen with dry grinding. Compared to dry grinding, wet grinding with the blender resulted in a more uniform particle distribution due to better mixing and the increased contact of coffee with the rotating knife. Wet grinding using the corundum stone mill yielded more very fine particles when using cold water compared to grinding with hot water.

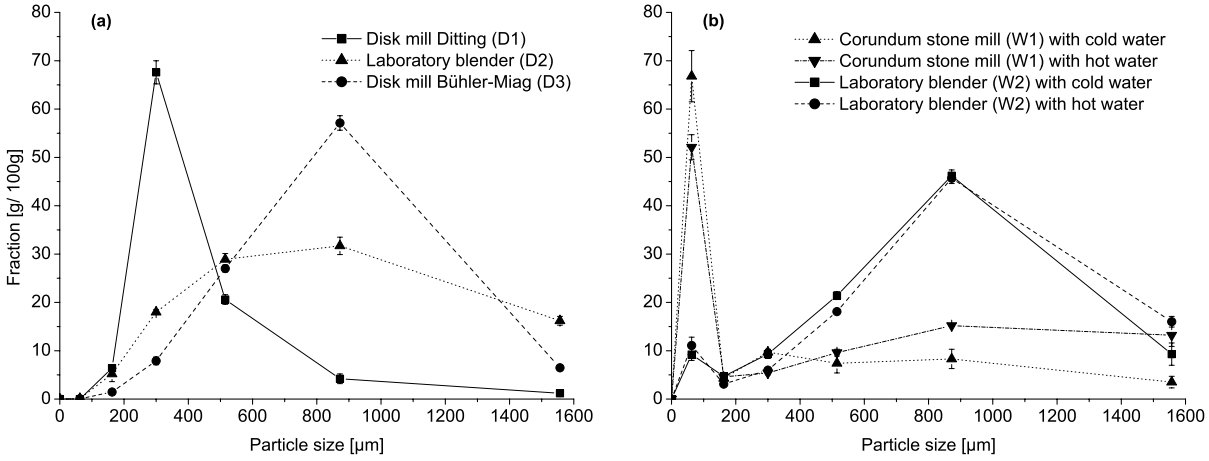

Figure 9.1 Particle size distribution of dry ground (a) and wet ground (b) coffee.

9.3.2 Aroma concentration in ground coffee

Tables 9.5 and 9.6 summarize the concentrations of aroma compounds obtained from the various grinding methods. Comparisons between wet and dry grinding methods are illustrated in Figure 9.2. The wet methods were compared to the dry grinding methods with as similar particle size distributions as possible. The coffees obtained from wet grinding with the corundum stone mill were compared to the dry ground coffees using the Ditting mill. The wet ground coffees obtained from the laboratory blender were compared to the dry ground coffees with the same laboratory blender or, for investigations on the hot extraction of cold wet and dry ground coffee, from the Bühler-Miag mill. However, as seen above, the very fine fraction obtained from wet grinding could not be reproduced in dry grinding of coffee.

Cold grinding with the blender and the corundum stone mill both resulted in significantly higher amounts of dimethyl trisulfide, 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, and 2,3-pentanedione when using wet grinding methods. In contrast, for dimethyl sulfide, hexanal and the less volatile compounds 4-vinylguaiacol, pyridine, 2-ethyl-3,5-dimethylpyrazine, and 2-ethyl-3,6-dimethylpyrazine, differences between dry and wet grinding methods were small and not significant.

It is known that, during conventional grinding, substantial amounts of volatile substances are released [120]. Water may help to retain the volatile compounds which otherwise would be lost during grinding. It was supposed that the release of volatile aroma compounds during grinding was closely connected to the release of carbon dioxide [5, 96]. To test this hypothesis, completely degassed coffee was ground conventionally and with water using the corundum stone mill. It was expected that, after complete degassing, the major part of remaining aroma compounds was bound within the coffee bean and only a very small part remained in gas phase within the cells. Therefore, only minor differences would be observed between the resulting concentrations of aroma compounds from wet and dry grinding. Since complete degassing of coffee beans can take several months [59], the coffee subjected to the experiment was stored for 11 months before grinding. To minimize aroma loss by oxidative degradation, storage took place in a valve bag under nitrogen atmosphere.

Figure 9.2 shows that differences between the concentrations of aroma compounds from wet and dry grinding were small. Only hexanal was found in significant higher amounts in the wet ground coffee, whereas dimethyl sulfide was found in significantly lower amounts after wet grinding. All the other analyzed compounds did not exhibit significant differences. This is an indication that higher aroma recovery from wet grinding of freshly roasted coffee is indeed caused by the trapping of volatiles and not by a better extraction because of the generation of smaller particles.

The recovery of ground coffee from water used in grinding is not practicable because of the high solubility of coffee in water. Therefore, reasonable applications of wet grinding would involve the use of the resulting coffee suspension for a subsequent extraction process. To combine grinding and extraction in one operation, wet grinding with the corundum stone mill was carried out with hot water and compared to dry grinding with the Ditting mill. The advantages of the wet grinding method with regard to the retention of aroma compounds were relinquished when hot water was applied in the grinding process (Figure 9.2). In addition, compared to the cold grinding processes, absolute concentrations of several highly volatile aroma compounds (i.e., dimethyl sulfide, 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, and 2,3-pentanedione) were substantially diminished in both hot wet and dry grinding (Table 9.4). It is assumed that because of the long contact time of hot water with ground coffee – the process took more than 5 min until grinding and sampling was complete – considerable losses of highly volatile compounds took place in the open grinding and sampling system.

As grinding with hot water led to losses of aroma compounds, an approach where coffee was ground with cold water, and then extracted with hot water in a closed system seemed to be more promising. Therefore, a two-step process involving cold grinding with subsequent hot extraction by heating the coffee suspension with microwaves was developed, as a step towards a possible industrial application of wet grinding. The grinding trials were carried out with both the blender and the corundum stone mill. For comparison with dry grinding methods, the coffee was ground with the disk mills (Ditting and Bühler-Miag), suspended in water, and directly extracted by

microwave heating in closed flasks to minimize losses of odorants. Figure 9.2 shows that, after wet grinding with blender and corundum stone mill, concentrations of 2-methylbutanal, 3-methylbutanal, pyridine, 2,3-butanedione, and 2,3-pentanedione were significantly higher compared to those from the respective dry grinding method. The concentration of dimethyl trisulfide was significantly higher in wet ground coffee with the corundum stone mill. The amount of 4-vinylguaiacol was significantly lower after wet grinding with the blender, while for concentrations of dimethyl sulfide, hexanal, 2-ethyl-3,5-dimethylpyrazine and 2-ethyl-3,6-dimethylpyrazine no significant differences were found.

The results of the present investigation show that it is possible to minimize the loss of aroma compounds released during grinding by using wet grinding processes. The close relationship of the internal carbon dioxide pressure with aroma stripping during grinding was demonstrated by wet and dry grinding of stored, completely degassed coffee. Due to the high solubility of roasted coffee even in cold water, the applications of wet grinding are restricted to processes with an extraction step after grinding. Coffee grinding with hot water in an open system, intended to combine grinding and extraction, resulted in high losses of aroma compounds. Therefore, a two-step process involving a grinding step with cold water and an extraction step with hot water in a closed system was proposed. Applying this approach, a higher recovery of aroma compounds was obtained.

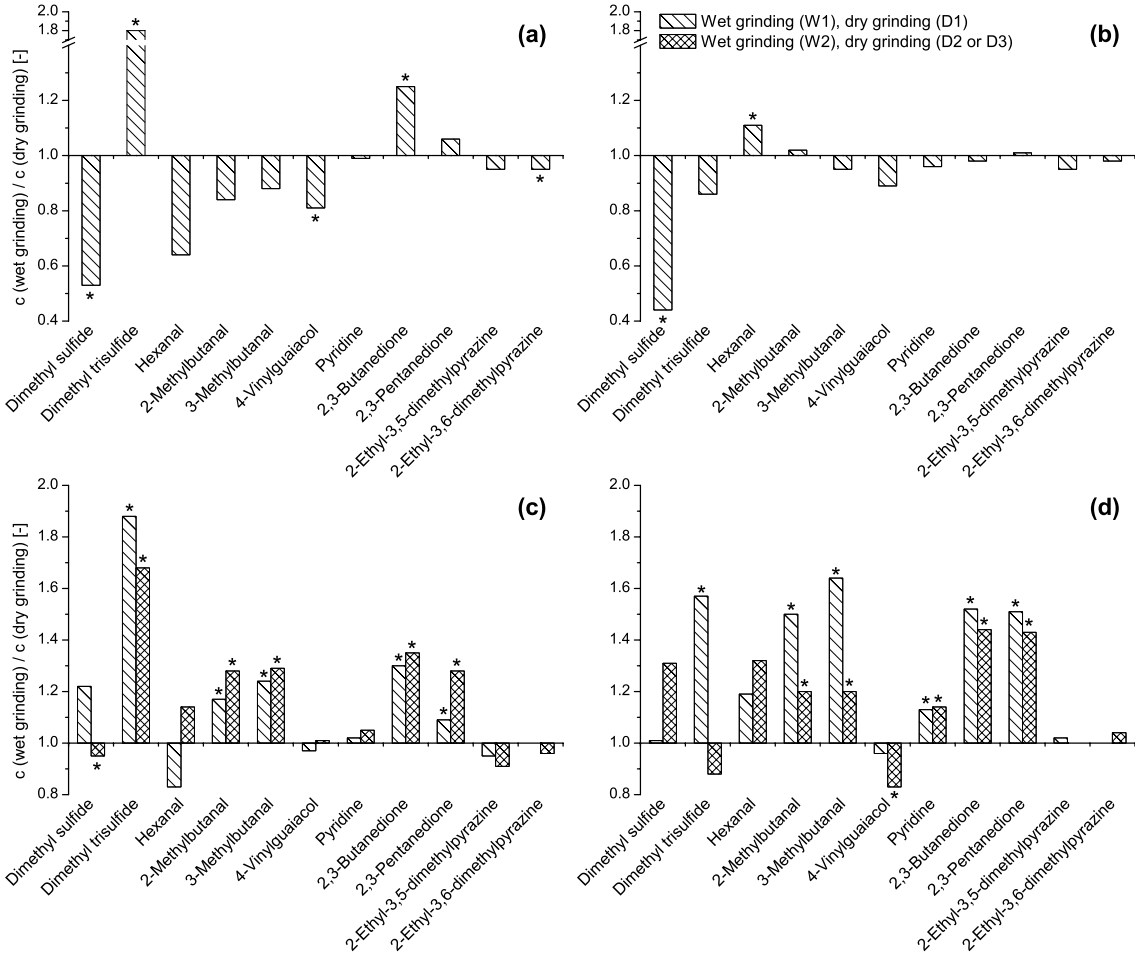

Figure 9.2 Relative comparison between wet and dry grinding methods. (**a**) Hot grinding (W1 compared to D1). (**b**) Cold grinding of degassed coffee (W1 compared to D1). (**c**) Cold grinding (W1 compared to D1, and W2 compared to D2). (**d**) Cold grinding with subsequent hot extraction (W1 compared to D1, and W2 compared to D3). Significant differences between wet and dry ground coffees are marked with an asterisk.

Table 9.3 Absolute concentrations of selected aroma compounds in dry and wet ground coffee (wet grinding experiments with cold water).

Compound	*Aroma concentration for grinding method [mg/ kg dm]* [a]					
	Cold grinding of freshly roasted coffee		Cold grinding of freshly roasted coffee		Cold grinding of degassed coffee	
	W1	D1	W2	D2	W1	D1
Dimethyl sulfide	1.4±0.1	1.18±0.05	1.14±0.04	1.2±0.1	0.13±0.01	0.22±0.03
DMTS [b]	0.23±0.02	0.12±0.01	0.21±0.03	0.12±0.02	0.26±0.02	0.30±0.01
Hexanal	0.97±0.03	1.2±0.1	0.9±0.2	0.78±0.04	0.37±0.01	0.33±0.01
2-Methylbutanal	24.7±0.5	21.0±0.5	26±1	20.7±0.4	16.7±0.7	16±1
3-Methylbutanal	15±1	12.1±0.3	15.4±0.6	11.9±0.5	7.54±0.07	8.0±0.4
4-Vinylguaiacol	27±1	28±2	23.3±0.5	23.0±0.6	21.7±0.6	24±3
Pyridine	144±1	142±5	152±13	146±9	169±3	176±5
2,3-Butanedione	25.0±0.5	19.2±0.6	27±1	19.6±0.6	16.2±0.4	16.6±0.3
2,3-Pentanedione	15.8±0.5	14.5±0.4	18.5±0.9	14±1	8.2±0.3	8.2±0.1
3,5-EDMP [c]	3.2±0.2	3.32±0.07	3.6±0.3	3.9±0.2	4.4±0.1	4.6±0.1
3,6-EDMP [d]	1.08±0.05	1.08±0.01	1.35±0.08	1.4±0.1	1.27±0.04	1.30±0.04

[a] Grinding methods according to Table 9.1.

[b] Dimethyl trisulfide

[c] 2-Ethyl-3,5-dimethylpyrazine

[d] 2-Ethyl-3,6-dimethylpyrazine

Table 9.4 Absolute concentrations of selected aroma compounds in dry and wet ground coffee (wet grinding experiments with hot water, and wet grinding experiments with cold water and subsequent hot extraction).

Compound	*Aroma concentration for grinding method [mg/ kg dm]* [a]					
	Hot grinding		Cold grinding and hot extraction		Cold grinding and hot extraction	
	W1	D1	W1	D1	W2	D3
Dimethyl sulfide	0.5±0.1	1.0±0.2	0.8±0.1	0.81±0.03	1.3±0.1	1.2±0.6
DMTS [b]	0.11±0.01	0.06±0.01	0.20±0.03	0.130±0.004	0.10±0.01	0.11±0.01
Hexanal	0.52±0.03	0.8±0.2	1.2±0.2	1.01±0.06	1.0±0.2	0.8±0.1
2-Methylbutanal	8±1	10±1	23±2	15±1	23±1	18.9±0.4
3-Methylbutanal	5.2±0.7	5.9±0.7	15±1	9.0±0.9	14.2±0.7	11.8±0.5
4-Vinylguaiacol	22±2	27±2	21.8±0.7	22.9±0.7	20±2	23.7±0.3
Pyridine	124±1	125±3	136±3	120±3	131±5	115±3
2,3-Butanedione	18±1	14±1	23.9±0.7	15.7±0.5	24.6±0.9	17±2
2,3-Pentanedione	9.2±0.7	8.7±0.8	13.1±0.4	8.7±0.4	13.8±0.8	9.6±0.3
3,5-EDMP [c]	3.1±0.1	3.26±0.09	3.36±0.02	3.3±0.1	3.2±0.3	3.2±0.5
3,6-EDMP [d]	1.08±0.01	1.13±0.02	1.14±0.03	1.14±0.04	1.08±0.09	1.0±0.2

[a] Grinding methods according to Table 9.1.

[b] Dimethyl trisulfide

[c] 2-Ethyl-3,5-dimethylpyrazine

[d] 2-Ethyl-3,6-dimethylpyrazine

10 Conclusions and outlook

10.1 Coffee roasting and aroma formation

For the sub-project on aroma formation during coffee roasting, roasting trials were carried out on a laboratory scale fluidizing-bed roaster which allowed full control over air flow, air temperature, bulk temperature and bean core temperature during the process. Therefore, the time-temperature conditions during the roasting process were fully traceable. The results obtained in the present investigation confirm that a degree of roast as defined by the coffee bean color can be obtained with different time-temperature combinations. However, the resulting coffees need not to be equivalent in terms of physical properties and aroma concentration. Table 10.1 shows a selection of physical properties and concentrations of aroma compounds in coffees roasted on the laboratory scale fluidizing-bed roaster. While the lightness of coffee was equal in all roasts, most of the other product properties were different. The reaction kinetics clearly changed when different time-temperature conditions were applied. In particular, high roasting temperature resulted in a fast formation and in higher peak concentrations of some impact odorants during roasting (i.e., methanethiol, 3-mercapto-3-methylbutyl formate, 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, *N*-methylpyrrole, and 4-vinylguaiacol). Other odorants did not exhibit a higher peak concentration, although their formation was faster during high temperature roasting (i.e., methylpropanal, 2,3-pentanedione, hexanal, 2,3,5-trimethylpyrazine, 2-ethyl-3,5-dimethylpyrazine). Pyridine and 2-furfurylthiol both required a high activation energy for their formation, and the increase was practically linear with roasting time. At a given color, the coffees with the longest roasting time exhibited the highest concentrations of pyridine and 2-furfurylthiol. With regard to the evolution of

dimethyl sulfide and dimethyl trisulfide, the impact of temperature was inverse. Although the increase of dimethyl sulfide concentration during the first stage of roasting was still slightly faster when high temperatures were applied, the peak concentration was smaller and a faster decrease was observed compared to the roasting processes with lower temperature. The evolution of dimethyl trisulfide was biphasic. A fast increase took place at a low degree of roast, then decrease and re-increase were observed. During the low temperature processes, dimethyl trisulfide concentration decreased at a considerably lower temperature compared to the high temperature roasting.

The results of this dissertation show that small changes in time-temperature conditions may lead to considerable differences in the concentrations of odorants. However, a significant concentration difference does not necessarily mean that the difference is perceivable. Therefore, the sensory impact of the differences in concentrations of odorants needs to be assessed.

The initial moisture content of green coffee beans had an additional impact on the formation of odorants during roasting of coffee beans. For the most part, a higher moisture content resulted in a slower increase of the bean core temperature during the first stages of roasting. Therefore, light roasts exhibited larger differences in concentrations of odorants than dark roasts.

There is no consensus in the question whether a coffee roasted on a fluidizing-bed roaster may be equivalent to a coffee produced on a traditional horizontal drum roasting equipment. The results presented in this dissertation suggest that coffees roasted on both types of roasters can be of similar quality. However, similar time-temperature conditions are a prerequisite, i.e., the roasting process cannot be accelerated by using fast fluidizing-bed roasting equipment to end up with the same coffee as with the horizontal drum roaster. Fast roasting always implies high energy impact leading to a faster volume increase, a higher extraction yield, faster carbon dioxide desorption [5], and different reaction kinetics for the formation and the elimination of aroma compounds.

Table 10.1 Comparison of selected physical properties and concentrations of some aroma compounds in high temperature–short time (HTST), low temperature–long time (LTLT), and profile roasting (Profile). For details on the roasting method, see chapter 4.

	Roasting method		
	HTST	LTLT	Profile
Color [L*]	21[a]	21[a]	21[a]
Organic roast loss [g/ 100 g wb]	8.54[a]	9.24[b]	10.10[c]
Water content [g/ 100 g wb]	1.30[a]	1.57[b]	1.73[c]
Density [g·cm^{-3}]	0.548[a]	0.588[b]	0.584[b]
2-Furfurylthiol [mg/ kg dm]	2.56[a]	3.35[b]	4.20[b]
3-Mercapto-3-methylbutyl formate [mg/ kg dm]	0.24[a]	0.13[b]	0.12[c]
3-Methylbutanal [mg/ kg dm]	11.3[a]	18.9[b]	12.1[a]
2,3-Pentanedione [mg/ kg dm]	11.5[a]	5.30[b]	5.67[c]
Pyridine [mg/ kg dm]	123[a]	146[b]	179[c]
2-Ethyl-3,5-dimethylpyrazine [mg/ kg dm]	1.2[a]	1.1[a]	1.1[a]

[a, b, c] Different letters indicate statistically significant differences ($p < 0.05$).

During roasting, substantial changes in the structure of coffee beans take place at macroscopic and microscopic scale (for an illustration of the changes in microstructure, see Schenker [5], p. 99-110). Geiger [6] investigated the development of the coffee bean structure during roasting. To optimize the roasting process, he recommended that time-temperature conditions should increase the product temperature slowly to limit damages of the intracellular structure. Geiger concluded that, with regard to structural development, the early stage of roasting is the most important phase. Therefore time-temperature conditions of a traditional drum roasting process are favored, and it would be interesting to compare the aroma stability of HTST roasted coffee to that of a traditionally roasted one.

The concepts for the reaction conditions within coffee beans during roasting are still fragmentary. A limited knowledge on the precursor compounds together with the particular conditions found within coffee beans during the roasting process (i.e. the compartmentalization, the increased pressure, the high temperature and the large surfaces), turn the prediction of reactions and the development of adequate models into a very complex matter. However, more insight into the reaction conditions would also considerably improve the general understanding of the roasting process. Model reactions may give indications on the nature of the reactions of the precursors, but the specific reaction conditions within the coffee bean are difficult to mimic. The most promising approach is the use of extracted coffee bean shells, where precursor compounds are re-infused into green coffee beans [25, 26, 121]. However, re-infusion is a delicate task. The distribution of the re-infused precursors within the green beans may not be uniform, and a large fraction may remain on or near the surface, which would influence the roasting kinetics of the reconstituted beans considerably.

The evolution of some odorants during roasting gave some indications to the reaction mechanisms. Formation of dimethyl sulfide and 4-vinylguaiacol started very early in drum roasting, when the temperature was comparatively low. This suggests a low activation energy, and hence a radical formation mechanism. The comparison of the formation and elimination kinetics of the structurally very similar α-diketones 2,3-butanedione and 2,3-pentanedione revealed that formation pathways were of different nature, and a proposed formation pathway of 2,3-pentanedione via the reaction of 2,3-butanedione with formaldehyde and loss of water [76] was not corroborated by the results obtained in this dissertation.

A high temperature required for the onset of formation of an aroma compound suggests a high activation energy. This was the case for 3-mercapto-3-methylbutyl formate, 2-furfurylthiol, pyridine, *N*-methylpyrrole, and, to a lesser extent, for 2,3-butanedione and 2,3-pentanedione.

10.2 Water quenching of roasted coffee and aroma stability

To prevent over-roasting, fast quenching has to be applied as soon as the desired degree of roast is achieved. The use of water increases the quenching efficiency because of the energy consumption by water evaporation. Spray quenching, which makes use of the evaporation enthalpy of water droplets, is the most efficient method [93] and is widely applied in practice. In film and immersion quenching, liquid water is used. Due to the formation of a stable water vapor layer, the heat transfer from the coffee bean to the liquid water is low. Therefore film and immersion quenching are less efficient than spray quenching with recurring contact of water with the surface of coffee beans.

Some extracts of high speed video recording of spray and film quenching are displayed in the Figures 10.1 – 10.5. The pictures were taken with a Memrecam fx6 high speed camera (NAC Inc., Stuttgart, Germany) with frame rates of 5000 (film quenching) and 10000 (spray quenching) frames per second. The first impacting droplets are quickly evaporated, while at the later stage of the quenching process with a lower temperature of the coffee bean surface, condensation of droplets occurs. The impact of a water drop on a hot surface of a coffee bean is displayed in Figure 10.5. Despite the high temperature of the bean (~ 200 °C), only a small amount of the water drop evaporated. A slight film boiling was observed at the border of the water drop only.

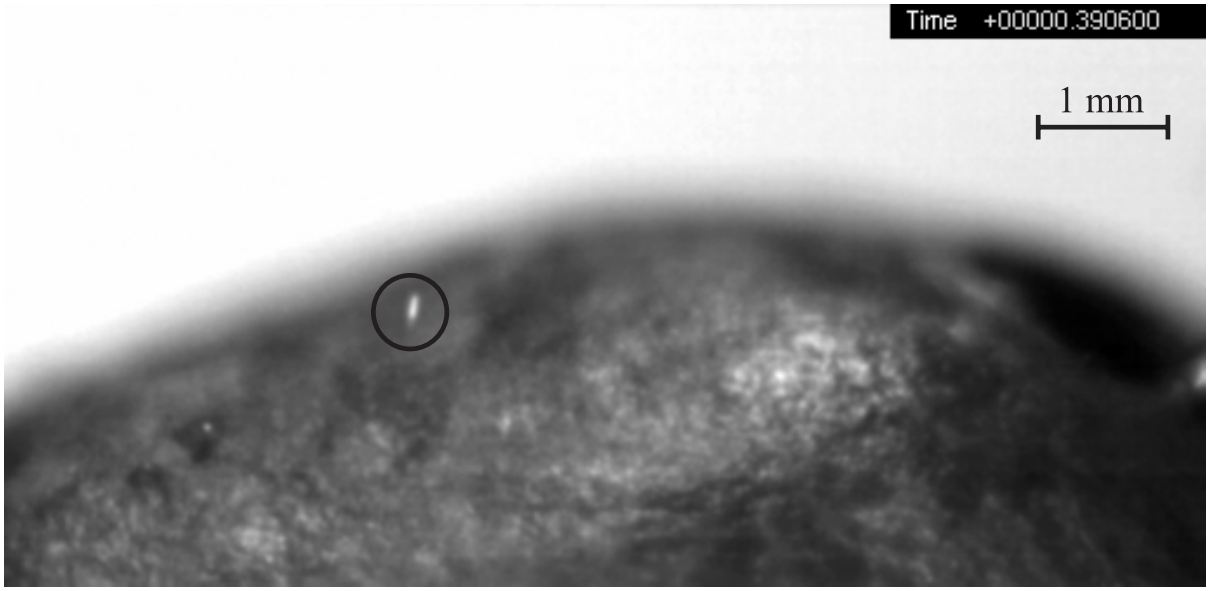

Figure 10.1 Hot coffee bean during spray quenching shortly before the impact of a water droplet on the surface (t = 0 s).

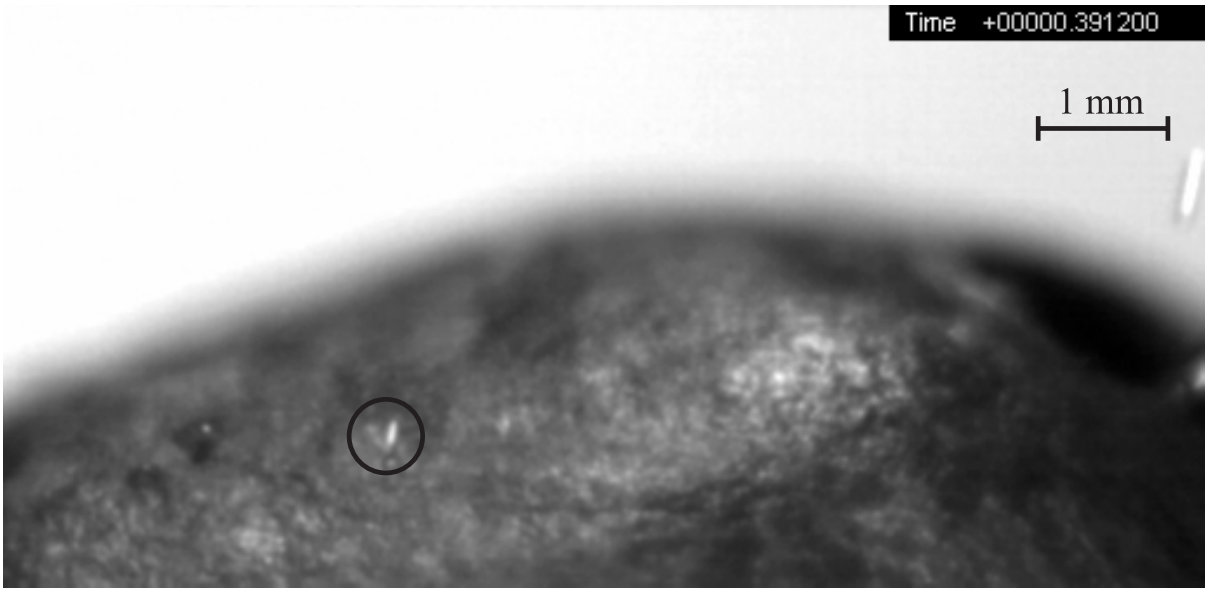

Figure 10.2 Impact of a water droplet on a hot coffee bean during spray quenching (t = 0.0006 s).

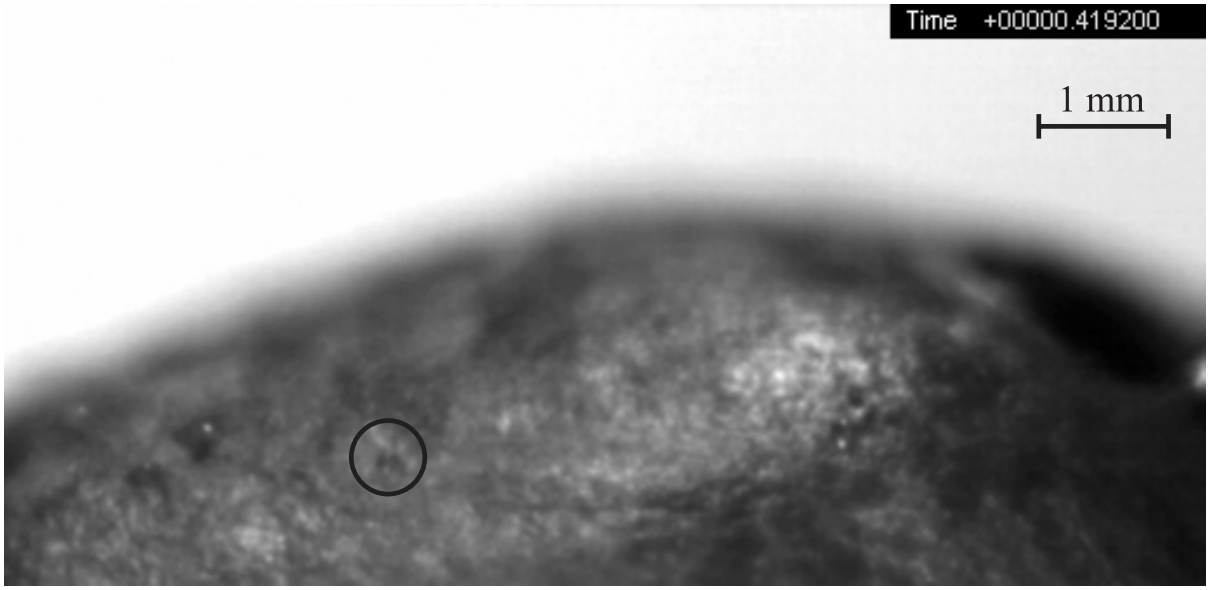

Figure 10.3 Coffee bean surface during water quenching. The water droplet evaporated shortly after the impact (t = 0.286 s).

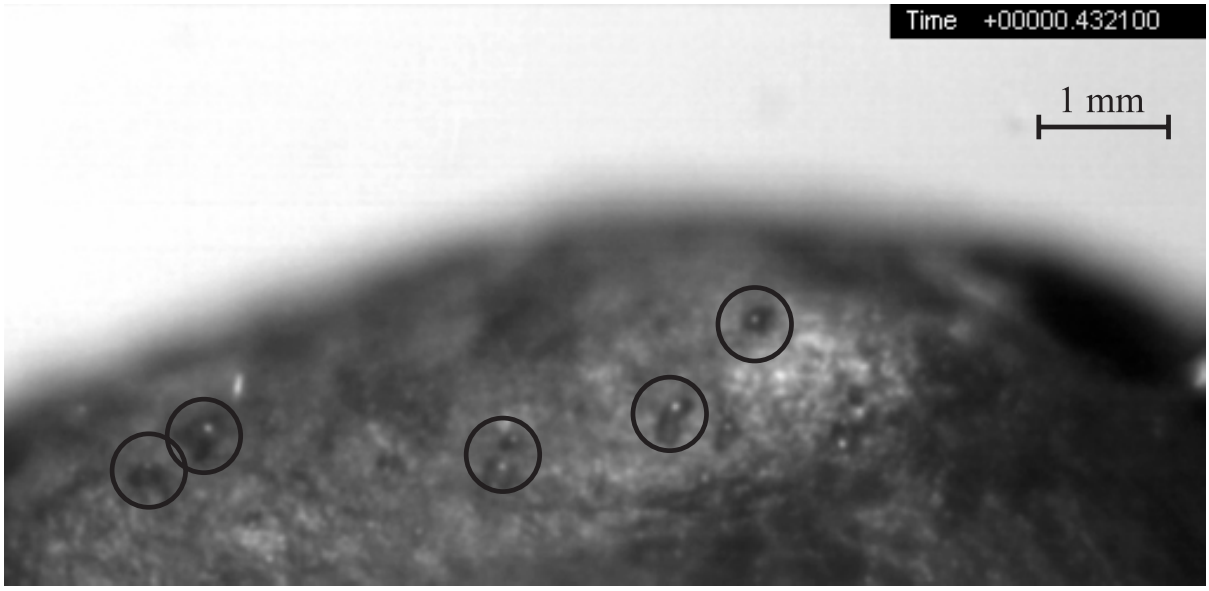

Figure 10.4 Last stage of spray quenching. The temperature of the coffee bean decreased, and the now impacting droplets condense on the surface (t = 0.415 s).

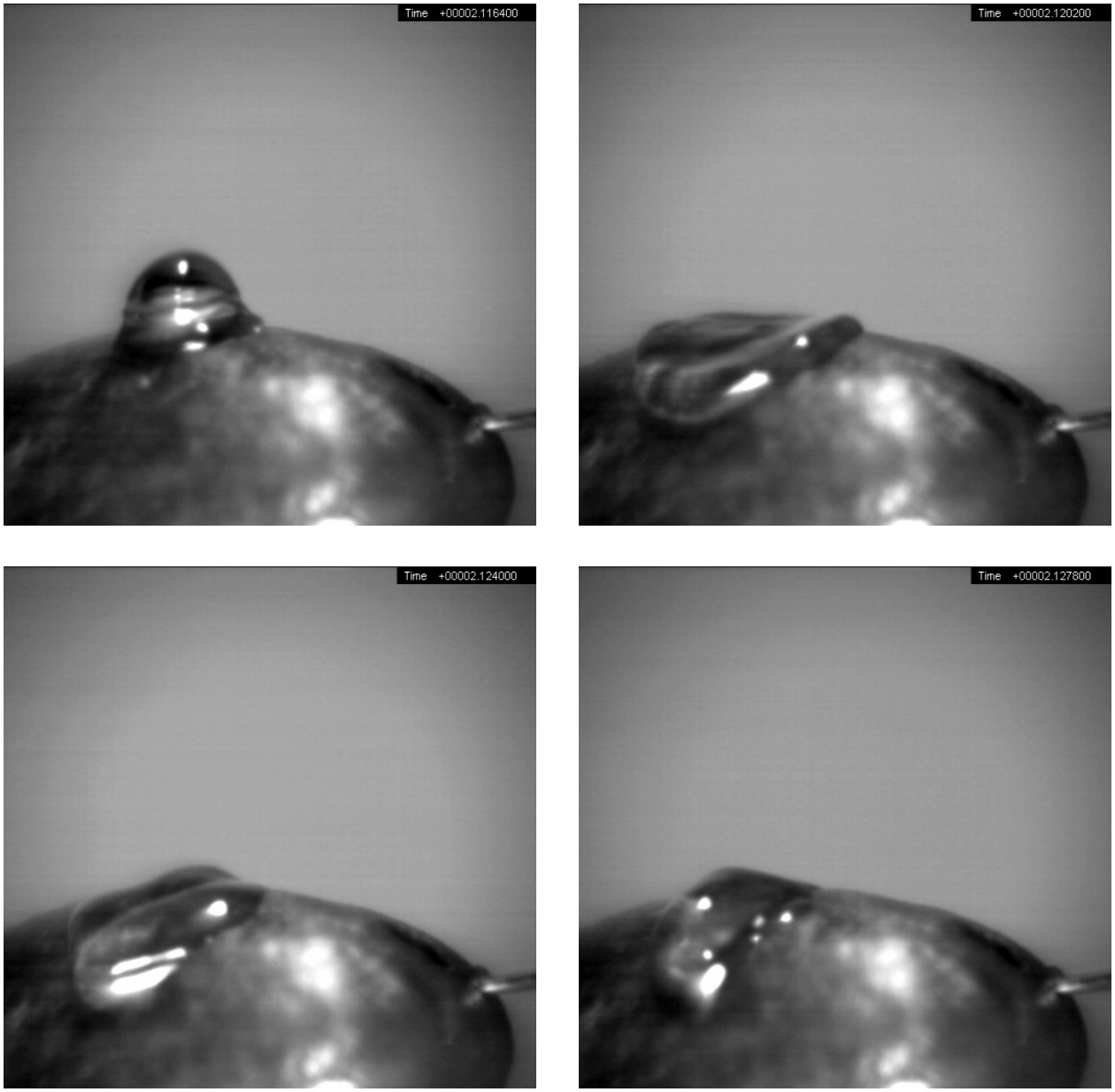

Figure 10.5 Impact of a water drop on a hot coffee bean: t = 0 s (top left), t = 0.038 s (top right), t = 0.076 s (lower left), and t = 0.114 s (lower right). Between 0.076 s and 0.114 s, a slight film boiling was observed during contraction of the water drop.

Water quench cooling is often related to loss of quality in roasted coffee. However, the assumption of Illy and Viani [9], that water quench cooling leads to the opening of pores, cell wall cracking and structure collapse because of the sudden drop in temperature was not corroborated by the results of this project. Indeed, water quench cooling without increase of moisture content resulted in a similar degassing behavior as air quenching. In addition, although faster degassing in water quenched coffees with increased moisture content was observed, a similar degassing behavior was obtained with air quenched coffee, which was re-moistened after quenching. And finally, no relationship between the quenching method and the intracellular porosity was found. The results suggest that the higher degassing rates of water quenched coffees are not directly related to the quenching method, but only to the increase of water content in the roasted coffee bean. It is assumed that high moisture content leads to changes in the state of cell walls, which in turn leads to an increased carbon dioxide permeability. The effect of the moisture content on carbon dioxide permeability was shown for paper, where carbon dioxide diffusivity was doubled by increasing the content of absorbed water from 0 to 0.1 g/ g paper [122]. It is supposed that the higher permeability is caused by a slight relaxation of the cellulose network. A similar effect of moisture on the permeability of roasted coffee cell wall polysaccharides is conceivable. The plasticizing effect of water in roasted coffee was demonstrated by measuring the firmness with a shearing test in a Kramer cell. The firmness of coffee beans increased almost linearly with increasing moisture content.

Coffee shelf-life is limited, particularly if coffee is stored under atmospheric conditions. Perceptible sensory changes have been reported after storage times of 6 to 8 weeks for coffee beans and 13 to 21 days for roast and ground coffee [1, 99]. Cardelli and Labuza found that the shelf-life of coffee depended on different factors, with oxygen content of the storage atmosphere being the most important [2], but water activity and temperature had a substantial impact on the storage stability as well. A water activity increase of 0.1 led to an increase of 60 % in the deterioration rate of roast and ground coffee.

The moisture content of roasted coffee impacts storage stability considerably, most probably because of the plasticizing effect of water, which increases the mobility of reactants and, in turn, increases reaction rates [106]. With better storage conditions (i.e. less oxygen partial pressure), larger differences were found during storage of coffees with different water contents. During the storage of roasted coffee beans and ground coffee at a normal atmosphere, only the evolution of dimethyl sulfide, dimethyl trisulfide, 3-mercapto-3-methylbutyl formate, and *N*-methylpyrrole was influenced by the moisture content. However, if the coffee was stored under nitrogen atmosphere, the majority of the investigated compounds was sensitive to the moisture content (i.e., dimethyl sulfide, dimethyl trisulfide, 3-mercapto-3-methylbutyl formate, 2-furfurylthiol, *N*-methylpyrrole, 2-methylbutanal, 3-methylbutanal, 2,3-butanedione, and 2,3-pentanedione)

Thiols as one of the most important class of odorants are strongly affected by the moisture of roasted coffee. In coffee beverages, staling of coffee due to thiol-matrix interactions and oxidative degradation of thiols is well investigated [26, 123-128]. However, similar studies for roasted coffee beans and ground coffee are scarce. The susceptibility of 2-furfurylthiol and 2-methyl-3-furanthiol to oxidation has been demonstrated by verifying their antioxidative capacity [129]. Possible degradation pathways of thiols are summarized in Figure 10.6. In coffee beans and ground coffee, mobility of reactants is limited, but oxidative degradation via hydroxyl radicals is still probable and, together with the plasticizing effect, might help to explain their faster degradation in coffees with increased moisture content.

A relationship between degassing of coffee beans and loss of aroma compounds was not found. Although degassing was faster in coffee beans with higher water content, the loss rate of most aroma compounds was similar. It is assumed that aroma stripping along with degassing in coffee beans is a negligible effect compared to the oxidative degradation of odorants.

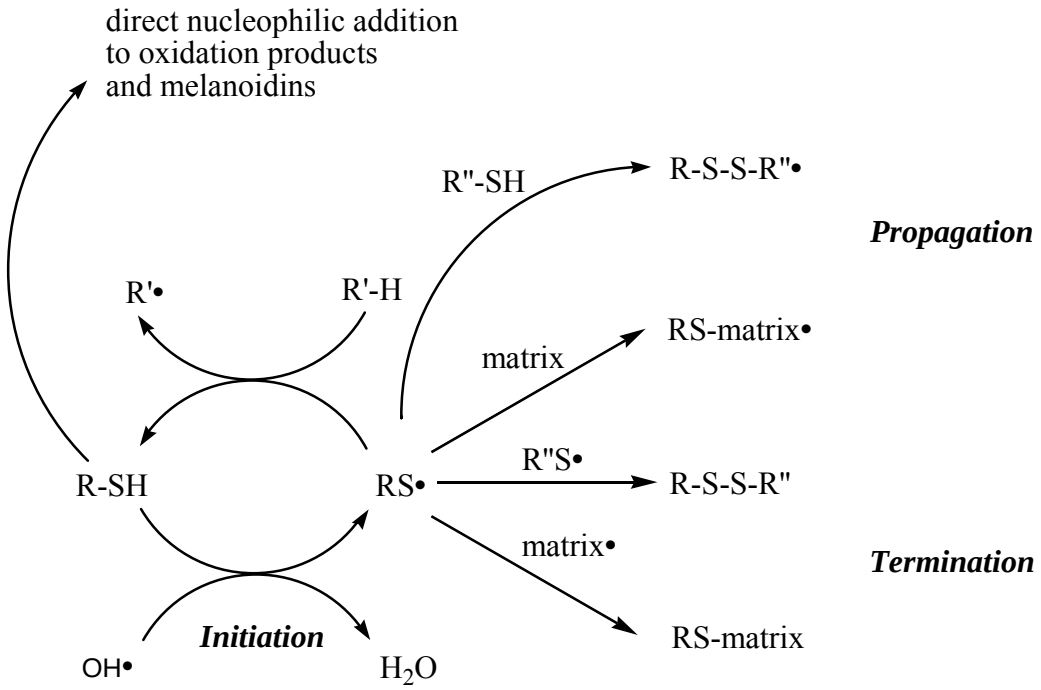

Figure 10.6 Possible degradation pathways of thiols (adapted from Charles-Bernard and coworkers [125]).

10.3 Grinding of roasted coffee

One sub-project dealt with the influence of water content and its plasticizing effect on grinding. Coarser particles resulted from grinding coffee with an increased water content. A resting time of several hours was necessary to allow an even distribution of water within coffee beans. There is evidence that directly after water quenching, water is very unevenly distributed, and hence there are areas with very high water content within the coffee beans, which may induce considerable changes in the local cell wall structure and its carbon dioxide permeability.

Since up to 50% of the entrapped carbon dioxide is liberated during fine grinding [59], it is probable that a large amount of volatile odorants are stripped with the carbon dioxide at the same time. An increased recovery of volatile odorants resulted from wet grinding methods compared to dry grinding. In addition, a completely degassed roasted coffee was ground with and without water. Contrary to the grinding trials with freshly roasted coffee, virtually no significant difference in the concentrations of volatile compounds was observed. This results prove that the higher concentration of odorants in wet ground coffee results from the entrapment of odorants which otherwise would be stripped off in dry grinding.

10.4 Roasting technology and product quality

A general problem in formulating measures to improve coffee quality is that the concept of quality is not easily defined. Coffee quality may imply very different facets such as aroma, taste, texture, mouthfeel, storage stability, absence of biological and chemical contaminants, health benefits, but also packaging, ease of preparation, and appearance [9]. In addition, smell and taste preferences may change according to time and location, which makes an unambiguous definition of coffee quality even more delicate. Studies which combine coffee roasting technology with sensory tests are relatively scarce [5, 65, 130].

From the results of the present dissertation, several conclusions with regard to coffee quality may be drawn:

1. The properties of roasted coffee depend on the time-temperature conditions applied during roasting. All changes in time-temperature conditions, e.g. acceleration of the roasting process, result in different physical properties and aroma profile.

2. Coffee aroma is complex, and aroma quality is rather a question of balance than of the simple amount of odorants only. Hence, improving the roasting process with the unique aim to increase the yield of odorants does not necessarily lead to an improved coffee aroma quality.

3. Variations in the raw material (e.g. blend composition, raw coffee moisture) influence the roasting process and must therefore be taken into account to obtain a constant product quality.

4. The shelf-life of coffee is decreased by a high moisture content. This is particularly the case if roast and ground coffee is packaged under protective atmosphere. Therefore, quenching of coffee at the end of the roasting process should not induce an increase of the moisture content.

10.5 Outlook

Coffee is a very complex product, and for a deeper understanding, much integrative research is needed to merge the individual pieces of knowledge to a general picture of coffee roasting. The compounds with the highest impact on coffee aroma are known, and their formation during roasting and fate upon storage are investigated to some extent. Additionally, some key taste compounds in coffee were identified recently [131, 132]. However, the knowledge on coffee taste compounds is still fragmentary. In addition, the understanding of the interactions of flavor compounds in sensory perception is very limited. To estimate the sensory significance of concentration differences in flavor compounds caused by the roasting process, more studies are needed. Undirected analytical approaches are promising tools for the establishment of correlations between coffee flavor compounds and sensory impressions [133]. Combining the knowledge on the impact of roasting on flavor compounds generation with data on sensory relevance will help to tailor the optimal roasting conditions needed for the production of a desired coffee. To expand the knowledge on precursor compounds, model reactions in a coffee bean-like environment are needed. The elucidation of reaction pathways within coffee beans by the use of stable isotope labeled precursor compounds, together with investigations on the influence of the coffee matrix on reaction conditions will lead towards a better predictability of the roasting process.

Staling of coffee is accelerated by a high moisture content. The plasticizing effect of an increased moisture content leads to a higher reactant mobility, which is supposed to be the main reason for the faster degradation of aroma compounds. However, the reaction mechanisms are not known in detail. The degradation pathways might be clarified by model reactions in a simulated coffee matrix at different water activities.

The impact of roasting conditions on structure and basic properties, such as volume, density, carbon dioxide desorption and de-oiling was shown in earlier studies [5, 6]. It would be interesting to know whether these structural differences induce changes in the aroma stability of roasted coffee.

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Publications, posters, and oral presentations

Publications

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Curriculum Vitae

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