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INVESTIGATIONS ON THE HOT AIR ROASTING OF COFFEE BEANS

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II Abbreviations

ABR	Air-to-bean ratio
AEDA	Aroma extract dilution analysis
AIC	Aroma impact compound
ANOVA	Analysis of variance
C.	*Coffea*
CH	Switzerland
CHARM	Combined hedonic aroma response measurements
CI	Characteristic ion
CIE	Comission Internationale d'Eclairage
CO_2	Carbon dioxide
cryo-SEM	Cryo scanning electron microscopy
D	Germany
db	dry basis
DMTA	Dynamic mechanical thermal analysis
DPFC	Digital pressure and flow control
ETH	Swiss Federal Institute of Technology
F	France
FD-factor	Flavor dilution factor
GB	Great Britain
GC	Gas chromatography
GC-FID	Gas chromatography with flame ionization detector
GC-MS	Gas chromatography mass spectrometry
GC-O	Gas chromatography olfactometry
HL	Temperature profile high /low
HTST	High temperature short time
IStd	Internal standard
LHC	Temperature profile low to high continuous increase
LSD	Least significant difference test
LTLT	Low temperature long time
MS	Mass spectrometry
MTMT	Medium temperature medium time
NMR	Nuclear magnetic resonance
O_2	Oxygen

ORL	Organic roast loss
PC	Personal computer / workstation / notebook
PDI	incorporated proportional, differential and integrational parts
PHL	Temperature profile pre-heating / high / low
PLHC	Temperature profile pre-heating / low to high continuous increase
prep-HPLC	Preparative high performance liquid chromatography
PT-100	Electrical resistance temperature probe
RI	Retention index
RIC	Reconstructed ion current (GC-MS)
RL	Roast loss
SDE	Simultaneous distillation/extraction
SEM	Scanning electron microscopy
SIDA	Stable isotope dilution assay
t-BME	Tertiary butyl methyl ether
TEM	Transmission electron microscopy
T_g	Glass transition temperature
t-test	Student's t-test
vpm	Volume per million
wb	wet basis

III Summary

Coffee is one of the most important internationally traded food commodities. After harvesting the ripe coffee "cherries" are processed to dry green coffee beans in the producer countries. In the consumer countries, roasting is the most important unit operation in converting green beans into roast coffee with its specific flavor. Apart from the primary process objective of flavor development, it is important to generate favorable bean properties for preservation of quality during storage. The present project contributes to the identification of important process factors and their influence on the product properties as a base for process optimization.

Roasting trials were mainly carried out with a fluidized-bed hot air laboratory roaster, allowing for coffee roasting under well-defined process conditions. The hot air temperature profile and the air velocity were carefully controlled and, in addition to batch pile temperatures, the bean core temperature was measured. Humid air roasting and water quench cooling were operated optionally. A roasting chamber with sightglasses combined with an optical setup including a stereo microscope enabled optical online observation of a single bean in process. Measurements and trials on an industrial scale were carried out in order to receive information on industrial roasting conditions, which served as a starting point and as a continuous standard for the laboratory trials. The structural, physical and chemical changes of the bean during roasting were followed by volumetry, porosimetry, microscopy, and thermal and chemical analysis. Instrumental aroma analysis was complemented with sensory analysis.

Green bean quality and initial water content in particular have a major impact on the process development and the resulting product properties. The temperature profile is the most crucial parameter in the process design. It determines both flavor formation as well as structural product properties. Different temperature profiles affect dehydration and the chemical reaction conditions in the bean which control

gas formation, browning and flavor development. A driving force for bean expansion as well as the structure resistance opposed to it are again temperature and dehydration related factors. High temperature roasted beans exhibit a greater bean volume, a larger cumulated pore volume and larger cell wall micropores than low temperature roasted coffee of identical degree of roast. These properties are assumed to increase the undesired mass transfer and to accelerate the staling process.

Hot air humidity must be considered as yet another important process parameter which influences the heat transfer rate and may affect various water content related developments. The amount of hot air in relation to the coffee batch size turned out to be critical for roaster design and operation. Low air-to-bean ratios resulted in coffee of superior cup-quality, whereas excessive air streams led to products of bland, dull and flat sensory properties. A lower ratio is assumed to prevent physical aroma stripping and excessive contact with oxygen and may create a favorable "microclimate" enclosing the beans. These findings also stress the important role of oxidation processes during roasting and storage.

Process optimization requires specification of a compromising target quality because not all desirable product properties can be maximized at the same time. High aroma quality is achieved with moderate roasting processes at medium temperatures. Provided there is a low air-to-bean ratio, an optimal roasting time for a medium degree of roast should be 6 min or longer, depending on the target flavor profile. Restrictive low temperature conditions yield a very stable product during storage, but a lack of aroma strength. High temperature conditions generally cause an unfavorable aroma profile and result in excessive gas formation and a very porous bean structure which is impairing quality retention during storage. Roasters should operate with a fairly high proportion of conductive heat transfer and at low air-to-bean ratios. For the most part, there may be no requirement for completely oxygen-free coffee technology. On the other hand, an oxygen-free final roasting stage may be worth to consider for further investigations.

IV Zusammenfassung

Kaffee ist eine der wichtigsten international gehandelten Rohwaren. Die reifen Früchte des Kaffeebaumes werden noch in den Anbauländern zu lagerfähigen grünen Kaffeebohnen verarbeitet. In den Konsumentenländern ist das Rösten der wichtigste Verarbeitungsschritt, wobei Grünkaffee in ausgeprägt duftenden, geschmackvollen Röstkaffee verwandelt wird. Neben dieser primären Prozess-Zielsetzung ist die Erzeugung von günstigen Produkteigenschaften wichtig, die dem drohenden Qualitätszerfall während der Lagerung entgegenwirken. Die vorliegenden Untersuchungen leisten einen Beitrag zur Identifikation von wichtigen Prozessfaktoren und deren Einfluss auf das Endprodukt als Basis zur Optimierung von Röstprozessen.

Röstversuche wurden vorwiegend mit einem Heissluft-Fliessbettröster im Labormassstab unter exakt definierten Prozessbedingungen durchgeführt. Das Temperaturprofil und die Luftzufuhr wurden genau gesteuert. Neben den gebräuchlichen Haufentemperaturen wurde auch die Kerntemperatur der Bohnen erfasst. Es konnte wahlweise mit trockener oder feuchter Luft geröstet oder zusätzlich mit Wasserquenche gekühlt werden. Eine Sichtglas-Röstkammer kombiniert mit einem Stereomikroskop erlaubte optische online-Beobachtungen einzelner Bohnen im Röstprozess. Die Messungen und Versuche an Industrieröstern ergaben Daten zu den industriellen Röstbedingungen, welche als Ausgangspunkt und Massstab für die Laborversuche dienten. Die strukturellen, physikalischen und chemischen Veränderungen der Bohnen wurden mit Volumetrie, Porosimetrie, Mikroskopie, thermischer und chemischer Analyse verfolgt. Die instrumentelle Aroma-Analyse wurde durch sensorische Prüfungen ergänzt.

Die Rohstoffqualität und insbesondere der Ausgangswassergehalt beeinflussen den Prozessverlauf und die Produkteigenschaften wesentlich. Die grösste technologische Bedeutung kommt jedoch dem Temperaturprofil zu. Die Rösttemperatur

bestimmt die Aromabildung und die strukturellen Veränderungen in entscheidendem Ausmass. Sie beeinflusst den Trocknungsprozess und bestimmt die spezifischen chemischen Reaktionsbedingungen, von welchen die Bildung von Gasen, Bräunungsprodukten und Aromastoffen stark abhängig ist. Die treibende Kraft zur Volumenzunahme und der entgegengesetzte Strukturwiderstand sind ebenfalls temperatur- und trocknungsabhängige Faktoren. Hochtemperatur-geröstete Bohnen weisen im Vergleich zu Tieftemperatur-gerösteten Kaffees verstärkte Expansion, grösseres kumuliertes Porenvolumen und grössere Zellwand-Mikroporen auf. Vermutlich fördern diese Eigenschaften einen unerwünschten Stofftransport bei der Lagerung und wirken sich negativ auf den Alterungsprozess aus. Die Heissluft-Feuchtigkeit darf ebenfalls nicht vernachlässigt werden, da sie den Wärmeübergang beeinflusst und sich vermutlich auf wassergehaltsabhängige Röstvorgänge auswirkt. Das Verhältnis von Heissluftmenge zu Chargengrösse (Luft-zu-Bohnen-Verhältnis, LBV) erwies sich als wichtige konstruktive und betriebliche Grösse. Ein tiefes LBV ergab Produkte von hoher Aromaqualität, während übermässige Luftströme generell zu Kaffees mit flacher und aromaschwacher sensorischer Charakteristik führten. Ein tiefes LBV schützt vor physikalischem Aromastoff-Austrag und übermässigem Sauerstoffkontakt und schafft ein vorteilhaftes "Mikroklima" um die Bohnen. Die Ergebnisse belegen die herausragende Rolle oxidativer Prozesse während der Röstung und der Lagerung.

Prozess-Optimierungen erfordern eine kompromissbereite Festlegung der Zielqualität, weil sich nicht alle im Produkt erwünschten Eigenschaften gleichzeitig maximieren lassen. Eine hohe Aromaqualität wird durch moderate Prozesse mit mittelhoher Temperaturführung erzielt. Bei tiefem LBV soll die Röstzeit für einen mittleren Röstgrad 6 min oder mehr betragen. Ausschliessliche Tieftemperatur-Bedingungen ergeben ein zwar stabiles, jedoch aromaschwaches Produkt. Hochtemperatur-Röstung bewirkt ein starkes, aber unvorteilhaftes Aroma, eine übermässige Gasentwicklung und eine sehr poröse Bohnenstruktur. Röstanlagen sollten einen mittleren bis hohen Anteil an konduktivem Wärmeübergang aufweisen und mit tiefem LBV operieren. Ein vollständiger Ausschluss von Sauerstoff in der gesamten Herstellungstechnologie ist unnötig. Hingegen sollte ein Sauerstoff-freier letzter Röstabschnitt für weitere Untersuchungen in Betracht gezogen werden.

1 Introduction

Coffee presents one of the world's most favorite beverages. It is greatly appreciated for its delightful smell and flavor as well as for the stimulating effects of caffeine. While the beverage is consumed mainly in Europe, North and Central America, the coffee plant grows at elevated altitudes in tropical and subtropical regions all around the world. More than 5 million tons of green coffee beans are annually produced worldwide. Among all internationally traded food commodities, coffee holds a unique position with the greatest trade volume in financial terms. Some 20 million people earn a living directly from coffee production. Post-harvest processing is accomplished in the producer countries, resulting in green coffee beans ready for shipping. In the consumer countries roasting is the most important unit operation in roast coffee manufacturing.

Hot air roasting of coffee beans is a traditional thermal process. Its primary objective is to produce roast coffee of the desired taste and aroma, but also to generate a dark color and a dry brittle texture. The bean that is exposed to roasting can be regarded as a natural complex "bioreactor" in which drying takes place, water is redistributed and extensive chemical reactions are induced, causing profound changes of both chemical composition and bean microstructure. Roasting results in a product of distinct quality concerning aroma and flavor, texture, extraction yield and appearance. Moreover, the product is subject to substantial quality changes from immediately after roasting and during storage. Therefore, the protection of aroma, the prevention of excessive oil migration and the control of gas desorption during storage presents another challenge in coffee technology. The behavior of products during roasting and the resulting product properties are influenced by a series of important process parameters, such as roaster design, heat transfer, characteristics of the heat transfer media, cooling and water quenching. Since the developments and interactions occurring in the bean during roasting are inadequately understood

the roasting process in practice is still designed and operated mainly on an empirical base.

The present investigation intended to contribute to a more fundamental insight into the coffee roasting process. They aim at the identification of important process factors and their influence on product properties so that process optimization becomes possible on a rational base. Thereby, industrial roasting conditions served as starting point and continuous standard. Consequently, some effort was devoted to monitor industrial roasters. The main part of the investigations was carried out with laboratory scale roasting under well-defined process conditions. The laboratory scale roasting equipment used in a preceding research project on nut roasting (Perren, 1995) was adapted to coffee roasting, in particular with the addition of a cooling unit, allowing for efficient fluidized-bed and water quench cooling. Structural, physical and chemical changes were followed during laboratory roasting and in simulation experiments using the technique of thermal analysis, thus establishing the relations between roasting conditions and the resulting product properties. Based on the preceding project on nut roasting (Perren, 1995) initial emphasis was put on coffee bean microstructure, using volumetry, porosimetry and microscopy. Investigations on coffee aroma, which is the most outstanding product property of roast coffee, were then introduced. Marked interactions between structure and physicochemical developments during roasting and storage could be established and evaluated for process optimization.

2 Literature review

2.1 Coffee in perspective

2.1.1 Taxonomy, appearance, cultivation and post-harvest processing

The genus *Coffea* belongs to the botanical family of *Rubiaceae* and comprises more than 70 different species. However, only the three species *C. arabica*, *C. canephora* and *C. liberica* are of commercial importance. As a result of modern breeding techniques some hybrids of *C. arabica* and *C. canephora* have recently been introduced with success. Since *Coffea* was first correctly described by Linnaeus in the mid eighteenth century, botanists have failed to agree on a precise classification system. The most widespread varieties are Typica and Bourbon for *C. arabica* and Robusta for *C. canephora*. Therefore, *C. canephora* is often simply referred to as *Robusta*. The geographical gene center of *Coffea* lies in the Abyssinian highlands of Ethiopia.

The coffee plant grows in tropical and subtropical regions of Central and South America, Africa and South East Asia, preferably in temperate and humid climates at altitudes between 600 and 2500 m. It is a shrub or a tree that may grow to a height of 2.5 to 4.5 m (*C. arabica*) and 4.5 to 6.5 m (*C. robusta*), depending on variety and growth conditions. Cultivated plants are generally kept at lower height. Oval shaped green leaves grow on the lateral branches together with clusters of white flowers. Each flower develops into a small ellipsoidical stone fruit of approximately 15 mm length, called "cherry". The cherry ripens within 7 to 11 months, whereby its color changes from green to red. The ripe cherry consists of a red exocarp (skin), a thick, sweet gelatinous-pectic mesocarp (pulp) and usually two seeds (coffee beans). Each seed is wrapped in a thin silverskin and protected by a parchment hull. This plant and fruit morphology has been described in detail by Illy and Viani (1995), Wrigley (1988) and Clifford and Willson (1985).

The two species *C. arabica* and *C. canephora* differ considerably in their botanical, genetic, agronomic, chemical and morphological characteristics. *C. arabica* varieties generally produce an oval convex seed with an S-shaped longitudinal slit (the central cut) on the flat side. *C. canephora* seeds are more round with a straight central cut. *C. arabica* usually grows at higher altitudes than *C. canephora* and is generally regarded as of superior quality. On the other hand, *C. canephora* is more resistant to pests and diseases. Illy and Viani (1995) provide a detailed survey on the characteristics of the two species.

Harvesting is carried out by non-selective stripping of whole branches or by selective hand-picking. The latter is very labour intensive, but results in a superior product quality because only ripe cherries are collected. The subsequent crop processing includes the separation of the beans from the pulp and is carried out by either the *dry* or the *wet* process (Illy and Viani, 1995, Thorn, 1995, Clarke and Macrae, 1987 and many other authors). The *dry method* presents the most traditional process and is simple and inexpensive. The harvested cherries are spread in small layers on tiled or concrete terraces and exposed to the sun and air for drying. The layers are raked over at regular intervals to prevent fermentation, and occasionally have to be covered to protect them from rain or low temperatures. Fermentation in heaps can optionally be included. After some four weeks the cherries are dry and the outer shell has become dark brown and brittle. The husk is finally broken up in dehullers and the beans are then stored in silos.

The *wet process* requires greater investment and more care, but is generally believed to better preserve the intrinsic qualities of the bean and to produce a superior coffee quality. In contrast to the dry method, during wet processing the pulp is removed from the bean prior to drying. As a first step, the pulp is removed in a pulping machine, ideally within the first 12 h after harvesting. The separated beans in their parchment hull are washed and then essentially subjected to a fermentation for 12 to 48 h. Then, they are sun dried or mechanically dried. At this stage, the wet process is completed and the beans are known as "parchment coffee". The parchment is removed only before export by a hulling or peeling step. This operation is followed by polishing, grading and sorting, marketing and shipping.

2.1.2 Historical, socio-cultural and economical aspects of coffee

As mentioned in section 2.1.1, the coffee plant originated in the highlands of Ethiopia, where it still grows wild today. There are numerous myths and legends on the discovery of coffee and its roasting and brewing. Coffee is said to have become a hot beverage as early as AD 1000. However, it was in Yemen, formerly called Arabia, where spreading and horticultural propagation of coffee began in AD 575. In those days, Yemen was one of the busiest places in the world and its main port, Mocha, was the centre (Thorn, 1995). By the 13th century coffee was an established component of daily life and culture in Arabia (Heise, 1996). It was from here that coffee began its great journey around the world. Via Mecca it first arrived at Cairo and Constantinople (Istanbul), from where travellers brought it to Europe. By the early 17th century, German, French, Italian and Dutch traders introduced coffee to their overseas colonies.

Coffee is one of the most important internationally traded commodities and is said to have the second largest trade volume in financial terms directly after oil. Some 20 million people worldwide obtain their income directly from the coffee production. The annual coffee production is between 5 and 6 million tons of green beans. In 1989 42.0 % of the world production were produced in South America, 20.4 % in Africa, 18.5 % in Asia and 17.9 % in North and Central America (D'Amicis and Viani, 1993). Major *C. arabica* producer countries in 1993 were Brazil (1,275,000 t), Colombia (1,080,000 t), Mexico (184,000 t), Ethiopia (180,000 t), Guatemala (177,000 t), El Salvador (165,000 t), Costa Rica (148,000 t) and Honduras (121,000 t). Major producer countries that mainly cultivate *C. canephora* were Indonesia (441,000 t), Ivory Coast (200,000 t), Uganda (177,000 t) India (169,000 t), the Philippines (111,000 t) and Cameroon (50,000 t) (Rehm and Espig, 1996). Brazil mainly applies dry processing, whereas Colombia produces wet processed *C. arabica* coffees.

Colombia is known as the largest producer of washed quality coffees in the world. More than any other producer, the country has been concerned to develop and promote its coffee product and industry. This effort, together with favorable geographical and climatic factors, has given Colombian coffee its reputation for

high quality and flavor. Colombian coffees generally provide good "body" and acidity, rich flavor, and are superbly balanced (Thorn, 1995).

The highest coffee consumptions are found in Europe. The Finnish are the biggest coffee consumers in the world with an annual per capita consumption of 12.6 kg (D'Amicis and Viani, 1993). The coffee consumptions of the other Nordic countries are also well above 10.0 kg p^{-1} yr^{-1}, while the figures are 7.5 kg for Switzerland, 4.7 kg for the United States and 4.4 kg for Italy. Coffee imports that are actually consumed in Switzerland come to more than 56,000 tons, and the annual average coffee consumption amounts to around 1000 cups per person.

2.1.3 Chemical composition of green and roasted coffee beans

Table 1 provides a general survey on the chemical composition of green and roasted coffee beans (Illy and Viani, 1995). Other comprehensive data and reviews on coffee components are provided by Clarke and Macrae (1985), Viani (1993) and Maier (1993). The two species *C. arabica* and *C. canephora* are different in composition. Arabica beans contain more lipids, sucrose and trigonelline, while robusta contains more caffeine and chlorogenic acids. The complex chemical reactions during roasting lead to a totally altered composition of the roasted bean. The composition in roasted coffee is highly dependent on the roasting conditions and the degree of roast in particular.

Lipids account for 15 to 18 g /100 g (db) of arabica beans. Coffee oil contains mainly triglycerides, the principal fatty acids being $C_{18:2}$ (40 ... 45 g /100 g db) and $C_{16:0}$ (25 ... 35 g /100 g db). The lipid fraction also includes a relatively large unsaponifiable fraction that is rich in free diterpenes (mainly cafestol and kahweol). The nitrogen fraction of coffee includes caffeine, trigonelline, nicotinic acid, free amino acids and proteins. Since coffee is very much appreciated by consumers for its stimulating effects, but is also subject to discussions on health risks, a lot of work has been devoted to the alkaloid caffeine. The acids of coffee present a fraction appreciable in quantity which is of chemical and sensory interest (Maier, 1987). Among them, the group of chlorogenic acids is the most remarkable one because of its high concentration in green coffee, and because of its antioxidative and cancer-protective effect. The sensorially perceived acidity is determined mainly by acetic

and citric acid. Melanoidins in roast coffee are poorly characterized so far (Viani, 1993). They constitute a major heterogeneous group of brown to black polymeric material that is formed at roasting. In contrast, a lot of research has been accomplished on the volatile fraction of roast coffee. A literature review on aroma precursors in green beans and aroma compounds in roasted coffee is provided in chapter 2.4.

Oligosaccharides and Polysaccharides constitute about one half of the raw bean dry matter (Viani, 1993). The polysaccharides present the principal structure building elements of the cell. Therefore, their composition and fate during roasting is crucial for the development of bean microstructure. Coffee polysaccharides have been studied extensively in the 1960s by Thaler and Arneth (1968a, 1968b, 1969) and Thaler (1975), and other authors. Thaler's group found four different fractions in green beans, composed of mannan, cellulose, galactan and araban. More recently, Bradbury and Halliday (1990), using high resolution GC-MS, identified cellulose, mannan and arabinogalactan as the principle polysaccharides in coffee. Arabinogalactan was described as principally $\beta(1 \rightarrow 3)$ linked galactan chain with frequent short side chains linked at C6 to galactose residues $1 \rightarrow 3$ linked to terminal arabinose residues. Mannan has been defined as a linear $\beta(1 \rightarrow 4)$ linked mannan with only about 1 one-residue galactose stub at C6 per 100 mannose residues. These structure models were partially criticized in a more recent study by Navarini et al. (1999), who employed NMR spectroscopy in combination with classical methods. Arabinogalactan and Mannan were isolated from hot water extracts of dark roasted coffee. Mannan was described as a branched $\beta(1 \rightarrow 4)$-D-mannan substituted with small amounts of galactose and arabinose (an arabinogalactomannan). Both polysaccharides are structurally related to those originally present in the green coffee beans, even if the arabinogalactan appears to be more altered by roasting (Bradbury and Halliday, 1990). Yet, it is not clear if the two polysaccharides in the isolate are individual components of a physical mixture, or if they are associated to form a complex assembly. Under the latter hypothesis, proteinaceous material may play an important role (Navarini et al., 1999). Leloup and Liardon (1993) found that roasting considerably reduces the molecular weight range of arabinogalactans and galactomannans in coffee cell walls.

Tab. 1: *Chemical composition of raw and roasted coffees in g /100 g db (Illy and Viani, 1995).*

Component	Arabica coffee		Robusta coffee	
	green	roasted	green	roasted
Polysaccharides	49.8	38.0	54.4	42.0
Sucrose	8.0	0	4.0	0
Reducing sugars	0.1	0.3	0.4	0.3
Other sugars	1.0	no data	2.0	no data
Lipids	16.2	17.0	10.0	11.0
Proteins	9.8	7.5	9.5	7.5
Amino acids	0.5	0	0.8	0
Aliphatic acids	1.1	1.6	1.2	1.6
Quinic acids	0.4	0.8	0.4	1.0
Chlorogenic acids	6.5	2.5	10.0	3.8
Caffeine	1.2	1.3	2.2	2.4
Trigonelline (including roasted by-products)	1.0	1.0	0.7	0.7
Minerals (as oxide ash)	4.2	4.5	4.4	4.7
Volatile aroma	traces	0.1	traces	0.1
Water	8 to 12	0 to 5	8 to 12	0 to 5
Caramelization and condensation products (by difference)		25.4		25.9

2.2 Roasting technology

2.2.1 General considerations on roasting

Roasting is generally defined as a dry heat treatment of foods with the intention to generate roast aroma compounds, to develop color, and often to create a crispy texture. These intentional product alterations make the explicit difference between roasting and simple drying (Perren, 1995). Heat can be transferred to the roasting goods by different modes. In differentiation to frying or roasting nuts in oil, roasting of coffee beans is mostly regarded as to be carried out in a gaseous atmosphere such as hot air or steam.

Roasting is applied to a number of foodstuffs, such as cocoa, nuts, chicory, coffee and other oil containing seeds. It is a time-temperature controlled process that usually involves dehydration, reaction of free amino acids and short-chained peptides with free mono- and disaccharides during nonenzymatic browning, protein denaturation and subsequent changes in texture (Perren, 1995).

2.2.2 Coffee roasting

Process

Roasting is the most important unit operation in converting green coffee beans into flavor-full roast coffee. The primary objective of the process is to produce a desired taste and aroma. Furthermore, coffee is roasted to generate a dark color and a dry and brittle texture that makes grinding and extraction possible (Clarke and Macrae, 1987, Johannessen, 1992). For coffee roasting in particular, temperatures higher than 190 °C are required (Dalla Rosa et al., 1980). Illy and Viani (1995) provide a summary table on the macroscopic effects of roasting on the coffee bean.

Types of roasters

The various principles of roasting systems can be grouped regarding different criteria:

Product flow

Coffee beans can be roasted in batch, usually with industrial batch sizes of some hundreds of kilograms, or in continuous systems. Continuous roasters are generally

designed for large hourly capacities, whereas batch roasters provide more flexibility in process layout and control.

Mechanical principle

The most commonly used systems are found to be the horizontal rotating drum, the vertical fixed drum with rotating mixing elements, the vertical rotating bowl and the fluidized-bed. The main task is to provide means for sufficient mixing of the beans in order to achieve homogeneous roasting and to prevent scorching of beans. Clarke and Macrae (1987) provide an illustrated summery of different industrial roasters.

Heat transfer

Heat can be transferred to the beans by heat conduction at direct contact with hot metal surfaces, by free or forced convection due to a streaming media (hot air), or by radiation. Roasters generally make use of all three types of heat transfer, but their relative contribution to the overall heat transfer may greatly differ. Although infrared roasting has been reported (Kino and Takagi, 1995), this method is very unusual for coffee. Since coffee is exclusively hot air roasted in industrial practice, it makes sense to limit distinction to systems with prevailing *conductive* heat transfer and systems with prevailing *convective* heat transfer. In this respect, it is also very useful to consider the operating air-to-bean ratio.

Air-to-bean ratio

The amount of hot air used in a roasting process in relation to the batch size of coffee beans is defined by Mahlmann (1986) as *air-to-bean ratio (kg air per kg green coffee)*. This ratio is a characteristic parameter in a roasting process, but only applies for a given degree of roast. According to Mahlmann, figures can range from 1 in a typical "conventional" process up to 150 in fully fluidized-bed systems.

Process factors of major importance

The quantity of heat transferred to the beans presents the most important parameter of the roasting process. It can be determined from the bean temperature and roasting time (Illy and Viani, 1995). According to a widespread opinion, the degree of roast in the product is correlated to the *final* roasting temperature (Sivetz, 1991, Illy and Viani, 1995). During the last decade, the time/temperature profile has been the most

extensively discussed issue in coffee roasting. Early traditional industrial roasting was carried out with conductive type equipment, applying slow heat transfer with long roasting times of more than 20 min. The introduction of gas fuel operated roasters enabled direct contact of beans with combustion gases and allowed for much faster heat transfer and fluidized-bed roasters (Illy and Viani, 1995, Sivetz, 1975). During the 1970s and 1980s, there was even a trend to ultrafast roasting with roasting times cut down to less than 90 s. Inventors claimed process and product benefits, since this process was regarded as more efficient, economic, and turned out to give a low-density high-yield product (Sivetz, 1975 and 1991, Hubbard et al., 1979, Stefanucci and Protomastro, 1982, Small and Horrell, 1993, and others).

However, low density coffee did also cause a series of troubles and reservations. The entire microstructure of low density high yield coffee beans was found to differ considerably from that in "regular" coffees (Kazi and Clifford, 1985, Puhlmann et al, 1986). Greater volume increase and more intense gas formation created a packaging problem (Radtke, 1975). Moreover, fast roasted coffees exhibited greater oil sweating which was regarded to be a sensory risk (Puhlmann et al, 1986). In addition, these products have a somewhat higher final water content. Hence, they are more affected by oxidation and staling during storage (Radtke, 1979, Radtke-Granzer, 1982, Hinman, 1991). Last, but most important, high yield roasting has not been optimized organoleptically (Illy and Viani, 1995). High yield coffees gave infusions that were bitter, burnt and astringent (Kazi and Clifford, 1985, Illy and Viani, 1995). For all these reasons, ultrafast roasting has been widely abandoned in industrial practice in recent years. Roasting times of more than 4 min are commonly applied again today. Still, empirically optimized temperature/time profiles vary considerably from manufacturer to manufacturer and are well kept secret. These questions must be further investigated so that process development can be put on a more fundamental scientific understanding.

The roasting process must be stopped by rapid cooling of the beans (Illy and Viani, 1995). This is generally achieved by excess cold air and/or a precise amount of water sprayed on the hot beans (water quench cooling). The water is supposed to fully evaporate on the bean surface rather than to greatly influence the bean water content. This cooling process makes use of the high evaporation enthalpy of water.

2.2.3 Dehydration and chemical reactions induced by roasting

According to Illy and Viani (1995) the roasting process can be roughly divided into a drying phase, a roasting phase, where a number of complex chemical reactions take place, and a final cooling phase. During roasting the beans loose weight, generally between 14 and 20 %, depending on the green bean quality, the process conditions and the target degree of roast (Clarke and Macrae, 1987). A major part of this weight loss is due to dehydration, whereas another substantial part (some 5 to 8 % for a medium degree of roast) is caused by a loss of dry matter, primarily as CO_2. The chemical reactions that convert organic matter into gaseous products also result in the formation of a considerable amount of water that is then again lost as water vapor (Clarke and Macrae, 1987). Illy and Viani (1995) reported that 70 % of the degradation products are water and 30 % carbon dioxide. Dehydration is widely regarded as a steady process. However, Puhlmann and Meister (1989) claimed a development of water release in three stages. They found a first stage of slow dehydration below 100 °C, a stage of accelerated but migration-limited dehydration and a final stage of maximal dehydration rates due to microstructural changes of the bean.

At first, chemical reactions are endothermic, whereas a number of authors state an exothermic final roasting stage. On the basis of calorimetric measurements, Baltes (1977) reported the net result of reactions in coffee to become exothermic at 150 °C. Raemy and Lambelet (1982) found a temperature of 140 °C. Illy and Viani (1995) as well as Viani (1993) claim that the process changes from endothermic to exothermic at a bean temperature of 160 °C, whereas Streuli (1973) reported exothermic reactions to start at 190 °C. Although Raemy and Lambelet (1982) claimed a self-heating effect in the beans, the few temperature curves reported in literature (Puhlmann and Meister, 1989, Da Porto et al., 1991, Illy and Viani, 1995, Nicoli et al., 1997) do not show an increase in the final roasting stages that can be clearly attributed to exothermic reactions.

The chemical reactions that take place during roasting have not yet been completely elucidated, the reasons for this being great difficulty in reproducing or simulating all the reactions that take place inside a bean in the laboratory. Nevertheless, significant information can be obtained by comparing the compositions of green and roasted

coffee (Illy and Viani, 1995, Clarke Macrae, 1985, Viani, 1993). Some of the more extensive and complex chemical reactions during roasting affect the carbohydrates of green beans and include Maillard reaction, Strecker degradation, pyrolysis, caramelization, mainly resulting in aroma, flavor and color compounds. Roasting leads to protein denaturation and degradation. Free amino acids, peptides and proteins with free amino groups react with reducing sugars to form glycosylamines and/or aminoaldoses and/or aminoketones by condensation. Amino acids react with α-dicarbonyls during Strecker degradation and form aminoketones (Illy and Viani, 1995). On roasting there is a reduction in the amount of citric and malic acid and an increase of many of the other acids, in particular quinic acid and volatile acids (Maier, 1987). Chlorogenic acids are strongly degraded (Leloup et al., 1995). The loss is about proportional to the degree of roast and can reach 80 % in dark roasted coffee. Caffeine is thermally quite stable, whereas trigonelline is partially degraded during the process. Triglycerides are little affected by roasting. The formation of aroma compounds is discussed separately in chapter 2.4.

2.2.4 Appearance and general properties of roasted coffee beans

In contrast to green coffee beans, roasted beans distinguish themselves by a certain "degree of roast". While it basically means the extent of roasting, and the state into which the beans have proceeded by roasting, there are several different possible criteria and definitions for the degree of roast. The overall weight loss or the organic roast loss may serve as an indicator for the degree of roast for a given raw material. The qualitatively determined or visually assessed external color of the beans is even more suitable in industrial practice (Clarke and Macrae, 1987). Color changes progressively during roasting from greenish-grey to a marked yellow, orange, brown, dark brown and almost black. Moreover it is said to be correlated with the bitter/acid ratio in the cup (Illy and Viani, 1995). Also for scientific purpose the instrumental color measurement is commonly regarded as the most appropriate measure of the degree of roast. However, color is a less reliable indicator in the case of ultrafast roasting, since the interior of the bean is less roasted than the outside (Illy and Viani, 1995). On the other hand, some authors also suggested chemical properties as an indicator for the degree of roast, such as the methylpyrazine ratio

(Hashim and Chaveron, 1996), isomers of quinic acid (Scholz-Böttcher and Maier, 1991) and the ratio of certain amino acid enantiomers (Nehrig and Maier, 1992).

The ability to retain the gases formed during roasting presents one of the most remarkable properties of coffee beans. It is well known, that roasted whole beans contain large quantities of entrapped carbon dioxide that is only released during more than 4 months of storage (Clarke and Macrae, 1987, Radtke, 1975). The amount of gas development is dependent on the degree of roast. According to Sivetz and Desrosier (1979), about half of the total CO_2 generated is retained in the roasted whole bean. Even though, measured at standard conditions NTP (20 °C, 101.3 kPa pressure), whole beans contain a quantity of approximately 2 to 5 ml CO_2 (Clarke and Macrae, 1987). This CO_2 must be held under considerable pressure within a roasted bean, which for a typical case was calculated by Clarke and Macrae (1987) to be 6.4 at (648 kPa). Radtke (1975) calculated even higher pressures of 800, 570 and 550 kPa, respectively, for 3 different fully roasted coffees in the cold state. A substantial part of the entrapped gas is only lightly bound in the bean, since it is easily released during grinding.

The gas desorption process during storage is often accompanied by migration of coffee oil to the bean surface. The extent of oil migration is dependent on the green bean quality and possible pre-treatments, such as decaffeination. Decaffeinated beans are known to be more delicate to roast, since they tend to more "oil-sweating" (Lee, 1999). On the other hand it is also known that oil migration in decaffeinated beans is controllable by the roasting conditions and the target degree of roast. Darker roasted beans tend to a more severe oil migration. Applying intensive heat during roasting is regarded as migration promoting and detrimental to the roast coffee quality. The mechanisms of this mass transfer are poorly understood, since they have not been extensively investigated so far.

The amount of dry matter that is transferred into the coffee beverage is dependant on a series of parameters, such as variety and origin of the raw material, the degree of roast and the roasting temperature, as well as the conditions during the extraction procedures (Clarke and Macrae, 1987, Nicoli et al., 1990, Hinz et al., 1997). Extraction yields greater than 50 % are achieved in industrial extraction technology by applying high pressures and temperatures. Conventional home-brewing leads to

an extraction yield below 30 % (Peters, 1991). The extraction mechanics are very complex and so far authors have failed to agree on a commonly accepted model of this process.

2.3 Structural properties of the coffee bean

2.3.1 Morphology of the green coffee bean

Green coffee beans do not exhibit a uniform and homogenous morphology. As illustrated in Figure 1, a specific folding, recognizable as a slice being folded upon itself, creates the typical shape with the central cut on the flat side (Bürgin, 1969, Dentan, 1985). At the periphery of the seed, there is one single layer of epidermal cells. The main bean part consists of parenchymatous storage cells (Dentan, 1985). In the middle part of a transverse section one can distinguish a thin layer of mucilaginous material in which is embedded the small embryo.

The cytoplasm of the parenchyma cells essentially contains lipids, proteins, carbohydrates and appreciable amounts of caffeine, chlorogenic acids and minerals (Dentan, 1985). The lipids are distributed homogeneously throughout the bean and located close to the plasmalemma, forming a layer of variable thickness. They are stored within numerous oil bodies with a diameter range of 0.2 to 0.3 µm (Wilson et al., 1997). These oleosomes are remarkably stable and do not aggregate or coalesce (Huang, 1996). Their surface is shielded by a layer of proteins, called oleosins. The stability of oleosomes seems to play an important role in the plant physiology during lipid biosynthesis and seed imbibition. The center of the cytoplasm is free of lipids and contains proteins and carbohydrates. Dentan (1985) described some sort of a vacuole in the cytoplasm filled with carbohydrates.

The parenchymatous cell walls of ripe coffee beans are particularly thick and do not enclose any intercellular spaces (Dentan, 1985). Reinforcement rings give them a nodular appearance in cross sections. The bulk of the full grown cell wall consist of the secondary wall (Dentan, 1977). In certain areas the cell wall is crossed by many plasmodesmata (Dentan, 1985). Wilson et al. (1997) analyzed freeze-fractures by SEM and found no evidence of additional pre-existing channels within the wall of green beans. They observed cellulose microfibrils and described them as organized

in polarized orientation by FF/TEM. The general model concept of the organization of the plant cell wall suggests a network of polysaccharide microfibrils that is stabilized by proteinatious cross-links and embedded in a gel of pectic-cellulosic material (Nultsch, 1996, Wilson and Fry, 1986). This complex cell wall architecture has been remarkably visualized with light micrographs of the onion primary cell wall in a study by McCann et al. (1990). They sequentially extracted polymers from the native wall and analyzed the remaining structure in the microscope. Both above mentioned studies do not directly apply to coffee beans. Nevertheless, they give useful hints on the general structural architecture of plant cell walls.

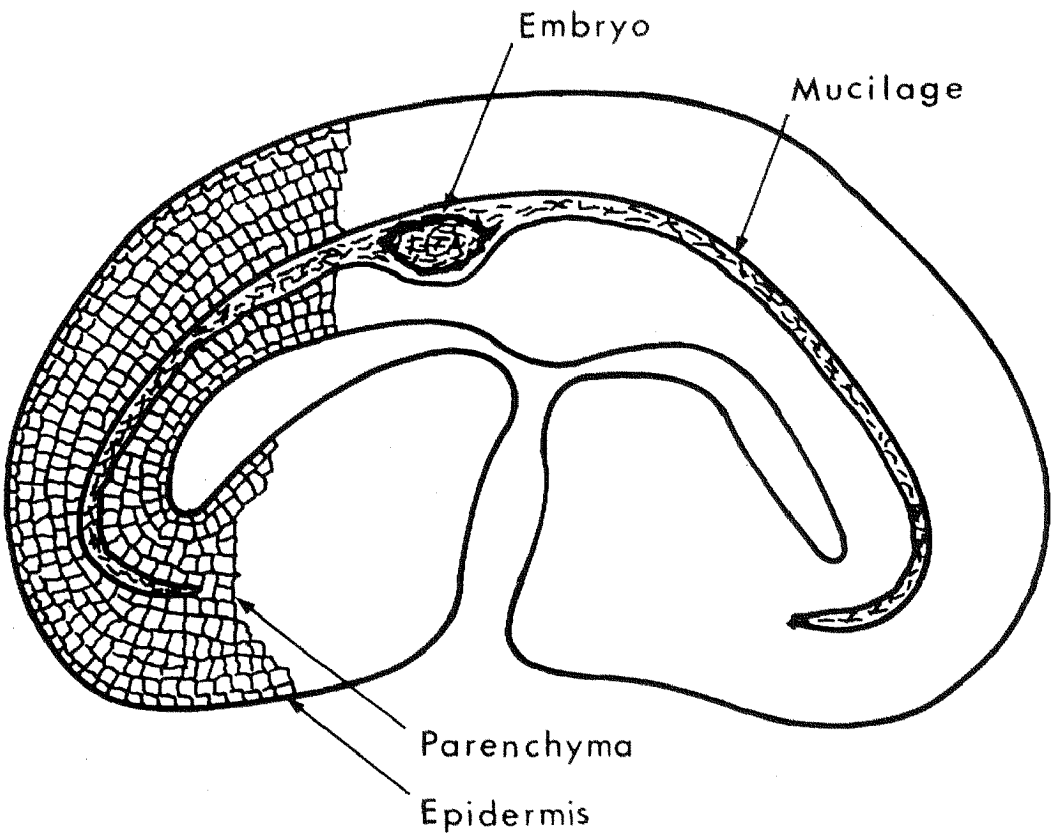

Fig. 1: *Schematic transverse section of a coffee bean (Dentan, 1985). A specific folding gives the bean its typical shape with a central cut on the flat side. The bulk of the bean consists of parenchymatous cells.*

2.3.2 Changes of macrostructure during roasting

The volume increase presents the most obvious macroscopic change of the bean structure during roasting. Clarke and Macrae (1987) described bean expansion as occurring progressively, but including a "popping phase", leading to considerable decrease of density. It is not quite clear from this statement whether the term "popping phase" applies only to sounds accompanying the expansion, or if the authors suggest a phase of instantaneous expansion. Volume increase and density decrease is a function of the degree of roast, but also of the speed of roasting (Clarke and Macrae, 1987). Dalla Rosa et al. (1980) found that the resulting bean volume is correlated with the final roasting temperature. Bean expansion is caused by a very rapid pressure build-up due to rapid formation of water vapor and gas within the bean (Illy and Viani, 1995). Illy and Viani (1995) reported a steady and continuous volume increase and found the development to be positively correlated to weight loss. They noted a swelling of the beans of 40 to 60 % at a weight loss of 18 %. No information on initial bean water content or roasting temperature was provided together with these data. Guyot et al. (1985) reported even greater expansion in the case of rapid roasting at high temperatures. Comparing final products of the same degree of roast, he found a significant influence of the roasting temperature on the volume development. This relationship was clearly confirmed in a comprehensive study by Ortolá et al. (1998) including *C. arabica* and *C. canephora* beans from six different origins. These coffees were roasted at temperatures of 220, 235, 250, 265, 280 and 295 °C to an identical degree of roast. Values of relative volume increase ranged for Colombian *Arabica* coffee from 1.59 to 1.84, and for *Robusta* from Uganda from 1.37 to 1.55.

Guyot et al. (1985) regarded the maximization of bean expansion as beneficial for quality. Also Small and Horrell (1993) aimed for maximum volume increase in order to produce high yield coffee. They reported that fast roasting (1 ... 3 min) of pre-dried (< 5 g /100 g wb) coffee beans leads to greatly expanded or "puffed" beans with a high extraction yield. Their physico-chemical model concept of bean expansion features the chlorogenic acids as key-components, since the authors detected a sharp decomposition of these acids with substantial CO_2 evolution in a temperature range close to the glass transition temperature T_g of the bean. Instanta-

neous pressure build-up during a softened stage of the bean would result in a "puffing" effect. Small and Horrell (1993) also realized the significant influence of the bean water content. They suggested to move the drying step outside the roaster in order to allow for more aggressive fast roasting conditions within the roaster. Concerning actual values of T_g, they refer to a value mentioned in a patent application by Brandlein et al. (1988). The patent authors stated T_g of coffee beans being around 216 °C. They described the softening effect of water in glass transition theory and attributed greater expansion of fast roasted beans to the higher water contents retained during high temperature roasting.

2.3.3 Changes of cell and pore structure during roasting

Chemical reactions, dehydration and the large volume increase during roasting are accompanied by profound structural changes of both the cell wall and the cytoplasm of the green bean. Wilson et al. (1997) reported the proteinaceous/polysaccharide cytoplasmatic matrix of green beans starts to denature after the initial stages of roasting. Oil droplets coalesce and finally form a layer that "flows" around the inner surface of the cell wall. A further series of publications dealt with the microstructure in fully roasted beans. Roasted bean tissue presents excavated cells with the, at first glance, unaltered cell walls building a framework. This structure has been extensively described using light microscopy, scanning electron microscopy (SEM) and image analysis (Bürgin, 1969, Dentan, 1977, Dentan and Illy, 1985, Puhlmann et al., 1986, Massini et al., 1990, Gutiérrez et al., 1993, Illy and Viani, 1995, Wilson et al., 1997). The voids of excavated cells can be regarded as macropores and, apart from possible major tissue cracks, make up for the main part of the bean porosity. Radtke (1975) reported porosity values in roasted beans ranging from 0.38 to 0.49 µm depending on the origin and pretreatment of coffee. Kazi and Clifford (1985) found different average cell sizes for "high yield" (34 ... 40 µm) and "regular" (21 ... 23 µm) coffees, respectively. Massini et al. (1990) described the development of pores in the course of roasting using SEM and reported the entire bean surface to be cracked after 10 min of roasting. However, their micrographs of the roasted bean surface seem to be difficult to interpret. Gutiérrez et al. (1993) presented a comprehensive investigation on coffee bean porosity. Various physical methods as well as SEM and image analysis were used to determine the porosity of coffees roasted at

different temperatures to the same degree of roast. Again, high temperature roasted coffee was found to have a statistically significantly greater macropore area than low temperature roasted products.

A number of authors assume that roasting alters the porosity of the cell wall (Saleeb, 1975, Puhlmann et al., 1986, Massini et al., 1990, Gutiérrez et al., 1993, Illy and Viani, 1995, Wilson et al., 1997). So far, very little is known about the formation of *micro*pores in the cell wall as affected by roasting conditions. The fate of the plasmodesmata during roasting is unknown. Saleeb (1975) concluded from gas adsorption measurements that the macropores of roasted beans are accessible through very narrow micropores of molecular magnitude (2.8 nm radius) which form a so-called ink-bottle structure. In contrast, Wilson et al. (1997), using electron microscopy, found two different types of micropores of an average radius of 50 nm and 5 nm, respectively.

Roasting-induced changes in pore structure have a major impact on the final product quality. The pore structure controls mass transfer phenomena during storage and may determine the high gas adsorption capacity and the gasdesorption properties (Saleeb, 1975, Radtke, 1975, Massini et al. 1990). Fine micropores are assumed to allow the mobilized coffee oil to migrate to the bean surface (Puhlmann, 1986, Illy and Viani, 1995, Wilson et al., 1997). Moreover, the loss of aroma compounds and the staling process are probably related to microstructure (see chapter 2.4.4).

2.4 Flavor profile of green and roasted coffee

2.4.1 Analysis of coffee flavor

Since the aroma of roasted coffee is based on a complex mixture of organic compounds that occur only in traces and are volatile by nature, a sophisticated methodology is required for qualified research on coffee aroma. Although instrumental analysis has been advancing on an incredible pace during the last three decades, the investigation of complex food aroma remains a demanding task. Generally, it involves the following steps (Marsili, 1997):

- Isolation and concentration of volatiles
- Separation
- Identification
- Quantification
- Investigation of sensory properties and impact on human aroma perception
- (Validation of analytical results with the help of models)

The methods used for isolation of food flavor compounds are most critical for the result of an aroma analysis. Sample preparation is complicated by a number of factors, such as low concentration levels, variation of volatility, instability, matrix-volatile interactions and the high complexity of aroma composition (Marsili, 1997). Headspace analysis and distillation techniques are the most suitable isolation methods (Clarke and Macrae, 1985). Solvent extraction and vacuum distillation are commonly used distillation techniques. However, each method implies preferential isolation of some compounds and discrimination of others. Therefore, it is strongly recommended to use at least two different isolation methods in order to be able to compare the results (Marsili, 1997).

The simultaneous distillation/extraction (SDE) according to Likens and Nickerson (1964) is one of the most widely used and valuable solvent extraction techniques for roast coffee. The SDE apparatus provides for the simultaneous condensation of the steam distillate and an immiscible organic solvent. Both liquids are continuously recycled, and thus the steam distillable, solvent soluble compounds are transferred from the aqueous phase to the solvent (Marsili, 1997). This method has been successfully applied to coffee in a series of investigations by various authors (e.g.

Bade-Wegner et al., 1993 and 1997, Holscher et al., 1990, Vitzthum et al., 1990). It is convenient, requires simple handling, gives good recovery and limits time consumption (Holscher and Steinhart, 1991). One of the disadvantages of the method was found to be the relatively great heat impact on the sample that might generate artefacts.

Vacuum distillation, more accurately described as direct solvent extraction with subsequent high vacuum transfer, presents another widespread isolation technique applied on coffee (e.g. Clarke and Macrae, 1985, Blank et al., 1991 and 1992, Holscher et al., 1990 and 1991). A solvent extract is obtained from ground coffee. The aroma fraction is then separated from the non-volatile compounds by means of a high vacuum transfer to a series of cryo-traps. It yields an aroma isolate with an odor that resembles very much the odor of the original sample. The main advantages of this method lie in the relatively low heat impact to the sample and improved isolation of polar and hydrophilic volatiles, since no water is in contact with the sample.

The complex composition of coffee aroma usually makes it impossible to separate all volatile compounds in one gas-chromatographic run. A pre-fractionation is generally required, which in most cases is carried out by column chromatography or preparative high performance liquid chromatography (prep-HPLC). A description of these procedures can be found in Bade-Wegner et al. (1993), Blank et al. (1992), Holscher et al. (1990), Vitzthum et al. (1990). Subsequent separation by gas chromatography (GC) requires a high performance capillary column. For the same reasons as outlined above for isolation techniques, it is recommended to use at least two different types of these stationary phases (Marsili, 1997).

Usually, the flame ionization detector (FID) is the preferred device for quantification of GC separated compounds. Accurate quantification can be difficult for certain flavor compounds which occur frequently in extremely low concentration levels (Grosch et al., 1990). Stable isotope dilution assay (SIDA) is a suitable technique to overcome this problem. Generally, the identification of compounds is performed by gas chromatography mass spectrometry (GC-MS).

Gas chromatography olfactometry (GC-O), sometimes referred to as "GC-sniffing", is an important analytical tool in aroma research because it characterizes the odors of single compounds emerging from the sniffing port of the instrument (Marsili, 1997). Here, the human nose acts as the detector used for evaluating the effluent of the GC column. Extract dilution techniques, such as CHARM (Acree et al., 1984) or AEDA (Grosch, 1993), provide means to even evaluate the relevance and impact of a single compound within the entire aroma profile. They involve stepwise dilution of the extract and are based on the principle, that the higher the dilution at which the compound can be detected by GC-O, the greater its contribution to the aroma of the food. However, GC-O also implies a series of limitations. Marsili (1997) describes the "out of context effect", the "contrast effect", human limitations and systematic limitations imposed by the test design. Therefore, the result of such an analysis should be checked and confirmed by sensory analysis of models (Marsili, 1997, Grosch, 1995).

2.4.2 Flavor of green coffee beans

Although green coffee beans are not consumed as such and are generally regarded as having no pleasant aroma or flavor, the volatiles of green beans were investigated, since they do possess a large number of volatiles (Clarke and Macrae, 1985). 55 new compounds were added to 52 volatiles already known by Vitzthum et al. (1975). Surprisingly, the authors identified even 13 pyrazines, although these are generally regarded as products resulting from heat treatment. They found that the odor of green coffee beans is mainly caused by methoxypyrazines. According to recent literature by Holscher and Steinhart (1995) more than 200 green coffee volatiles have been identified so far. Only a small number of these compounds actually have an aroma impact on the typical flavor of green coffee. Holscher and Steinhart (1995) also added some 30 newly identified volatiles from their experimental work. They found that a majority of all identified compounds possess a carbonyl function and are known breakdown products generated during autoxidation of lipids. The list includes hydrocarbons (e.g. ethane, i-pentane, etc.), aldehydes and ketones (e.g. ethanal, propanal, n-butanal, 2-butanone, 2,3-butanedione, 2,3-pentanedione etc.), acids, esters, lactones, nitrogen compounds, sulfur compounds (e.g. methional) ethers, halogens, phenols and furans (e.g. 2-methyl-

furan, furfural, etc.). Among the newly identified compounds were for instance hexanal, (E)2-nonenal, (E,Z)2,4-decadien-al, (E,E)2,4-decadienal, linalool, β-damascenone, 3-methyl-2-buten-1-ol and 2- as well as 3-methylbutyrate. Moreover, most of these compounds are also found in roast coffee.

2.4.3 Flavor profiles of roasted coffee

The chemical reactions that are induced by roasting produce a vast amount of different volatiles. So far, more than 800 different volatiles from a wide range of chemical classes have been identified in roast coffee (Nijssen et al., 1996, Flament, 1989). Investigations on the Maillard reaction and the volatile fraction of roast coffee have been reviewed among others by Clarke and Macrae (1985), Clarke (1990), Ho et al. (1993) and Reineccius (1995).

The reaction pathways of roast aroma formation have been reviewed by Holscher and Steinhart (1994). As they are of a very complex nature, a number of studies has been devoted to aroma formation in model systems. Stahl and Parliment (1993) reported on the generation of 2-furfurylthiol in cysteine-ribose model systems and found increasing quantities with increasing temperatures and roast time. Also Hofmann and Schieberle (1998a) investigated the formation of 2-furfurylthiol in various precursor systems. They suggested that different formation pathways for 2-furfurylthiol may run in parallel during food processing. The authors also found the formation of various pyrazines, 2-acetyl- and 2-propionyl-2-thiazoline from cysteine and carbohydrates to be dependent on the system water content (Hofmann and Schieberle, 1998b). Heat treatment in dry systems and increasing temperatures favored pyrazine formation. Bohnenstengel and Baltes (1992) reported on well known and newly identified volatiles resulting from asparagine/glucose and aspartic acid/glucose mixtures under roasting conditions.

So far, very little information is available on the formation development of aroma compounds in coffee beans *during* roasting and the influence of different roasting conditions. Silwar and Lüllmann (1993) reported on this subject in an investigation with *Robusta* coffees. Coffee samples were roasted on a laboratory scale roaster at different temperatures for a constant length of time of 5 min, resulting in products of various degrees of roast. The authors stated from cup testing that aroma formation

starts around 170 °C, when a peanut-like roast note can be perceived. At 180 to 190 °C coffee-like flavor arose, whereas the "real" flavor of roasted coffee only appeared at 220 to 230 °C. After passing this point, the flavor was judged to be slightly over-roasted (240 °C) and typically over-roasted (250 ... 260 °C). This study did also demonstrate a continuous increase of the total amount of volatiles with increasing temperature up to 250 °C, followed by decreasing quantities beyond this temperature. Similar developments were described for furans and pyrazines. Furans and caramel compounds were found to be fully developed at 230 to 240 °C. 2-furfurylthiol continued to be formed up to 260 °C. The formation of pyrazines generally reached a maximum at 250 °C. Beyond this temperature they are assumed to be incorporated in melanoidins. Still, the group of pyrazines is heterogeneous and the respective compounds were found to react individually.

Another recent study by Mayer et al. (1999) dealt with the influence of coffee origin and the degree of roast on concentrations of aroma compounds in blends of *C. arabica*. For a series of compounds, the authors found considerable differences in concentration depending on the origin of blend. The degree of roast (light, medium and dark) had the greatest impact on propanal, 2(5)-ethyl-4-hydroxy-5(2)-methyl-3(2H)-furanone, guaiacol, 4-ethyl-guaiacol, 2-furfurylthiol, 3-methyl-2-buten-1-thiol and methanethiol. In blends of Colombia and Kenya coffees guaiacol and 2-furfurylthiol developed unhindered and were greatly increased with increasing degree of roast. Other compounds such as 2,3-butanedione and 2,3-pentanedione developed to a maximum for a medium degree of roast and exhibited lower concentrations in dark roasted coffees.

In recent years, more research has been addressed to the sensory relevance of volatile compounds and the identification of key odorants in coffee. Olfactometric investigations revealed an impressive variety of different aroma qualities in coffee. However, they also showed that only a small number of potent aroma compounds actually dominate the sensory perception (Holscher et al., 1990). These most important aroma contributors were termed *aroma impact compounds*, *aroma key compounds*, *character impact odorants* or just *potent odorants*. An overview on selected frequently cited aroma impact compounds is provided in Table 2.

Tab. 2: *Selection of frequently cited aroma impact compounds in roasted Arabica coffee.*

Compound	References (incomplete)
2,3-Butanedione (= Diacetyl)	Blank (1992), Grosch (95, 96), Semmelroch (1995a, 96)
ß-Damascenone (= 2,6,6-Trimethyl-1,3-cyclohexadienyl)	Holscher (1990), Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a, 1995b, 1996)
2,3-Diethyl-5-methyl pyrazine	Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a, 1995b, 1996)
2-Ethyl-3,5-dimethyl pyrazine	Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a, 1995b, 1996)
4-Ethyl guaiacol	Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a, 1995b, 1996)
5-Ethyl-3-hydroxy-4-methyl-2[5H]-furanone (= Abhexon)	Blank (1991, 1992), Grosch (1996), Semmelroch (1995b, 1996)
2-Furfurylthiol (= Furfuryl-mercaptan) (= 2-Furanmethanthiol)	Holscher (1990), Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a, 1995b, 1996)
Guaiacol	Holscher (1990), Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a, 1995b, 1996)
3-Hydroxy-4,5-dimethyl-2[5H]-furanone (= Sotolon)	Blank (1991, 1992), Grosch
4-Hydroxy-2,5-dimethyl-3[2H]-furanone (= Furaneol)	Holscher (1990), Blank (1991, 1992), Grosch (1996), Semmelroch (1995b, 1996)
2-Isobutyl-3-methoxy pyrazine	Holscher (1990), Grosch (1996)
3-Isobutyl-2-methoxy pyrazine	Blank (1991)
Linalool	Blank (1991, 1992)
3-Mercapto-3-methylbutylformiate	Holscher (1990, 1991), Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a, 1995b, 1996)
Methional (= 3-Methylthio-1-propanal) (= 3-Methyl-mercapto-propionaldehyde)	Holscher (1990), Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a, 1995b, 1996)
2-/3-Methyl butanal	Grosch (1995, 1996), Semmelroch (1995a, 1996)
3-Methyl-2-buten-1-thiol	Holscher (1990, 1991), Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a)
2-/3-Methyl butyric acid	Holscher (1990), Blank (1992)
2-Methyl-3-furanthiol (= 3-Mercapto-2-methylfuran	Holscher (1990), Blank (1991, 1992), Grosch (1995, 1996)
2,3-Pentanedione	Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a, 1996)
2,3,5-Trimethyl pyrazine	Blank (1991, 1992), Grosch
Vanillin	Blank (1991, 1992), Semmelroch (1995a, 1995b, 1996)
4-Vinylguaiacol	Holscher (1990), Blank (1991, 1992), Grosch (1995, 1996), Semmelroch (1995a, 1995b, 1996)

Tressl and Silwar (1981) investigated sulfur-containing aroma compounds and determined the threshold of 2-furfurylthiol. They found that in concentrations as low as 0.01 to 0.5 ppb 2-furfurylthiol was perceived like freshly roasted coffee. From 1 to 10 ppb it possessed the aroma of stale coffee with a sulfury note. Thus, the authors stated that 2-furfurylthiol may be considered either as an aroma impact compound or an off-flavor compound, depending on the concentration. Vitzthum et al. (1990) regard 2-methyl isoborneol as responsible for the harsh, earthy and moldy aroma character of *Robusta* coffees. Holscher et al. (1990) determined the aroma impact compounds of roasted colombian coffee. As the most important compounds, they listed 2-methyl-3-furanthiol, 2-furfurylthiol, methional, 3-mercapto-3-methyl-butylformate, 2-isobutyl-3-methoxy pyrazine, 2-metylbutyrate, β-damascenone and furaneol. Three of the animal-like, catty smelling sulfur-containing aroma impact compounds were further described by Holscher and Steinhart (1991). Another extensive list of aroma impact compounds was provided by Blank et al. (1991 and 1992). 3,5-dimethyl-2-ethyl pyrazine, β-damascenone, 3-mercapto-3-methylbutylformate and 2-ethyl-3,5-dimethyl pyrazine turned out to be the three most powerful aroma contributors of ground coffee in this study. However, these investigations also displayed that the situation in ground coffee may considerably differ from the one in the beverage. Semmelroch et al. (1995b), using stable isotope dilution assays, showed that the quantities of 14 aroma impact compounds differed significantly between *Arabica* and *Robusta* coffees. Grosch et al. (1995) provided another comprehensive list of aroma impact compounds in coffee. Semmelroch et al. (1995b) determined from headspace analysis the following key odorants in ground coffee powder: 2,3-butanedione, 2,3-pentanedione, 3-methyl-2-butenthiol, methional, 2-furfurylthiol and 3-mercapto-3-methylbutylformiate. A subsequent investigation by Semmelroch and Grosch (1996) with stable isotope dilution assays and sensory experiments yielded yet another list of aroma impact compounds of coffee brews. A summery on studies concerning the aroma of roasted coffee was given by Grosch et al. (1996). Finally, a recent investigation on the influence of various aroma impact compounds on sensory perception indicated a great influence of 2-furfurylthiol and 4-vinylguaiacol.

Concerning the aroma composition, some interesting parallels to coffee can be found in other roasted foodstuffs. 2-ethyl-3,5-dimethylpyrazine, 2,3-butanedione, 1-octen-3-one and 3-methylbutanal were identified as important contributors to the aroma of roasted chicory (Baek and Cadwallader, 1998). Ziegleder (1991) reported on the aroma fraction of roasted cocoa. About 20 aroma compounds were identified for the first time. The listing also includes major contributors to coffee aroma, such as 4-hydroxy-2,5-dimethyl-3[2H]-furanone (furaneol), 2-/3-methyl butyrate, guaiacol, 2,3-butanedione and linalool. Another comprehensive source for comparison of coffee, cocoa and tea is provided by Flament (1989).

Sensory perception of coffee beverages is not exclusively determined by aroma compounds, but also by other important flavor compounds, such as organic acids like acetic acid and citric acid, and bitter components. In addition, the content of solids in the beverage contributes to the "body" of the beverage and therefore affects the sensory product properties. Illy and Viani (1995) provide a detailed description of the factors that constitute the "cup quality" of a coffee beverage.

2.4.4 Staling of roast coffee

Since the unprotected aroma of freshly roasted coffee is subject to severe quality losses during storage, aroma freshness becomes a crucial quality parameter. It was realized early that adequate packaging can significantly extend shelf-life of roast coffee. On the other hand, it is not easy to measure the freshness of coffee. Vitzthum and Werkhoff (1979) suggested the use of certain quantity ratios of selected indicator substances, such as 2-methylfuran in relation to 2-butanone or methanol in relation to methylfuran. They showed the promotion of staling due to elevated storage temperatures, as well as the accelerated staling process of ground coffee as compared to whole beans. Kwasny and Werkhoff (1979) used the same measure for freshness and found greater staling rates in dark roasted coffees as compared to light roasts. Arackal and Lehmann (1979) confirmed the beneficial effects of newly developed vent packaging materials on shelf-life. Tressl et al. (1979) pointed out the important role of furfurylmercaptan in the staling process. Spadone and Liardon (1989) used a combined approach for the investigation of staling, including headspace analysis, multivariate statistics and sensory analysis. The authors reported significant qualitative changes of roast coffee, even when stored under the

best possible conditions. High product humidity and elevated temperatures were found to be the most detrimental storage parameters. O_2 had an influence on coffee samples stored in cans. Similar extent of aroma modification was detected for sample series gassed at levels of 1 % and 3 % O_2, whereas maximum staling was found in coffee samples packed in air. Rather unexpectedly, the author found both O_2 dependent and independent chemical reactions involved in the staling process. Kallio et al. (1990) investigated the development of headspace volatiles during storage of ground coffee in air tight packages filled with CO_2 and air, respectively. Surprisingly, they reported similar rates of alteration of most of the volatiles analyzed for both storage conditions, though conceded methodological limitations. Steinhart and Holscher (1991) suggested that coffee freshness is constituted by low-boiling components, such as low-molecular sulfur compounds, Strecker-aldehydes and α-dicarbonyls. The authors regarded methane thiol as the most important indicator of coffee freshness. Leino et al. (1991) characterized the headspace of stored *C. arabica* and *C. canephora* coffees and the sensory properties of the respective beverages. The ratios of 2-methylfuran/2-butanone, acetone/propanal and 2-methylfuran/propanal were used as indicators of coffee freshness. Storing the coffee for 18 months at room temperature led to several changes in the aroma compounds profile, whereas the perceived odor intensities did not change during storage. Hence, the concluded that certain compound ratios are suitable to monitor the ageing process, but are inadequate to predict the sensory quality of the beverage. In a further study these ratios were used to investigate the staling process of two commercial Finnish coffee blends (Leino et al., 1992). Holscher and Steinhart (1992a) used headspace cryo-focusing analysis, GC-olfactometry and statistical discriminant analysis. As reported earlier, they found again great correlation between the loss of methanethiol and the loss of coffee freshness during storage. In an additional study Holscher and Steinhart (1992b) formulated a two step model concept of staling in roast coffee. They stated that a first step is determined by physico-chemical processes that lead to a decrease of volatiles. A second step is characterized by oxidative reactions, resulting in aroma-relevant oxidation products.

3 Experimental

3.1 Raw material

Raw material selection was basically targeted to maximum continuity of coffee quality over a long-term period. Green beans of defined varieties and single origin were used in order to minimize product inhomogenity. Still, using different lots from the same supplier but from different crop years, the coffee quality varied in a considerable, but acceptable range. Coffees were obtained from two Swiss import companies.

Main experiments

In general, if not specified otherwise, a wet-processed *C. arabica* Linn. variety from Colombia with a water content of 10 to 11 g / 100 g (wb) was used. Some experiments were carried out with a wet-processed *C. arabica* Linn. variety from Costa Rica.

Comparison

For trials with the intention of a comparison of different raw materials, coffees from both species *C. arabica* and *C. canephora* were roasted. Wet-processed *C. arabica* beans originated in Colombia, Costa Rica and Guatemala, dry-processed Santos was imported from Brazil. Beans of *C. canephora* originated in Uganda.

Blends

In trial series involving industrial scale roasting a commercial blend of 100 % *C. arabica* beans was used. Furthermore, a number of roast coffee brands was purchased for color comparison.

3.2 Roasting

3.2.1 Laboratory roasting trials

Fluidized-bed hot air laboratory roaster

Roasting experiments were carried out with a fluidized-bed hot air laboratory roaster in batches of 100 g green beans. The roaster was built by G.W. Barth GmbH & Co., D-Freiberg/Neckar, for a research project on nut roasting (Perren, 1995) and adapted for coffee roasting. It allowed for coffee roasting under well-defined process conditions with accurate control of hot air temperature, air velocity and bean core temperature. Fluidized-bed roasting and cooling were performed in separate sections. Steam injection into the hot air inlet and water spray injection into the cooling air provided options for humid atmosphere roasting and water quench cooling, respectively.

A schematic drawing of the roaster is given in Figure 2, and technical data are provided in Table 3.

Roasting section: Air of ambient temperature was sucked in by a radial fan RD2 (Elektror, D-Esslingen/Neckar). Air velocity was controlled by means of a flap valve in the inlet stream in front of the fan and measured by an airflow meter (Schiltknecht, CH-Gossau/ZH). The air was heated to roasting temperatures by two parallel electrical heaters S10000 8D8 (Leister, CH-Kägiswil). Optionally, satura-

Tab. 3: *Characteristic technical data of the laboratory roaster.*

Hot air temperature	20 ... 300 °C
Max. deviation of hot air temperature (isothermal processes)	± 1 °C
Hot air velocity	1.0 ... 3.0 ms^{-1}
Hot air flow rate	0.47 ... 1.41 m^3 min^{-1}
Capacity	100 g green beans
Cooling air flow rate	0 ... 2.8 m^3 min^{-1}
Cooling time for 100 g beans to achieve $T_{bean} < 40$ °C (without water quenching)	60 s

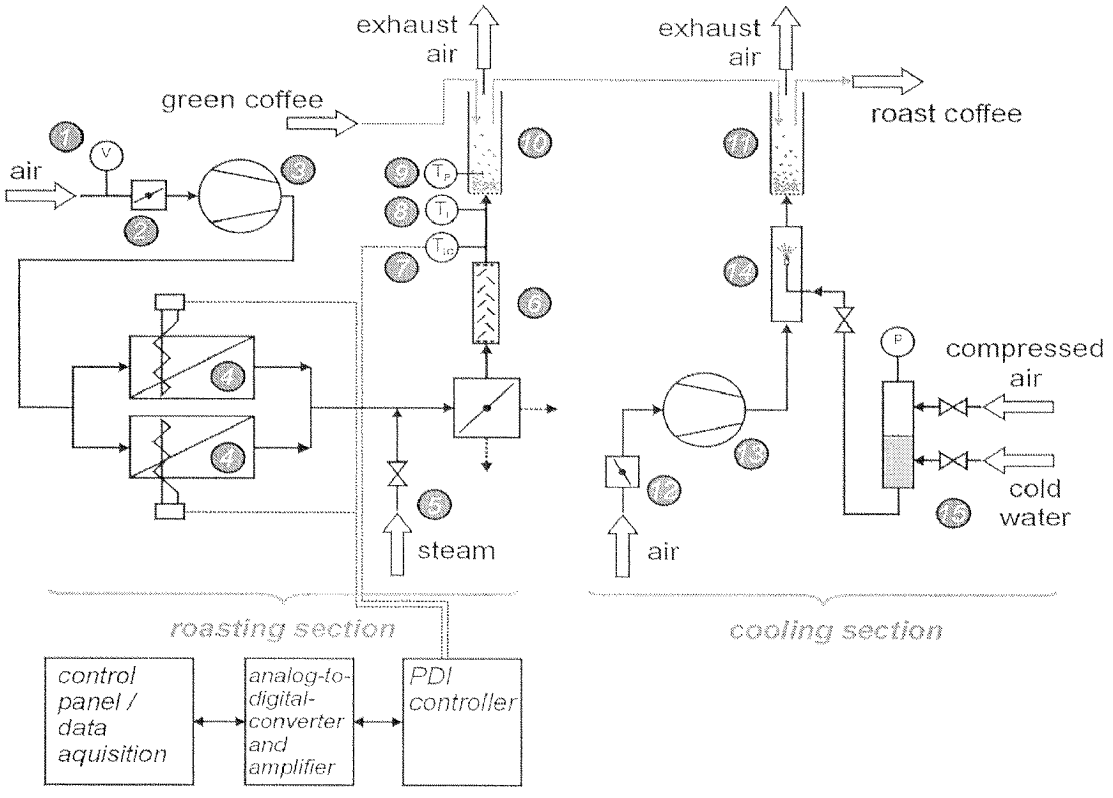

Fig. 2: *Fluidized-bed hot air laboratory roaster. 1: Airflow meter for inlet air velocity. 2: Inlet air flap valve. 3: Inlet air radial fan. 4: Electrical heaters. 5: Optional steam injection. 6: Static air mixing element. 7: Temperature probe PT100 for* $air_{in(controller)}$ *temperature. 8: Thermocouple for* air_{in} *temperature. 9: Thermocouple for recording coffee pile temperature. 10: Roasting chamber. 11: Cooling chamber. 12: Cooling air inlet flap valve. 13: Cooling air radial fan. 14: Water quench spray injection. 15: Pressurized water container.*

ted steam was fed to the hot air stream (176 g m^{-3} air). The air stream was equilibrated by a static mixing element ME SMV-X DN100 (Sulzer Chemtech, CH-Winterthur). The roasting chamber for batch roasting consisted of a stainless steel tube of 10 cm diameter and a height of 24 cm with a wire mesh bottom for air inlet and a removable wire mesh cover on the top. Silver skins coming off during roasting were collected at the air outlet by a vacuum suck in system. Hot air tempe-

rature was measured by a PT100 temperature probe right before the roasting chamber and used to control the heater's power.

Cooling section: The roasted beans were transferred manually to the cooling section by removing the roasting chamber and pouring the beans into the cooling chamber. An air stream of ambient temperature ensured a fast fluidized-bed cooling of the beans in the cylindric cooling chamber. For water quench cooling cold water was sprayed through a hollow cone nozzle 212.054.17.AC (Lechler, D-Metzingen) into the air stream before the chamber.

The control and data acquisition system consisted of a PDI-controller KS 4580 (Philips, D-Kassel), an analog-to-digital converter/amplifier MIDAS (DMP, CH-Hegnau-Volketswil) and a PC with the software FLOWCHART (ComTec, D-Jülich).

Measurement of bean core temperature

For determination of bean core temperature 2 or 3 beans per batch of 100 g green coffee were prepared for placement of thermocouples in the bean core. Fine holes were drilled into the bean tissue using a hand drill of 0.3 mm diameter. A thermocouple type K with 0.25 mm diameter (Thermocoax, F-Surèsnes) was inserted into the holes in a barb arrangement as illustrated in Figure 3a. Special attention was paid to ensure that the point of measurement lay in the bean core tissue and not in the folding gap. The mounted thermocouples were installed in a special fixation device described by Perren (1995) and in a patent by Perren et al. (1994), by which the thermocouples could be lead into the cylindric roasting chamber. Additional thermocouples were placed in the vicinity of the beans in order to measure pile temperatures. The batch of green beans was added to the chamber before transferring the entire setup into the pre-heated laboratory roaster. This arrangement allowed for partially free motion of the thermocouple-equipped beans within the fluidized batch without loosing them. All thermocouples were connected with the data acquisition system of the roaster and temperatures were monitored and recorded online. At least 10 temperature curves from individual beans were averaged in order to overcome bean inhomogenities.

Single bean roasting and optical online process recording

A roasting chamber with sightglass and an optical setup including a stereo microscope was developed for optical online process recording. Two plane and thermoresistant sightglasses (7×12 cm) were installed parallel in a cylindric stainless steel roasting chamber (Ø 10 cm, height: 27 cm) changing the shape of cross section gradually from circular to nearly square in the glass part and back to circular again. One green coffee bean was prepared for core temperature measurement and fixed by two tightened thermocouples inserted as illustrated in Figure 3b. Again, the special fixation device described by Perren (1995) was integrated in the roasting chamber in order to lead the thermocouples inside. A stereo microscope SZ 6045TR (Olympus, CH-Volketswil) was placed in a horizontal position in front of the sightglasses. For bright illumination four cold light sources were focused on the bean. A color 3CCD video camera KY-F55B (JVC, CH-Oberwil) was attached to the stereo microscope for image acquisition. Pre-heating of the roaster was only partially possible.

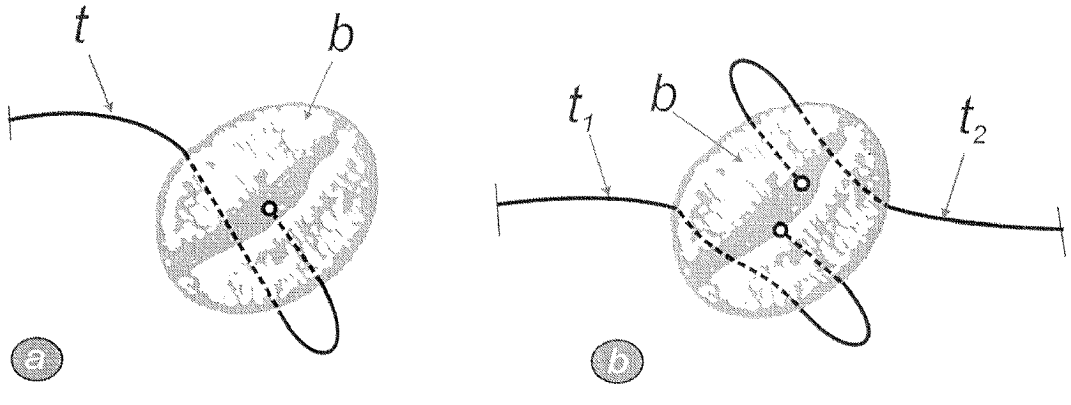

Fig. 3: *Fixation of thermocouples in the bean for measuring bean core temperature. 3a: Scheme for one thermocouple (t), allowing for partially free motion of the bean (b). 3b: Scheme with two thightened thermocouples (t_1 and t_2) to keep the bean (b) in a fixed position for optical observation.*

Isothermal roasting processes

Isothermal processes are suitable to investigate the general influence of temperature in the roasting process. For the majority of experiments green coffee beans were roasted in either a high-temperature short-time roasting process (HTST) at 260 °C, or in a low-temperature long-time process (LTLT) at 220 °C according to the process characteristics as given in Table 4. In some experiments, a medium-temperature medium-time process (MTMT) with a hot air temperature of 240 °C and a roasting time of 300 s was applied. In order to be able to compare the two main processes roasting was targeted to the same degree of roast, based on roast loss and final product color. Typical product properties are also presented in Table 4.

Tab. 4: *Roasting parameters for the HTST and LTLT process and typical properties of roasted products.*

	HTST roasting	*LTLT roasting*
Process parameters:		
Hot air temperature	260 °C	220 °C
Hot air flow rate	1.08 m^3 min^{-1}	1.08 m^3 min^{-1}
Hot air velocity	2.3 m s^{-1}	2.3 m s^{-1}
Roasting time	155 ... 180 s	540 ... 720 s
Cooling air flow rate	1.41 m^3 min^{-1}	1.41 m^3 min^{-1}
Product properties (typical values):		
Color (L*/a*/b*)	24.06 / 9.26 / 11.33	24.02 / 9.27 / 11.17
Roast loss (RV)	15.33 %	15.81 %
Water content	2.68 g /100 g (wb)	2.15 g /100 g (wb)

Roasting processes with temperature profile

In industrial practice coffee is not roasted under isothermal conditions. Therefore, the effects of pre-heating, continuous temperature increase or reduced temperature in the final stage of roasting on product properties were studied by developing four temperature profile processes (Table 5), (a) high temperature with a reduced final stage (HL), (b) continuous temperature increase from low to high (LHC), (c) pre-

heating temperature with subsequent LHC process (PLHC), (d) pre-heating temperature, high temperature at medium stage and reduced temperature at final stage (PHL).

Tab. 5: *Temperature-time profiles for non-isothermal roasting processes (Set values).*

Process	*Temperature*	*Time*	*Total roasting time*
HL	240 °C	150 s	
	220 °C	210 s	360 s
LHC	continuous increase 150 → 240 °C	270 s	
	240 °C	55 s	325 s
PLHC	150 °C	180 s	
	continuous increase 150 → 240 °C	270 s	
	240 °C	50 s	500 s
PHL	150 °C	180 s	
	no hot air flow (technical)	90 s	
	240 °C	140 s	
	220 °C	210 s	620 s

Roasting of beans with adjusted initial water content

Trial series dedicated to the influence of initial green bean water content on roasting properties were carried out by adjusting the original water content of 11.1 g / 100 g (wb) of a *C. arabica* variety from Costa Rica. Reduction of water content was achieved by vacuum freeze drying and resulted in products with water contents of 7.3, 5.5, 5.0 and 3.2 g /100 g (wb) bean, respectively. An increase of water content was accomplished by exposing the beans to a humid atmosphere with a water activity of $a_w = 0.90$ at a temperature of 37 °C for variable periods of time. Green beans with water contents of 14.4, 15.9 and 18.2 g /100 g (wb) bean were obtained.

3.2.2 Industrial roasting trials

Roasting trials and measurements on industrial scale were carried out in three different roasting systems. Commercial roasting conditions were recorded in the Probat RZ 3500Y and the Gothot Rapido-Nova systems. With the Barth CR-1250 system a series of new roasting processes were tested.

Recording of the roasting conditions in a Probat RZ 3500Y roaster

Description of the system

The RZ 3500Y (Probat, D-Emmerich) is a batch roasting system of the rotating-bowl type (Clarke and Macrae, 1987) as shown in Figure 4 and was operated at a capacity of 320 kg green beans. Coffee beans are fed into the center of a rotating horizontal bowl with a vertical shaft and are carried to the periphery of the bowl through centrifugal force assisted by hot air entering from the bowl bottom. On reaching a fixed multi-plate ring, they fall back to the center in spiral-shaped circuits surrounded by hot air. At the end of the roasting, the beans are discharged over the periphery and fall down into the cooling bowl that works on similar principles. Water quenching is applied first in the roasting chamber, and then in the cooling chamber. Exhaust air is partially recirculated to the burner.

Measurements

A shaft cover on top of the roaster provided access to the roasting chamber. Through this cover, 4 thin stainless steel tubes (Ø 2.5 mm) of various lengths (0.5 ... 1.2 m) were inserted into the roasting chamber, each of them leading one thermocouple type K of 1.0 mm diameter (Thermocoax, F-Surèsnes) to the points of measuring (MP_2 in Figure 4). Additional thermocouples were inserted through existing pipework into the hot air supplies and the air discharge stream near to the roasting chamber (MP_1 and MP_3 in Figure 4). Thermocouples were connected to a converter/ amplifier MIDAS (DMP, CH-Hegnau-Volketswil) and a PC-notebook with data acquisition software. A dew-point hygrometer was placed at MP_1 (Figure 4) to measure air humidity. The coffee was roasted in a 3-stage process with a total roasting time of approx. 270 s. In order to record roasting dynamics, samples were removed at regular intervals during roasting, cooled immediately and analyzed.

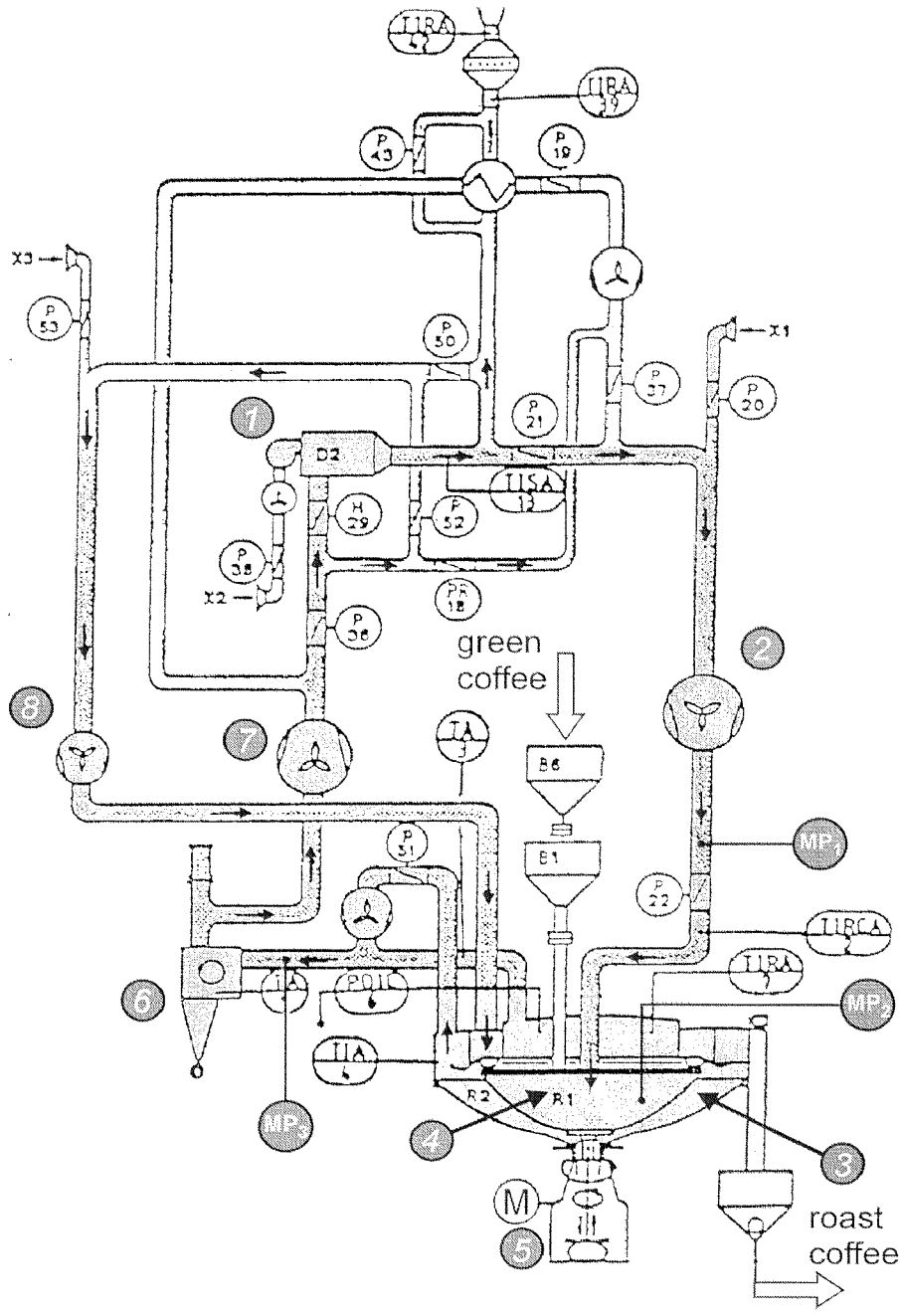

Fig. 4: *Probat RZ 3500Y industrial roasting system with a capacity of 320 kg (operation manual, Probat, D-Emmerich). 1: Burner. 2: Hot air supply blower. 3: Rotating cooling bowl. 4: Rotating roasting bowl. 5: Bowl drive. 6: Air discharge cyclone. 7: Air discharge blower. 8: Cooling air supply. MP: Points of temperature measurements, 1: Air inlet. 2: Roasting chamber. 3: Air discharge.*

Recording of the roasting conditions in a Gothot Rapido Nova roaster

The Rapido-Nova roaster (Gothot, D-Emmerich) consisted of a vertical drum for a coffee batch of 400 kg and a set of rotating paddles to increase the rate of heat transfer. A standard-type roaster of this kind has been described and illustrated by Clarke and Macrae (1987). In a similar way as for the Probat RZ 3500Y, 4 thermocouples were inserted into the roasting chamber and measurements were carried out in the same manner. A two-stage process with a total roasting time of approx. 354 s was used.

Roasting trials with a Barth CR-1250 roaster

The CR-1250 roaster (G.W. Barth Ludwigsburg GmbH & Co., D-Freiberg/Neckar) is a 50 kg batch roaster based on the design principles of the partially fluidizing nut roaster NR (Barth), described by Perren (1997). Different roasting processes with various temperature-time profiles were carried out, targeted to different degrees of roast.

3.3 General analytical methods

3.3.1 Roast loss

The overall weight difference between the green coffee batch and the roasted batch immediately after roasting and cooling was defined as *roast loss* (RL):

$$RL = 100 \cdot \frac{m_{green} - m_{roast}}{m_{green}} \quad (\%) \qquad \text{(equation 1)}$$

where: m_{green}: weight of green coffee beans (g)

m_{roast} : weight of roasted coffee beans (g)

The loss of organic dry matter was defined as *organic roast loss* (ORL) and was calculated by taking the water content of green and roasted beans and the roast loss into account:

$$ORL = 100 - \left[(100 - RL) \cdot \frac{dm_{roast}}{dm_{green}} \right] \quad (\%) \qquad \text{(equation 2)}$$

where: RL: roast loss (%)

dm_{green}: dry matter of green beans (g / 100 g, wb)

dm_{roast}: dry matter of roasted beans (g / 100 g, wb)

3.3.2 Color

Color was measured with a tristimulus colorimeter Chroma Meter CR-310 (Minolta, CH-Dietikon) with a reflection area of 19.6 cm^2. Samples of coffee beans were ground finely in a household two-disk coffee grinder Espresso E20 (Turmix, CH-Rapperswil). The ground coffee was transferred into a petri dish and gently pressed to form an even surface. Color values were depicted in the CIE $L^*a^*b^*$ color space. Chromaticity was defined $C^* = \sqrt{a^2 + b^2}$.

3.3.3 Water content

Roasted coffee beans

Samples of roasted beans were ground finely in a household two-disk coffee grinder Espresso E20 (Turmix, CH-Rapperswil). Gravimetrical determination of roast coffee water content was carried out using either oven dehydration or an infrared dehydration apparatus.

Oven method: The determination was carried out according to the Swiss Food Manual (1973). 5 g ground coffee were dried at 103 °C for 5 h.

Infrared dehydration: Approximately 1 g ground roast coffee was weighed accurately into the loading tray of an infrared dryer LP 16 (Mettler, CH-Greifensee). The coffee was dried at 120 °C for 10 min.

Green coffee beans

Green coffee beans are hard and tough and not suitable for grinding. However, after a first dehydration step, the beans become more brittle and ready for grinding.

Therefore, a two-step dehydration procedure was used according to the Swiss Food Manual (1973). A pile of 100.0 g green beans was oven dried for 2 h at 103 °C and the weight loss recorded. The beans were then ground to particles smaller than 0.63 mm. A quantity of 5 g ground coffee was oven dried again during 5 h at 103 °C. The total water content was calculated combining the two weight losses.

3.3.4 Extraction yield

The determination of extraction yield was carried out according to the Swiss Food Manual (1973). A sieving fraction of ground coffee with a particle size between 0.25 and 0.63 mm, accounting for more than 30 % of the total coffee weight, was used for the analysis. A quantity of 10.0 g coffee was extracted with 200 mL water under specified conditions. 25 mL of the filtered extract were carefully evaporated on a water bath and oven dried for 3 h at 103 °C. The extraction yield is given as percent dry extract based on coffee dry matter.

3.3.5 Surface oil

Batches of roasted beans were stored in 500 mL septum flasks as used for gas desorption analysis. Oily beans were spread on a soft plate and thoroughly blotted off from the surface oil with absorbent Kleenex paper. Coffee oil residues on the flask were removed by ethanol. The amount of surface oil was then determined gravimetrically.

3.3.6 Antioxidative potential

The antioxidative potential of roast coffee due to the formation of antioxidant compounds during roasting was estimated by modifying a method for measuring the oxidation induction period as described by Hadorn and Zürcher (1974). Roast coffee was ground finely and 200.0 mg thereof with a particle size < 500 µm were put into the reaction vessel of a 679 Rancimat (Metrohm, CH-Herisau) together with 5.0 g soy oil. The reaction vessel was heated and kept at 100 °C and an air stream led through the oil. Headspace exhausts were lead into a water-filled measuring vessel and water conductivity was continuously measured. A sharp increase in conductivity indicates the end of the induction period.

3.4 Characterization of structural and physical properties of coffee beans

3.4.1 Volumetry

A displacement method based on a system described by Mohsenin (1986) was used to determine bean volume and bean density. A small container was filled with peanut oil (density 910 kg m^{-3} at 25 °C) and placed on a balance. A lot of 30 g of roasted beans was weighed into a wire basket which was suspended on a support beside the balance. The basket was immersed into the oil and moved up and down for 15 s in order to release air bubbles trapped between the beans. Immersion was carried out likewise with the empty basket. From the weight difference of the immersed basket with and without coffee beans and using oil density the bean volume was calculated. Bean density was computed as ratio of bean weight in air and bean volume. Relative bean volume was based on the volume of green beans, taking into account the weight loss during roasting.

3.4.2 Mercury porosimetry

Mercury porosimetry makes use of the properties of mercury as a non-wetting liquid and is based on the measure of mercury intrusion into the pores of a sample at various pressures. Higher mercury pressures allow for the intrusion of increasingly smaller pores. The inversely proportional relationship between the size of an intrudable circular pore and the applied mercury pressure is described by the Washburn equation (Adamson, 1990):

$$r = \frac{-2 \cdot \gamma_{Hg} \cdot \cos\theta_{Hg}}{p} \qquad \text{(equation 3)}$$

where: r: pore radius (m)

γ_{Hg}: surface tension of mercury ($\gamma_{Hg} = 0.5 Nm^{-1}$)

θ_{Hg}: contact angle of mercury ($\theta_{Hg} = 130°$)

p: pressure (Pa)

A mercury-porosimeter Carlo Erba 2030 (Carlo Erba Strumentazione, I-Rodano), with a macro- and a micropore unit was used. About 0.4 g roast coffee (4 - 6 bean halves) were placed in a dilatometer and evacuated in the macropore unit for some 15 min. The dilatometer was carefully filled with mercury and the sample was checked for macropores by increasing the pressure gradually to 100 kPa (1 bar). The dilatometer was then transferred to the micropore unit, where the pressure was gradually increased to 400 MPa (4000 bar) during 45 min and the volume of intruded mercury recorded. Pressure values were converted into values of "equivalent pore radius" using the Washburn equation. Assuming a mercury contact angle of 130° and a surface tension of 0.5 Nm^{-1}, measured macropores ranged from r = 50 µm to 6.43 µm and micropores from 6428 nm to 1.61 nm. The pore radius corresponding to the maximum in the distribution function was defined r_{main} = maximum $dV/d \log (r/r_0)$, where V is the cumulated pore volume and r_0 = 1 m (normalization, dimensionless exponent). The r_{50} value describes the equivalent pore radius at which 50 % of the total cumulated pore volume is filled with mercury. Porosity ε was defined as the ratio of absolute volume per g bean and absolute volume of intruded mercury per g bean.

In applying high pressures to foods a thorough evaluation of potential artefacts due to sensitive structures and careful interpretation of the results is required. This was accomplished for roast coffee beans by means of cryo-scanning electron microscopy and energy-dispersive X-ray microanalysis (Schenker et al., 1998). Further successful applications of mercury porosimetry to food have been reported for roasted nuts (Perren, 1995), air dried vegetables (Karathanos, 1996) and other foods.

3.4.3 Dynamic mechanical thermal analysis (DMTA)

DMTA was used to investigate softening phenomena of coffee bean structure during heating. Green coffee beans were manually ground with sandpaper to slices of approximately 3 mm thickness and with two parallel plain sides. One slice per run was clamped in a plate plate measuring geometry of a Solids Analyzer RSA II (Rheometrics, NJ-Piscataway, USA). A constant pre-load of 0.5 kg was kept on the sample while carrying out dynamic testing (oscillation) at a frequency of 1 Hz and

a strain amplitude of 1 % of the slice thickness. The temperature was continuously increased from ambient to 260 °C with a heating rate of 5 °C min^{-1}. The RSA II was operated with Firmware version 5.0.0 and Rhios software version 4.2.2. Storage modulus G' and loss modulus G'' were calculated online.

3.4.4 Electron microscopy

Cryo-scanning electron microscopy (Cryo-SEM)

The bean tissue structure was investigated by cryo-SEM, with a Philips 515 microscope (Philips, The Netherlands) equipped with a SEM cryo unit SCU 020 (Bal-Tec, FL-Balzers). Pieces of beans were frozen in liquid nitrogen, fractured by a scalpel and transferred to the cold stage of the preparation chamber. The samples were exposed to -80 °C for 10 min under $p < 2 \cdot 10^{-4}$ Pa and cryo-sputter-coated with 15 nm platinum. The specimens were examined at a temperature below -130 °C at an accelerating voltage of 12 kV.

Energy-dispersive X-ray microanalysis

Elemental analysis was performed in a Philips SEM, equipped with a Tracor® Northern energy-dispersive X-ray analysis system and as described in detail by Frey et al. (1996). The microscope was operated at an accelerating voltage of 25 kV and a working distance of 12 mm. Elemental mapping was carried out by energy window mapping. The spatial resolution was 64 × 64 pixels with a dwell time of 0.1 s. All spectra in the spot mode were acquired at a magnification of 10 000 for 60 s (live time) and a dead time of 24 s (40 %) in the energy range of 0 to 13 keV.

Scanning electron microscopy (SEM) of chemically fixed specimens

Small bean pieces were fixed by a 4 % glutaraldehyde solution in 0.1 cacodylate buffer (pH 7.4) at 4 °C, rinsed in the same buffer, post-fixed by 1 % Osmium tetroxide in cacodylate buffer at 4 °C and again rinsed in the same buffer. Specimens were dehydrated in a graded series of ethanol, transferred into water free acetone and critical point dried. They were sputter-coated with 50 nm of Au/Pd and analyzed with a field emission SEM Hitachi S-700. Images were recorded digitally with a Gatan Digi-Scan interface at an accelerating voltage of 10 kV.

Analysis of the microfibril network in the cell walls was carried out likewise using an in-lens field emission scanning electron microscope Hitachi S-900. Small tissue bars were fixed by a 3 % glutaraldehyde solution in 0.1 cacodylate buffer (pH 7.4) at 4 °C, rinsed in the same buffer, dehydrated in a graded series of ethanol, defatted in diethylether, transferred into acetone and subjected to critical point drying. The specimen was glued with conducting carbon colloid in a holder, placed into a freeze-fracture device BAF 300 and fractured at room temperature. Electron beam evaporation was carried out with 200 Hz of platinum carbon from an angle of 45 ° and 100 Hz of carbon perpendicular with rotating sample. The sample was transferred into the microscope. Micrographs were recorded digitally using the BSE-image with a Gatan Digi-Scan interface at an accelerating voltage of 10 kV.

Transmission electron microscopy (TEM)

Specimen preparation for TEM analysis was carried out with a modified procedure according to Angermüller and Fahimi (1982). Small bean pieces were fixed in half-strength Karnovsky's fixative at room temperature for 1 hour. After washing in 0.1 M phosphate buffer postfixation was done for 1 h in 1 % osmium tetroxide in 0.1 M imidazole buffer. Samples were then rinsed in distilled water and dehydrated in a graded series of ethanol with stepwise embedding in Epon/Araldite resin. Ultrathin sections were cut using a Reichert-Jung ultramicrotome and stained with uranyl acetate and lead citrate, before examining in a Hitachi H-600 transmission electron microscope at 100 kV. Images were recorded digitally using a Gatan slow-scan CCD camera.

3.5 Gas desorption measurement and gas analysis

Sample preparation

Batches of 100 g green beans were placed in 500 mL septum flasks immediately after roasting. Each flask was closed tight with a special rubber septum of 12 mm thickness and then evacuated in the headspace analysis system with a Trivac D8B vacuum pump (Leybold, D-Köln) during 2 min. The flasks were stored at room temperature in darkness while bean gas desorption took place.

Headspace analysis

Sampling of headspace was carried out with the equipment and method described by Bertoli (1989) and Margadant (1991). Total headspace pressure was recorded. Two gas chromatographs were operated in parallel to monitor O_2, N_2, CO_2 and CO on one hand, and short-chain hydrocarbons and other gases on the other hand. Details on analytical conditions are given in Tables 6 and 7.

Tab. 6: *Analytical conditions for determination of O_2, N_2, CO_2, CO and Ar in coffee headspace.*

Gas chromatograph	Fisons GC 8340 (Brechbuehler, CH-Schlieren)
Packed column 1 (right)	Porapak Q 80/100 mesh; 3 m × 2 mm glass
Packed column 2 (left)	Molecular sieve 5Å 60/80 mesh; 3 m × 2 mm glass
Hot wire detector	Body temperature 150 °C; filament temperature 240 °C; attenuation 1; gain 10×
Oven temperature	60 °C, isothermal
Injector temperature	100 °C
Carrier	Helium 5.0
Carrier flow column 1	24.0 mL min^{-1} (DPFC flow mode)
Carrier flow column 2	75.0 mL min^{-1} (DPFC flow mode)
Polarity	Polarity change after elution of column 1 peaks
Sample injection	Electro-activated measuring valve with 2 sample loops of 250 µL volume each
Software	Chrom-Card, version 1.17

Tab. 7: *Analytical conditions for determination of short-chain hydrocarbons and other gases in coffee headspace.*

Gas chromatograph	Fisons 8330 (Brechbuehler, CH-Schlieren)
Packed column	Alumina F1, 60/80 mesh; 3 m × 2 mm glass
FID-detector	310 °C; Range 1; attenuation 0
Oven temperature programming	Iso-stage 1: 90 °C, 1 min Rate 1: 15 °C min^{-1} Iso-stage 2: 300 °C Cooling
Injector temperature	250 °C
Carrier	Helium 5.0
Carrier flow	DPFC flow mode, 20.0 mL min^{-1}
Detector gases	Air 120 kPa; Hydrogen 60 kPa; no make up gas
Sample injection	Measuring valve with 2 mL sample loop
Software	Chrom-Card, version 1.17

The total amount of gases released from the beans was calculated from the headspace pressure. An external standard gas mixture of CH_4, C_2H_6, C_3H_8, nC_4H_{10}, nC_5H_{12} and nC_6H_{14} (2 vpm each, in N_2; Garbagas, CH-Zurich) was used for quantitative determinations of hydrocarbons. Identification of peaks was accomplished by comparison of retention times from reference substances.

3.6 Analysis of coffee aroma compounds and flavor

3.6.1 General methodological considerations

Due to the technological nature of the present project on coffee roasting, the analytical effort in the analysis of coffee volatiles was restricted, as otherwise flavor research would have been a full project on its own. The methodology chosen in the present work intended to employ the most important elements of qualified aroma analysis and, at the same time, to limit time-consumption by making minor methodological concessions. Nevertheless, two different techniques for isolation of volatiles were applied in order to avoid potential artefacts in the most critical step of flavor analysis. A single high resolution capillary column catered for maximum separation performance, however, with no pre-fractionation of the isolates. Aroma relevance of a compound was evaluated using gas chromatography olfactometry. Quantification was performed in a relative manner by comparing between differently roasted products. Stable isotope dilution analysis was not used.

3.6.2 Isolation of the volatile fraction

Simultaneous distillation/extraction (Likens-Nickerson)

Simultaneous distillation/extraction (SDE) was carried out with a Likens-Nickerson apparatus (Likens and Nickerson, 1964, reviewed by Marsili, 1997). The procedure appropriate for coffee has been described by Holscher et al. (1990). A portion of 30 g ground coffee was combined with 500 mL distilled water and an internal standard of 2-Butanol (Fluka 19025, CH-Buchs) and was extracted with 50 mL solvent (pentane / diethyl ether mixture 1:1) for 2 h. After drying with anhydrous sodium sulfate the extract was concentrated to less than 1 mL by means of a Vigreux column (10 cm height, Ø 1 cm).

Vacuum distillation

A modified apparatus according to Schieberle and Grosch (1983) and described by Holscher et al. (1990) was used for vacuum distillation, comprising 3 cryo-traps connected with a vacuum pump Trivac 4/8B (Leybold, D-Köln). 100 mL solvent (pentane / diethyl ether mixture 1:1) were added to 30 g ground coffee and to an internal standard of 2-Butanol (Fluka 19025, CH-Buchs). The mixture was frozen

with liquid nitrogen and exposed to vacuum distillation at room temperature for 3 h ($p < 0.005$ mbar) and in a second step at 70 °C for 2 h ($p < 0.008$ mbar). Dehydration and concentration of the isolate was carried out as described above.

3.6.3 Gas chromatography FID (GC-FID)

A GC with flame ionization detector (FID) was used for separation and semi-quantitative evaluation of aroma compounds from isolates as well as for characterization of an extensive series of reference substances. The analytical conditions for separation are given in Table 8. Peaks in the chromatograms were characterized by retention indices (RI) calculated according to Van den Dool and Kratz (1963). The relative amount of a compound X was defined as:

$$Q_{FID_X} = \frac{A_X}{A_{ISTd}} \quad (-) \qquad \text{(equation 4)}$$

where: Q_{FIDx}: relative amount of compound X as compared to the internal standard
A_X: peak area of compound X
A_{ISTd}: peak area of internal standard

Tab. 8: *Analytical conditions for GC-FID analysis of coffee volatiles.*

Gas chromatograph	Hewlett Packard GC 5890 series II (Hewlett Packard, CH-Basel)
Capillary column	Supelcowax 10, 60 m, ID 320 µm, film thickness 0.25 µm (Supelco, CH-Buchs)
Detector	FID, 250 °C
Injector temperature	220 °C
Oven temperature programming	Iso-stage 1: 46 °C, 3 min Rate 1: 4 °C min^{-1} Iso-stage 2: 240 °C, 5 min
Carrier	Helium 5.0
Carrier flow	90 kPa column head pressure
Injection volume	1 µL
Injection mode	Split 1:12
Software	Chemstation, version A.03.34

3.6.4 Gas chromatography mass spectrometry (GC-MS)

Analytical conditions for GC-MS measurements (Table 9) were kept close to those applied in GC-FID analysis. Peak retention indices (RI) were calculated according to Van den Dool and Kratz (1963). In alternative to semi-quantitative evaluation via GC-FID, relative amounts of a few compounds were calculated using GC-MS peak areas (RIC), corresponding to equation 4. In some cases of co-eluted compounds a semi-quantitative evaluation according to equation 5 was applied, based on a characteristic ion of the compound in question. Compounds were generally identified by comparison of mass spectra and RI with reference substances.

Tab. 9: *Analytical conditions for GC-MS analysis of coffee volatiles*

Gas chromatograph	Fisons 8065 (Brechbühler, CH-Schlieren)
Mass spectrometer	SSQ 710 (Finnigan MAT, CA-San Jose, USA)
Capillary column	Supelcowax 10, 60 m, ID 320 µm, film thickness 0.25 µm (Supelco, CH-Buchs)
Injector temperature	220 °C
Oven temperature programming	Iso-stage 1: 46 °C, 3 min Rate 1: 4 °C min^{-1} Iso-stage 2: 240 °C, 5 min
Carrier	Helium 5.0
Carrier flow	90 kPa column head pressure
Injection volume	0.5 µL
Ionization potential	70 eV
Interface heating	240 °C
Mass range	40 ... 300 amu
Software	ICIS, version 7

$$Q_{MS(CI)_X} = \frac{A_{(MS)X} \cdot S_{CI}}{A_{(MS)ISTd}} \cdot 100 \qquad \text{(equation 5)}$$

where:
- $Q_{MS(CI)X}$: Relative amount of compound X as compared to the internal standard, based on characteristic ion
- $A_{(MS)X}$: MS peak area (RIC) of compound X and co-eluted compound
- S_{CI}: peak area share of characteristic ion (%)
- $A_{(MS)ISTd}$: MS peak area (RIC) of internal standard

3.6.5 Aroma extract dilution analysis by gas chromatography olfactometry (GC-O)

The GC-FID system was equipped with a column end split, leading to a sniffing port for olfactometry (Marsili, 1997). Aroma extract dilution analysis was carried out with un-diluted isolates and dilutions 1:4, 1:16, 1:32, 1:64, 1:128, 1:256, 1:512 and 1:1024. Each sequence of GC effluents was sniffed by at least two persons. They marked onset and end point of a perceivable odor by pressing a button and indicated odor quality to an assistant person. The online acquired data of a complete dilution series were processed into CHARM response chromatograms (Acree et al., 1984; reviewed in Marsili, 1997). The FD-factor for a specific compound was defined as the greatest dilution at which this compound was still perceivable in the GC effluent. It represents a measure for the aroma relevance of a compound. Aroma compounds with a FD-factor higher than 256 were regarded as key compounds. Compounds with a FD-factor of 1024 or more were specified as "aroma impact compound" (AIC) for the respective roast coffee.

3.6.6 Sensory evaluation

Sensory evaluation by an expert panel

A quantity of 12 g ground roast coffee was placed in a porcelain drinking bowl, and 0.3 L boiling water was poured over it. The coffee suspension was stirred and allowed to cool down to approximately 50 °C, while coffee particles deposited. Three expert coffee tasters sipped the beverage using spoons.

Flavor profiling

Flavor profiling by a trained industrial panel of 10 panelists was carried out in a standard sensory room and with a professional support service. Filter coffee was prepared immediately before sensory analysis, using 55 g ground coffee per liter water. Profiling of samples according to selected sensory attributes was carried out using a 10 cm line scale ranging from "attribute not marked" to "very marked", provided with a mark for the reference. Data were evaluated statistically by analysis of variance (ANOVA), least significant difference test (LSD) and Student's t-test.

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4 Results and discussion

4.1 Characterization of process dynamics

4.1.1 Heat transfer and development of bean temperature

The heat impact and the temperature required to roast coffee are high as compared to other roasted food products, such as nuts, malt or chicory. In general, temperature must exceed 190 °C for a minimal length of time to provide a sufficiently reactive roast environment. Therefore, the residence time and a relevant process temperature must be measured to describe the overall thermal impact. Usually, the temperature of the bean pile is recorded for practical reasons although the measurement of the bean core temperature would be preferable for more precise description of the roasting process.

The development of pile and bean core temperature during isothermal roasting in the laboratory roaster is shown in Figure 5. The high air to bean ratio resulted in a rapid convective heat transfer. The temperature increase was steady without any discontinuities such as described for hazelnuts (Perren, 1995). After a similar, short initial heating stage in all three processes, heating rates were found to be dependent on the hot air inlet temperature. The bean core temperature was exceeded by the batch pile temperature in each process. Neither of them ever reached hot air inlet temperature. Even during excessive roasting beyond usual degrees of roast a constant temperature difference between the hot air inlet and the bean core remained. This difference disappeared completely when bean models made from aluminium were heated. Therefore, it seems unlikely that an undesirable heat flow off through the very thin thermocouple has affected the measurements. The results point rather to a particular situation regarding the proportions of heat conduction, convection of heat and radiation due to the small batch size in the laboratory roaster.

Figure 6 shows the bean temperatures during roasting in industrial roasters as compared to the temperature development in the laboratory roaster. Generally, industrial roasting systems use much lower air to bean ratios as the laboratory roaster, resulting in lower heat transfer to the beans. Nevertheless, product temperatures that exceed 225 °C were achieved in the final stages of industrial roasting. When roasting was carried out to the same degree of roast, both industrial roasting times were found to be between those of the HTST and LTLT laboratory processes.

A series of industrial roasting trials with the Barth CR-1250 roaster and experiments with various temperature profiles demonstrated (data not shown here), that final bean temperatures are generally not related directly to the degree of roast. Coffee batches of identical degree of roast may originate from roasting processes with different end temperatures. Therefore, data on bean final temperatures supplied by many authors are merely of relative value because they only apply for a given raw material and given process conditions.

Internal heat generation due to exothermic chemical reactions in the beans has been suggested by various authors (Baltes, 1977, Raemy and Lambelet, 1982, Illy and Viani, 1995). However, a substantial additional temperature increase in the final roasting stages caused by such reactions was neither found in the laboratory nor in the industrial roasting processes. In the laboratory roaster, the expression of an exothermic stage in temperature curves during excessive roasting might have been suppressed by radiation phenomena or by superior inverse heat transfer from the beans to the air. In the industrial trials the target degree of roast may have been too low and the process terminated before proceeding into any exothermic final stage. In fact, only the observed unhindered temperature increase in spite of reduced air flow rate and heat transfer in the final stage may suggest the existence of an exothermic stage. The heat generation as measured by differential thermal analysis might be too moderate to greatly influence bean temperatures in a roasting process, or substantial influence occurs only with high degrees of roast. The present results are consistent with the few literature data on temperature development (Da Porto et al., 1991; Severini et al., 1991; Illy and Viani, 1995), where also no significant additional temperature increase in the final roasting stage is shown.

A more detailed analysis of the temperature development during roasting with the Probat RZ system is provided in Figure 7. Pile temperatures differed considerably depending on the position in the rotating bowl. The actual bean core temperature was lower than the pile temperatures. Therefore, literature data concerning product temperature development must be interpreted with due care, as they are most often termed as bean temperature, while in fact they generally represent pile temperatures. From Figure 7 it may also be noted that with the Probat RZ roaster a reduction of heat transfer in roasting stages 2 and 3 of the 3-stages process is achieved by reduction of air flow rate instead of hot air inlet temperature.

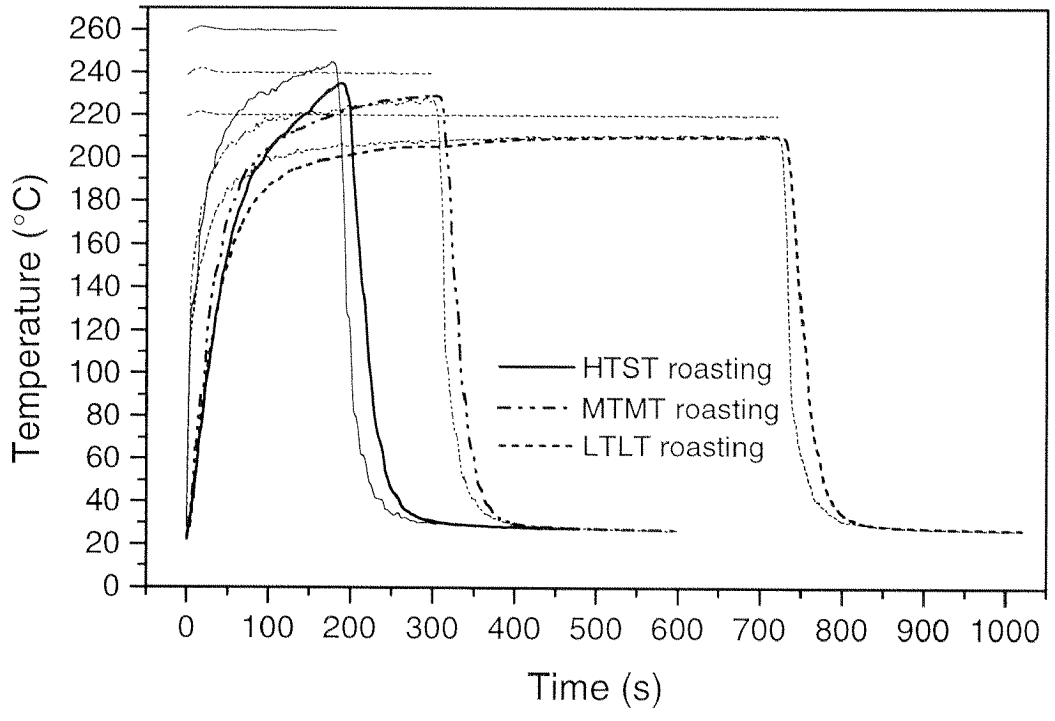

Fig. 5: *Temperature of bean pile (thick curves) and bean core (thin curves) during isothermal laboratory roasting at 260 °C (HTST), 240 °C (MTMT) and 220 °C (LTLT), and subsequent cooling. Curves are averaged (HTST: n=6, MTMT: n=10, LTLT: n=10).*

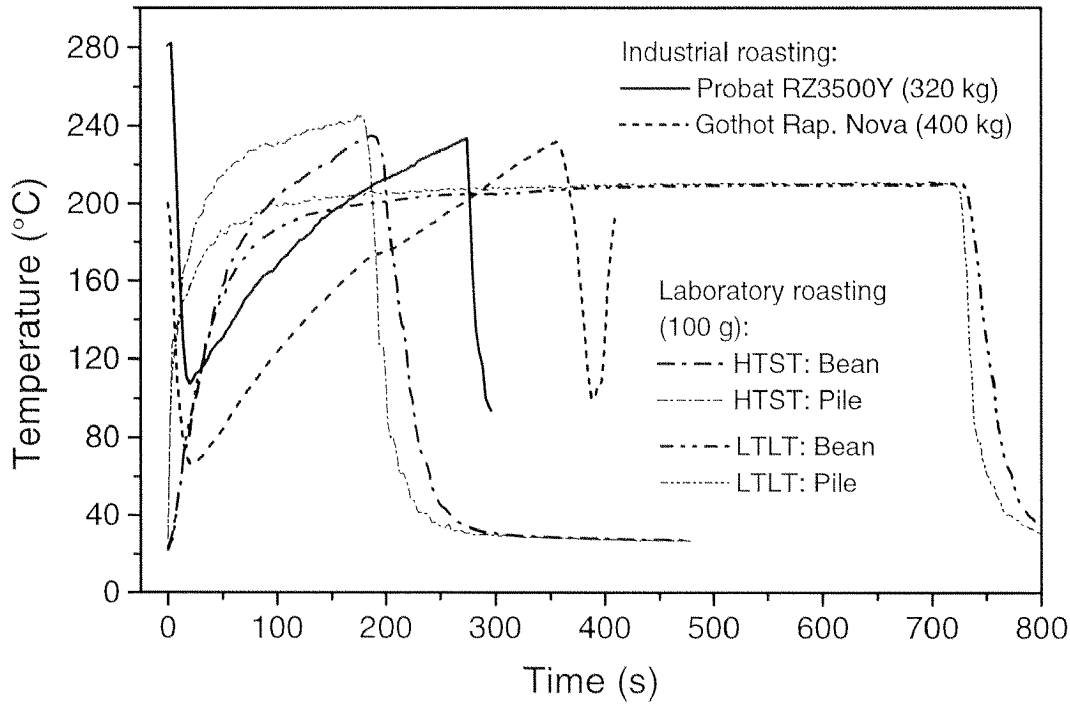

Fig. 6: *Temperature development in the laboratory roaster and in industrial roasters during roasting to the same degree of roast. (Industrial roasting: blend of 100 % C. arabica, laboratory roasting: C. arabica, Colombia).*

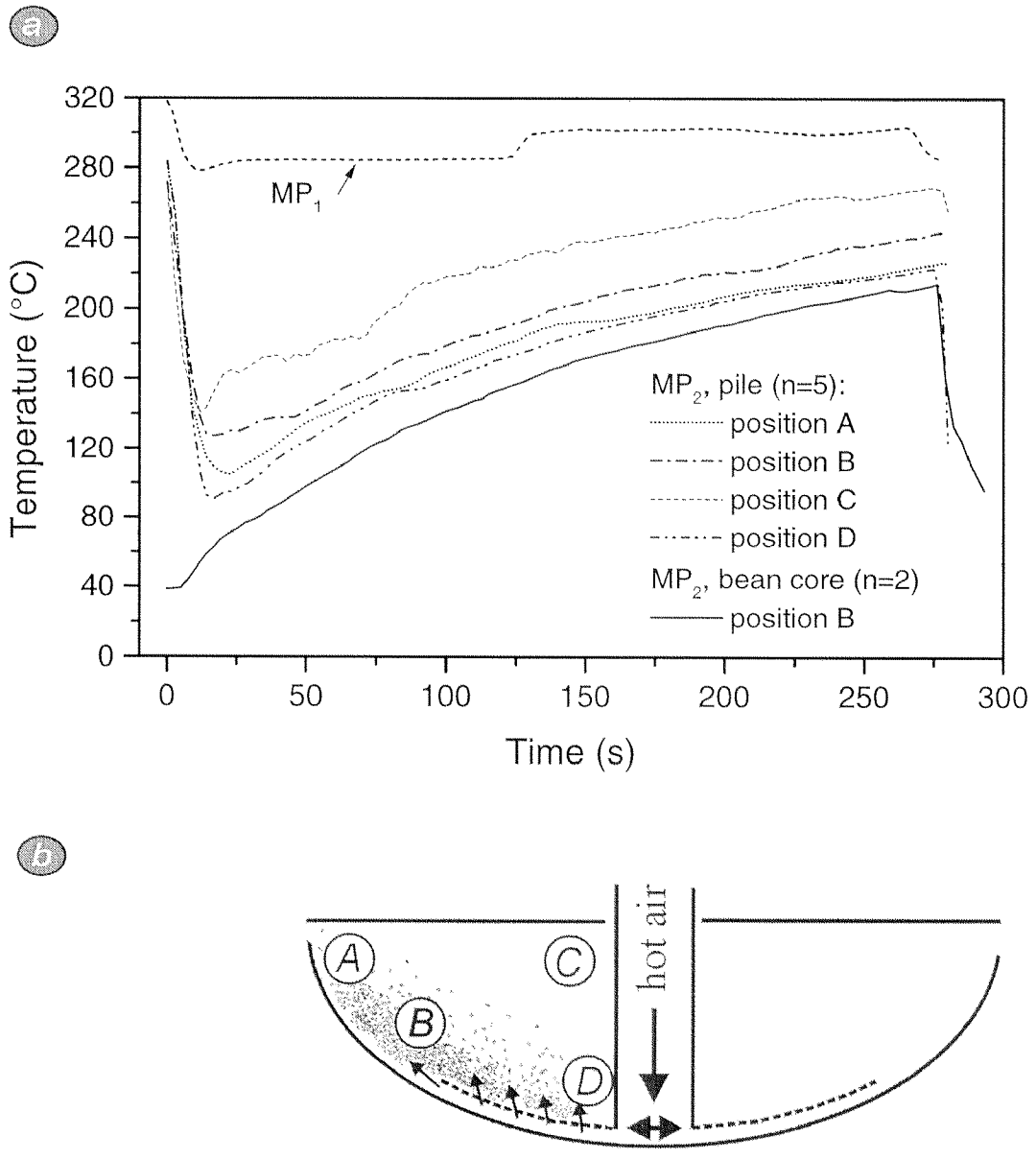

Fig. 7: *Industrial roasting with the roaster Probat RZ3500Y (Commercial blend of 100 % C. arabica). 7a: Hot air inlet temperature (MP_1) and temperature at different positions in the roasting bowl (MP_2) during roasting. 7b: Cross section of the roasting bowl with the locations of measuring position A, B, C and D.*

The properties of green coffee, in particular the initial water content, affects the temperature curves. Figure 8 presents the temperature curves during HTST laboratory roasting of coffee beans with different initial water content. For these measurements, coffee with a water content of 11.1 g /100 g (wb) was dried or humidified as described. Higher initial water contents result in slower heat transfer. In industrial practice, this fact makes far-reaching standardization of the green bean water content mandatory. Small and Horrell (1993) even suggested pre-drying of green beans before entering the roasting process in order to improve the temperature development for achieving high yield coffee.

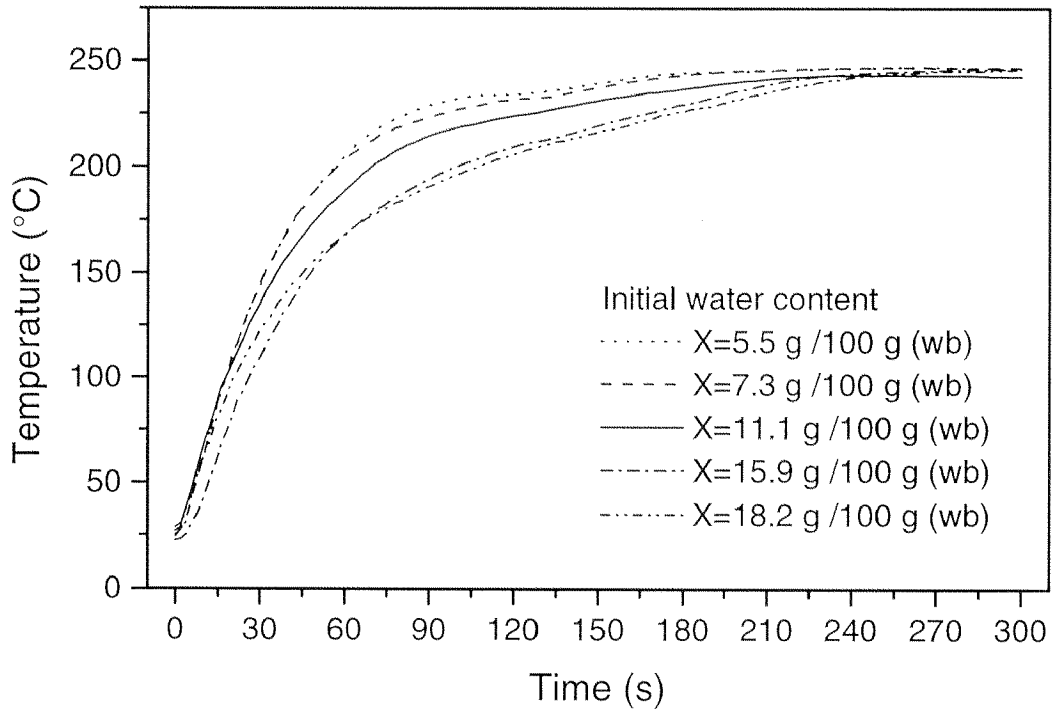

Fig. 8: *Influence of initial water content of green beans on the pile temperature during isothermal HTST laboratory roasting. Original water content X = 11.1 g /100 g wb (C. arabica, Costa Rica).*

4.1.2 Dehydration and loss of organic matter

During the roasting process, the water in the green beans is vaporized, and dry matter is partially transformed into volatiles. Moreover, a substantial amount of water is generated as a result of chemical reactions and again vaporized. Generally, coffee beans loose between 14 and 20 % of their weight during roasting, depending on green bean quality, roasting conditions and the degree of roast.

The relationship between roast loss (RL), organic roast loss (ORL) and water content for HTST and LTLT roasting is shown in Figure 9. The greatest rate of roast loss was found in the early process stages, mainly caused by dehydration, whereas loss of organic matter was initiated later during more progressive roasting. The roasting temperature was found to have a major impact on bean weight loss and dehydration. Dehydration, RL and ORL proceeded faster and more extensive during HTST roasting than during LTLT processing. Low temperature processing even seems to be incapable of ever achieving ORL values as high as in HTST roasting. The results confirm the conclusions made by Dalla Rosa et al. (1980) that the loss of dry matter is much more controlled by temperature than by residence time.

Dehydration during isothermal roasting took place in a steady and continuous manner. Stepwise dehydration due to different dehydration mechanisms as suggested by Puhlmann and Meister (1989) was not observed and must have been the result of their particular roasting conditions. It should be noted that accurate determination of water content in coffee beans is difficult. Roasted beans are very hygroscopic and may take on some water from surrounding air, while some water may be lost during grinding. Moreover, gases are also removed during analysis of water content, and thus, affecting the result. Therefore, data on water content have to be interpreted with due care.

Figure 10 compares dehydration in the laboratory and industrial roasting processes. The decrease in bean water content was delayed in both industrial processes as compared to laboratory roasting, which is primarily due to a different temperature development. In industrial roasting, the major part of water was removed only during the second half of the process. Both industrial final products exhibited identical colors, but a slightly lower water content was achieved with the Gothot Rapido Nova process.

The effect of roasting time on the final water content and RL of products with identical color was confirmed with laboratory roasting trials as shown in Figure 11. Longer roasting times resulted in products of slightly lower water content and greater RL as compared to short time roasted samples. The findings are in agreement with data on final water content provided by Kazi and Clifford (1985) and by Hinman (1991), and indicate a diffusion-limited dehydration process.

Figure 12 shows the influence of initial water content on roasting behavior. A high initial water content lead to greater dehydration rates and a faster increase of RL. Water contents converged after a certain time, and the final products did not differ in moisture nor in ORL. They did, however, differ in RL. ORL seems to be only slightly affected by different initial water contents. The additional energy consumption required to vaporize the additional water causes a delay in temperature increase in beans with higher initial water content (Figure 8).

The humidity of hot air presents another important parameter influencing the roasting process. Figure 13 demonstrates significant differences during isothermal laboratory roasting in dry and humid hot air at the same temperature. RL and ORL progress slightly faster at elevated air humidity. Even dehydration runs slightly faster after an initial lag phase. It can be assumed that the heat transfer in humid air is more efficient due to its greater specific heat capacity. The effect of a smaller vapor pressure gradient between the beans and the humid air may be compensated by a faster temperature increase and therefore cause a faster progress of roasting.

Measurements of air humidity revealed, that a substantial amount of water can be found in the hot air of industrial roasting systems. As a major part of the hot air is recirculated for economical reasons, water from the beans and from water quench cooling may accumulate and generate a humid atmosphere in the roasting chamber. Further investigations on air humidity and its effects on product quality are required.

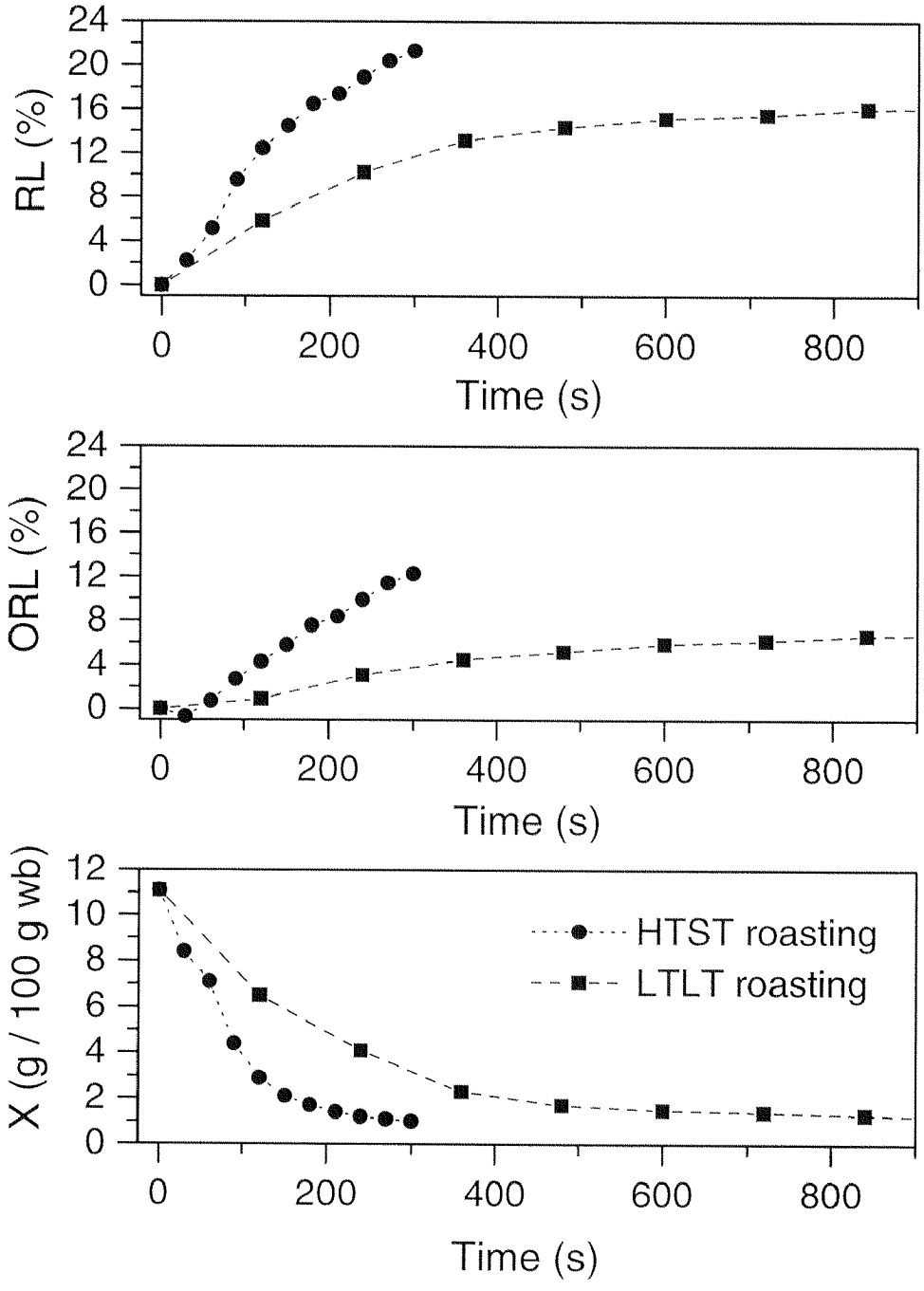

Fig. 9: *Development of roast loss (RL), organic roast loss (ORL) and bean water content (X) during isothermal HTST and LTLT laboratory roasting (C. arabica, Costa Rica).*

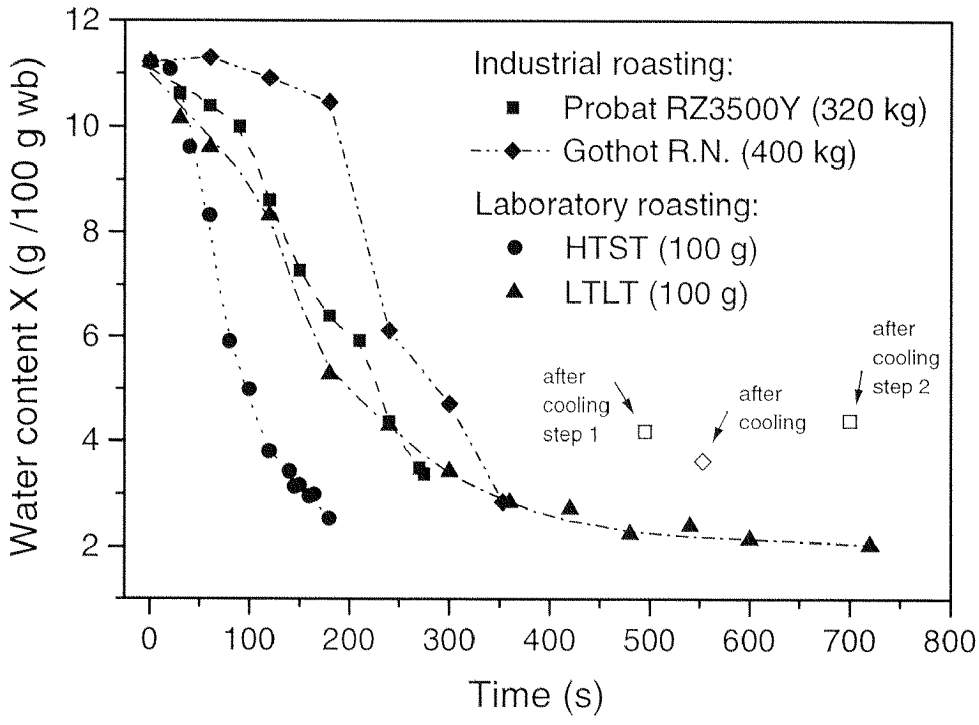

Fig. 10: *Dehydration of coffee beans during laboratory and industrial scale roasting (Commercial blend of 100 % C. arabica).*

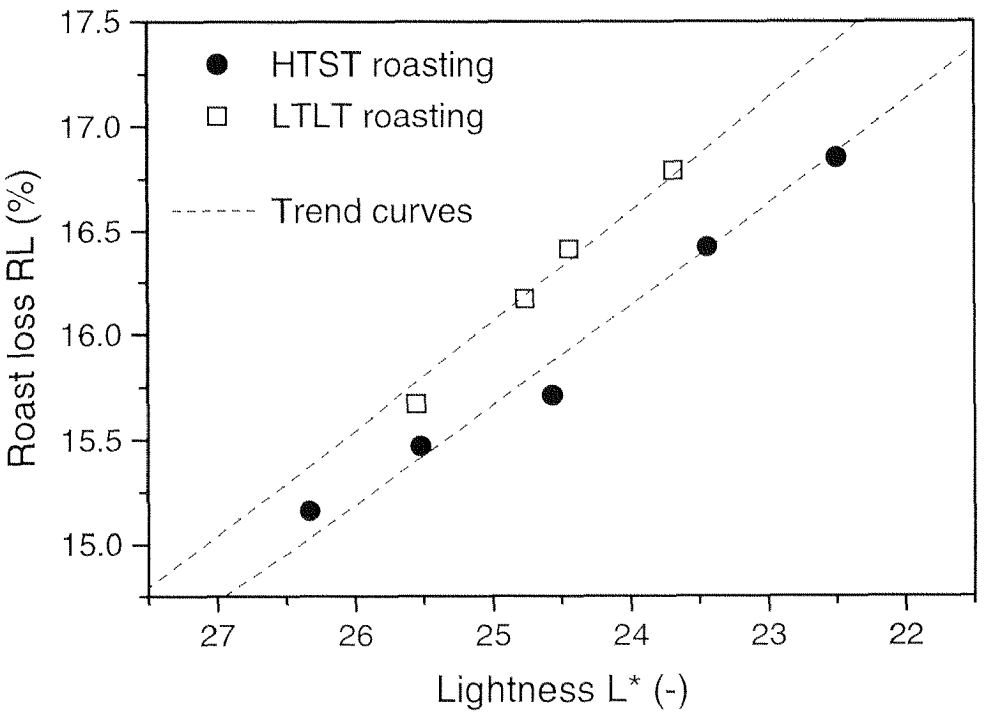

Fig. 11: *Relation between roast loss and lightness of HTST and LTLT roasted coffees in a range of medium degree of roast.*

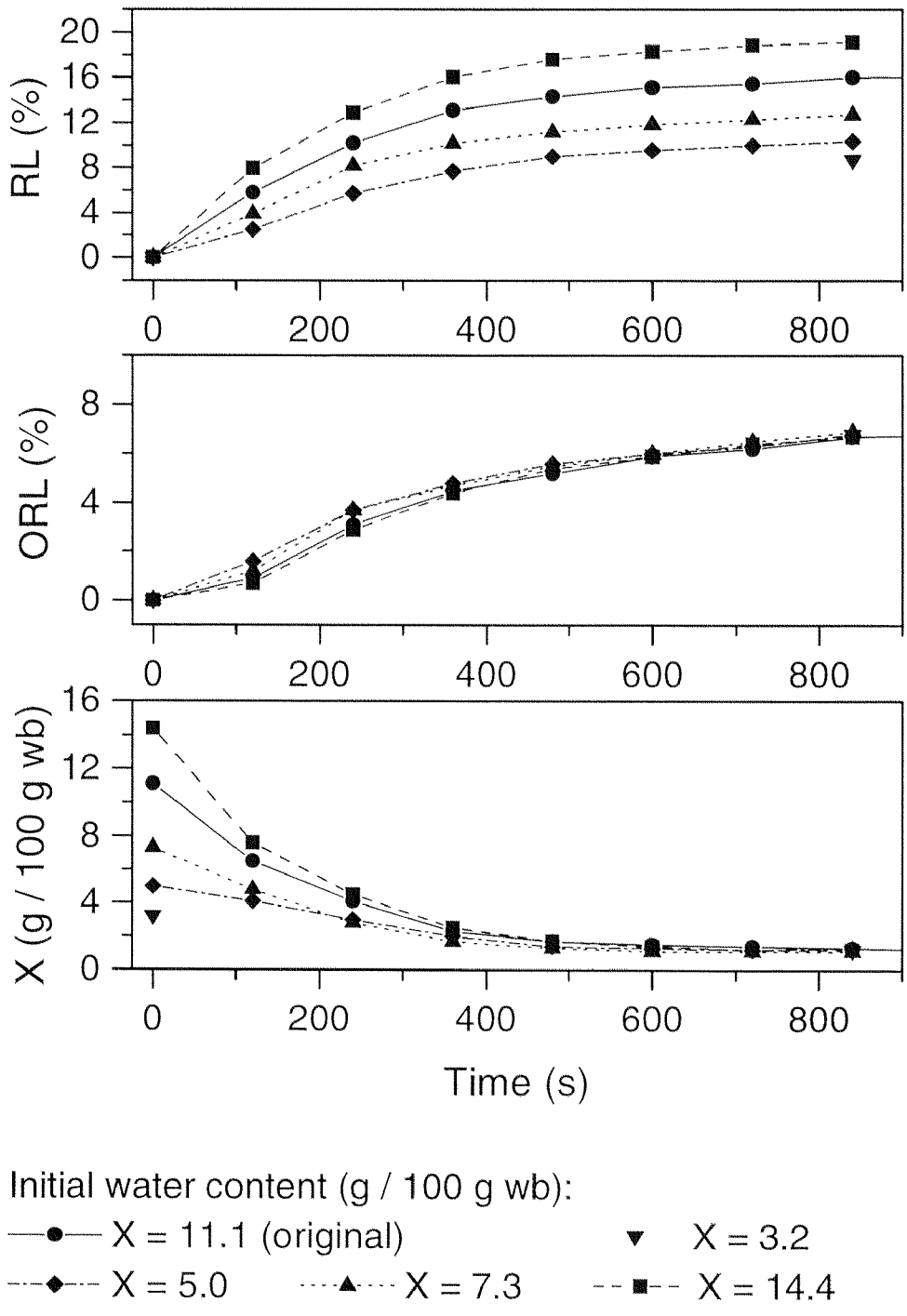

Fig. 12: *Influence of initial water content of green beans on roast loss (RL), organic roast loss (ORV) and water content (X) during isothermal HTST laboratory roasting (C. arabica, Costa Rica).*

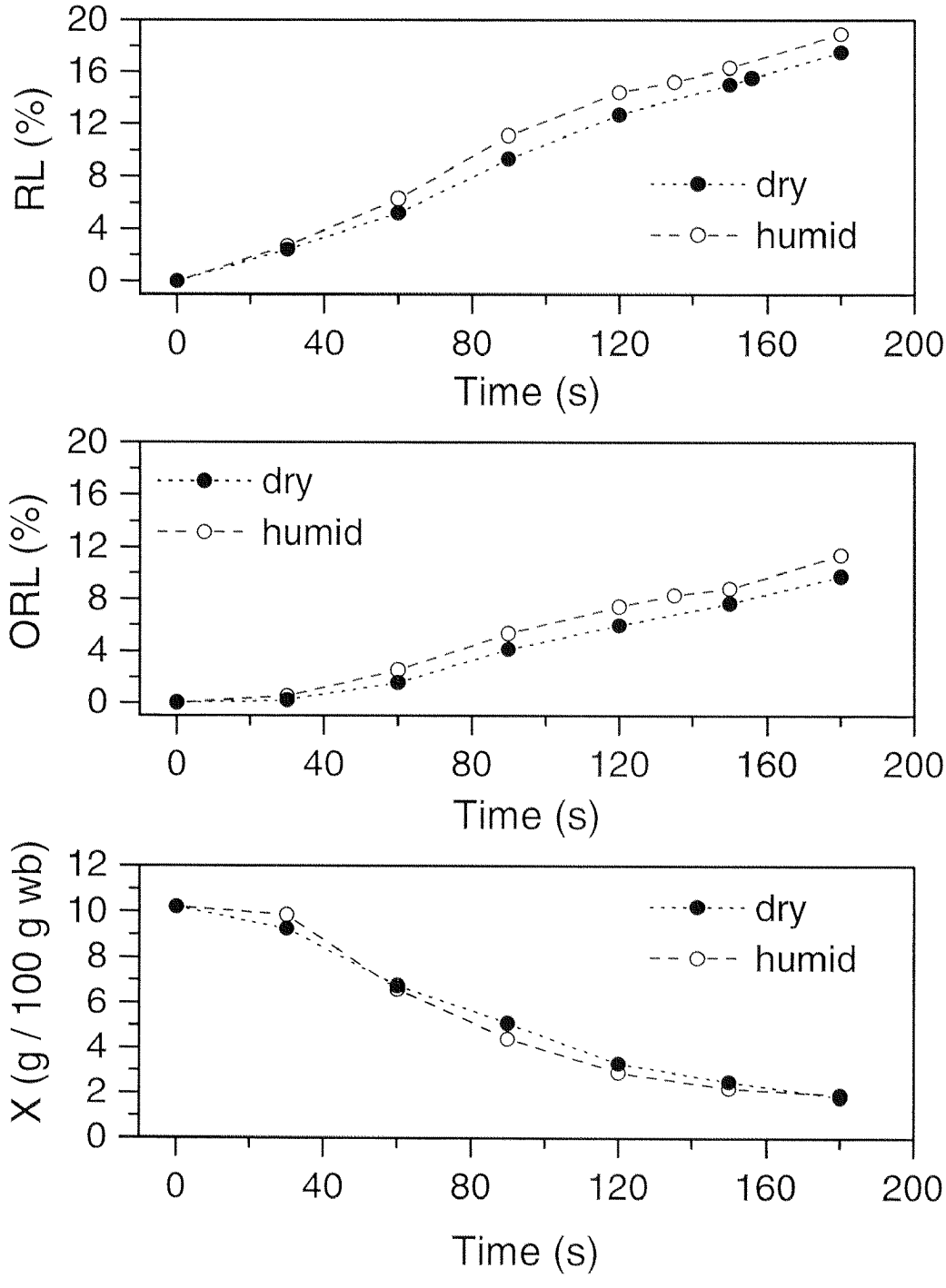

Fig. 13: *Influence of roasting air humidity (dry vs. humid) on roast loss (RL), organic roast loss (ORL) and bean water content (X) during isothermal HTST laboratory roasting.*

4.1.3 Development of bean color

During roasting, the color of coffee beans change from pale green-grey to yellow, orange, brown and finally dark brown and black. This color development is shown in Figure 14 for the HTST and the LTLT laboratory processes in the CIE $L^*a^*b^*$ color space as well as in the L^*C^* plane. The color changed faster with higher temperatures, but followed the identical pathways regardless of the type of process. Lightness decreased continuously, whereas chromaticity first increased in an early stage of roasting (yellow phase), and then decreased again continuously.

The decrease of lightness in isothermal processes seems to follow a first order type of reaction. It was found to be highly correlated with RL and ORL. Therefore, color is a suitable indicator of the degree of roast for a given raw material. However, roasting trials with beans from different origin revealed that the relationship between RL and color can vary in a wide range depending on the green been quality.

Figure 15 illustrates the development of bean color in laboratory and industrial scale roasting. Browning rates leveled off during laboratory roasting, although the highest bean temperatures are achieved in the final roasting stages. Apart from temperature and concentration of reactants the presence of water seems to be a key factor for non-enzymatic browning in coffee. From a certain point of dehydration onwards the rate of non-enzymatic browning gradually falls, as the bean enters a more and more glassy state (cf. chapter 4.2.2). The effect of glass transition on rates of non-enzymatic browning is known for other food systems (Karmas et al., 1992). In turn, the influence of temperature on color development is in parallel to the influence on organic roast loss. Temperature seems to set a limit of maximum color development that cannot be overcome by longer residence time. Higher temperatures led to a greater browning potential and potentially lower L^* values. Roasting below 190 °C allows only for moderate color development and incomplete roasting (Dalla Rosa et al., 1980). As was expected from the different temperature development in laboratory and industrial roasting, the color development in industrial roasting was greatly delayed. In the Gothot roaster, the color change was not initiated before 180 s of roasting, but a high rate of lightness decrease was found during the second half of roasting.

While using the same color describing system, color values for a given coffee product measured by different authors and devices can vary considerably. The color characteristics of 18 different roast coffee brands (commercially available, mainly from the Swiss market) are given in Figure 16. The data are intended to relate L^* values in the present thesis to usual degrees of roast found in commercial products. Within a narrow range of degrees of roast the relationship between lightness and chromaticity is almost linear.

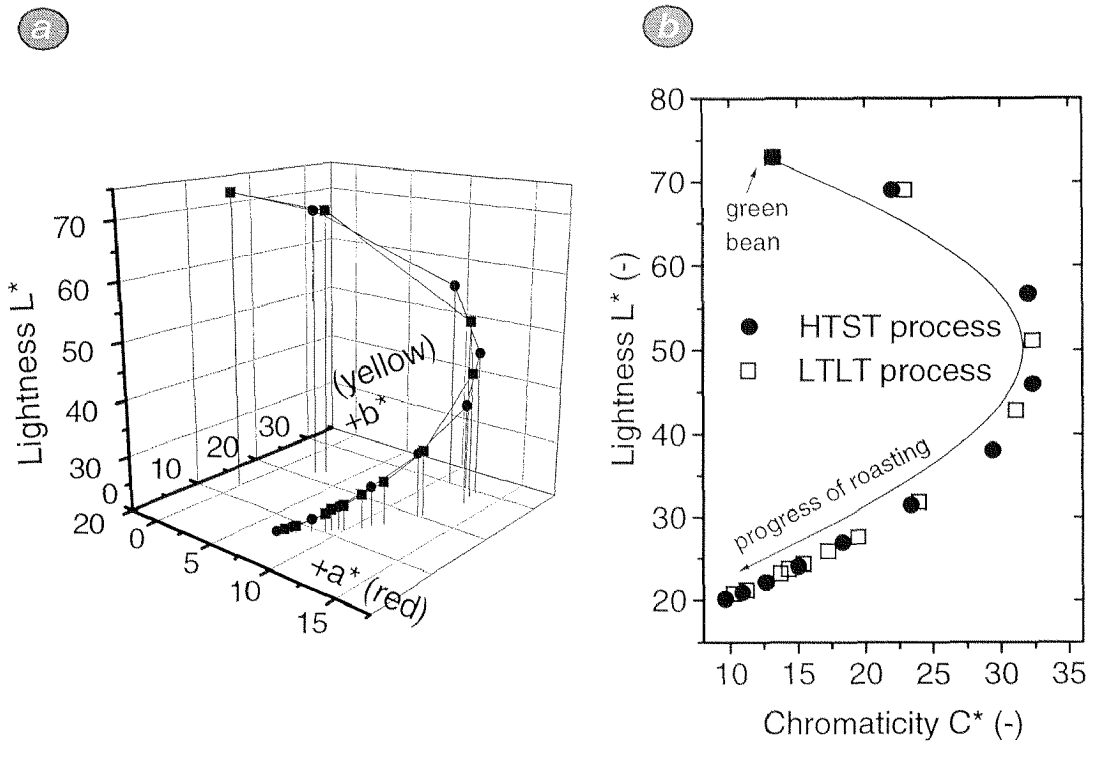

Fig. 14: *Development of bean color during HTST and LTLT laboratory roasting. 14a: Presentation in the CIE L*a*b* color space. 14b: Presentation in the L* C* plane.*

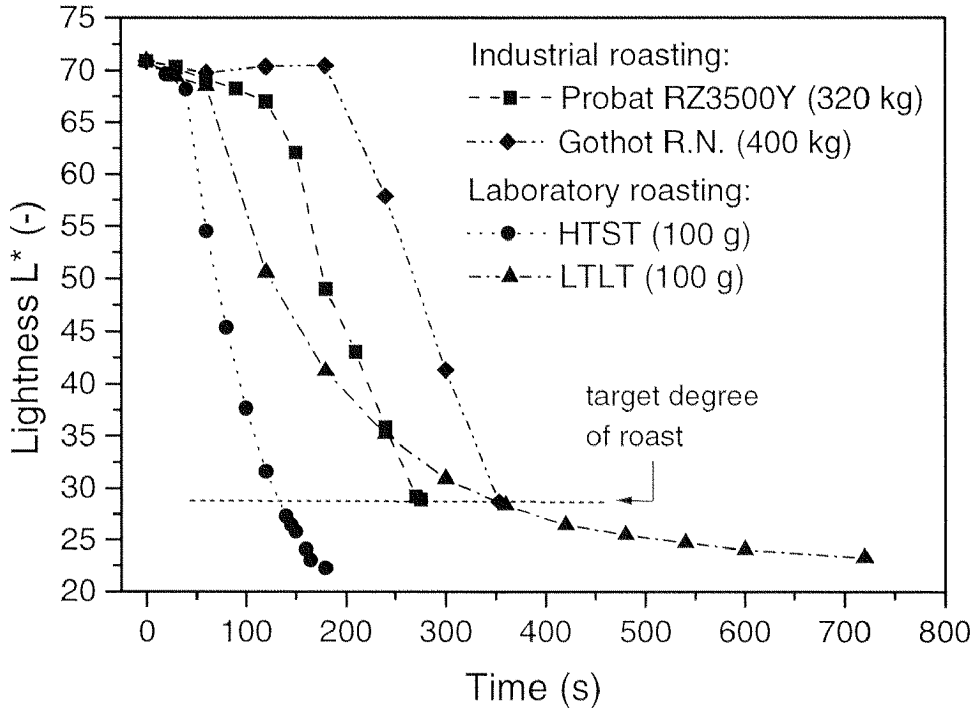

Fig. 15: *Decrease of lightness L* during laboratory and industrial scale roasting (Commercial blend of 100 % C. arabica).*

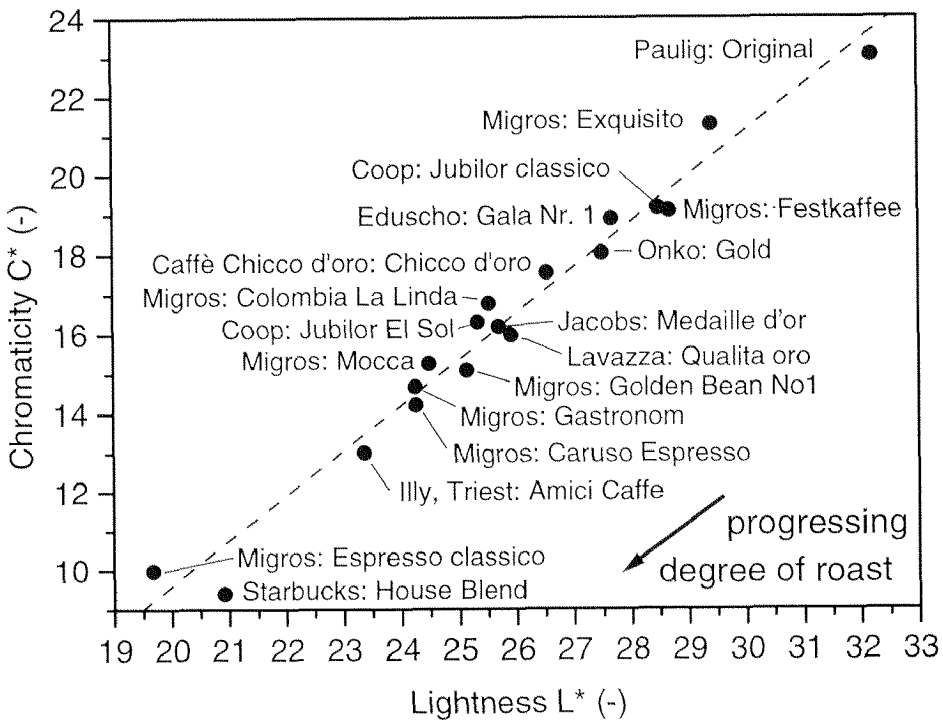

Fig. 16: *Relationship between lightness L* and chromaticity C* within the range of commercial degrees of roast and color characteristics of 18 different roast coffee brands.*

4.1.4 Gas formation

During roasting, a substantial amount of gases is formed as a result of pyrolysis and Maillard reaction. Figure 17 illustrates gas formation during HTST and LTLT isothermal laboratory roasting, measured as headspace pressure after storing bean samples for 4 months. Any gas loss during roasting itself was not taken into account. As expected from the development of dry matter loss, the major part of gases was formed only in the second half of the process. For a given raw material the rate of gas formation was highly dependent on the roasting conditions, as the higher roasting temperature in HTST led to greater rates than the lower temperature in LTLT.

Figure 18 presents the influence of LTLT, MTMT and HTST laboratory roasting to the same degree of roast (color) on the amount of different gases released during storage. The increase of total gas in final products with increasing degree of roast and higher roasting temperatures observed here was also reported by Radtke (1975) and Meister and Puhlmann (1989). CO_2 is the most dominant component in coffee gas. CO and N_2 present further major components. The influence of process parameters on CO_2 formation follows the trend observed for total gas formation. In contrast, CO and N_2 quantities seem to be independent of the roasting temperature. Clarke and Macrae (1987) have provided a percentage value for CO_2 of 87 %. In our case, the percentage of CO_2 in the total coffee gas was shown to be dependent on the applied roasting temperature.

Figure 19 shows the development of short-chain hydrocarbons, that went in parallel with the development of the amount of total gas. High formation rates were found in the second half of the process. During HTST the same compounds as during LTLT roasting were formed, but in greater amounts with the exception of pentane (Figure 20). Since methane, ethane and pentane are secondary products of lipid oxidation, their presence might have indicated progressing of oxidation reactions. However, the influence of roasting temperature on headspace concentrations of these oxidation products was not consistent. Hence, most probably they cannot be accounted for lipid oxidation. Munari et al. (1997) reported a coinciding picture of an overall increase of minor volatiles formation during roasting. Although their

work shows that the development of single aroma compounds such as 2 methyl propionaldehyde, methylfurane or 2,3 butandione may differ considerably from the general trend. The subject of aroma compounds formation is covered in chapter 4.3.3.

Tertiary butyl methyl ether (t-BME) was identified in the roast coffee headspace (Figure 20) and found to be formed during roasting (Figure 19). A similar trend in formation of this unexpected compound was found in each case with several coffee bean varieties from different origin. Artefacts due to the headspace analysis procedure were carefully ruled out. t-BME is known as a widely used solvent in wet chemistry, is volatile and has a characteristic odor. So far, it has not been described as a roast coffee component, except for one study by Wang et al. (1983) where t-BME has been mentioned in the context of contaminants. Ethers in general are not well known to contribute to the volatile fraction of foods. However, since all functional groups to produce t-BME can be found in other compounds occurring in roast coffee, chemical formation of t-BME in coffee does not seem unreasonable. Still, the formation pathway of t-BME is unknown. t-BME is dependent on the roasting conditions in the same way as the majority of other minor coffee gas components. It may contribute to the aroma of roast coffee.

Considering the fact that the major part of gases formed during roasting remains within the bean and is only released during storage, the great amount of entrapped gases must cause an extensive pressure build-up inside the bean. If the measured headspace gas pressures are related to the free volume within the beans and the roasting temperatures are taken into account, a model of bean pressure build-up can be developed as shown in Figure 21. Gases lost during roasting were not considered. The model goes in parallel with the gas formation, except for a temporary stagnation at the stage of greatest volume increase. The model suggests that the bean pressure may easily exceed 10 bar (1000 kPa), and it confirms that the highest bean pressures are found in the final roasting stages. At the end of excessive high temperature roasting, bean pressures of more than 20 bar can be assumed. Radtke (1975) calculated bean pressures of three different fully roasted coffees in the cold state to be 8.0, 5.7 and 5.5 bar. Assuming a final process bean temperature of 230 °C, the pressures at this temperature are 13.5, 9.62 and 9.28 bar, respectively. Thus, they are exactly

within the same pressure range as in the model outlined above. On the other hand, it is conceivable that the internal gas is only partially pressure-effective, since a substantial part of the gas may be present in an absorbed state. At any rate, the gases together with water vapor are the driving force for bean expansion during roasting.

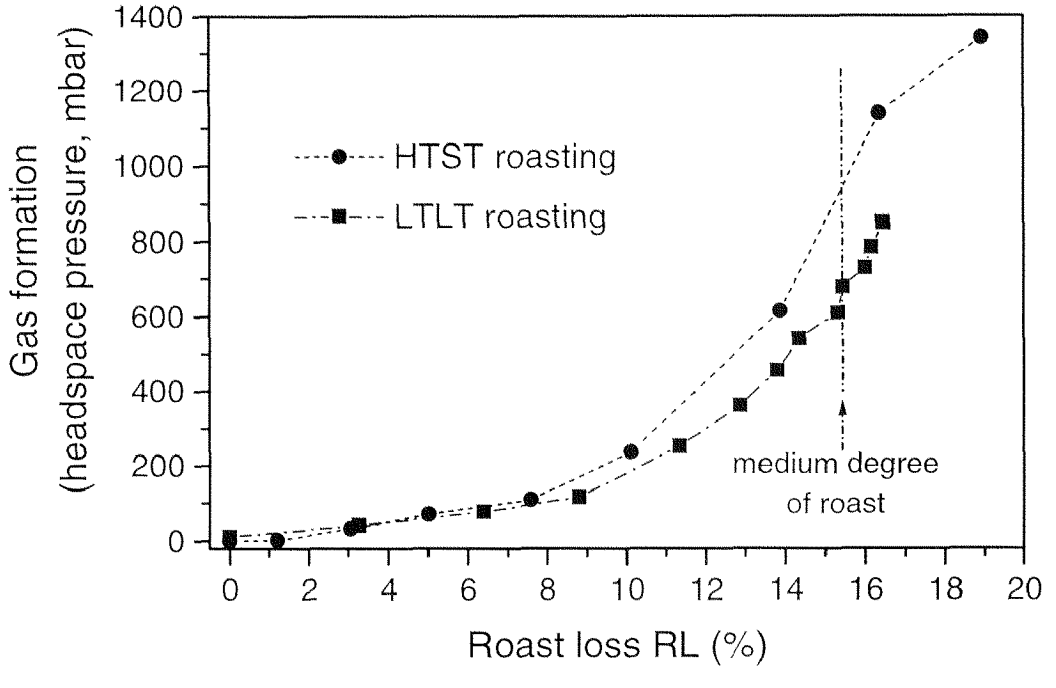

Fig. 17: *Gas formation during HTST and LTLT laboratory roasting expressed as headspace pressure after 4 months storage, and related to progressive roasting as expressed by RL. Data represent released gases from immediately after roasting to complete gasdesorption. Gas losses during roasting are unconsidered.*

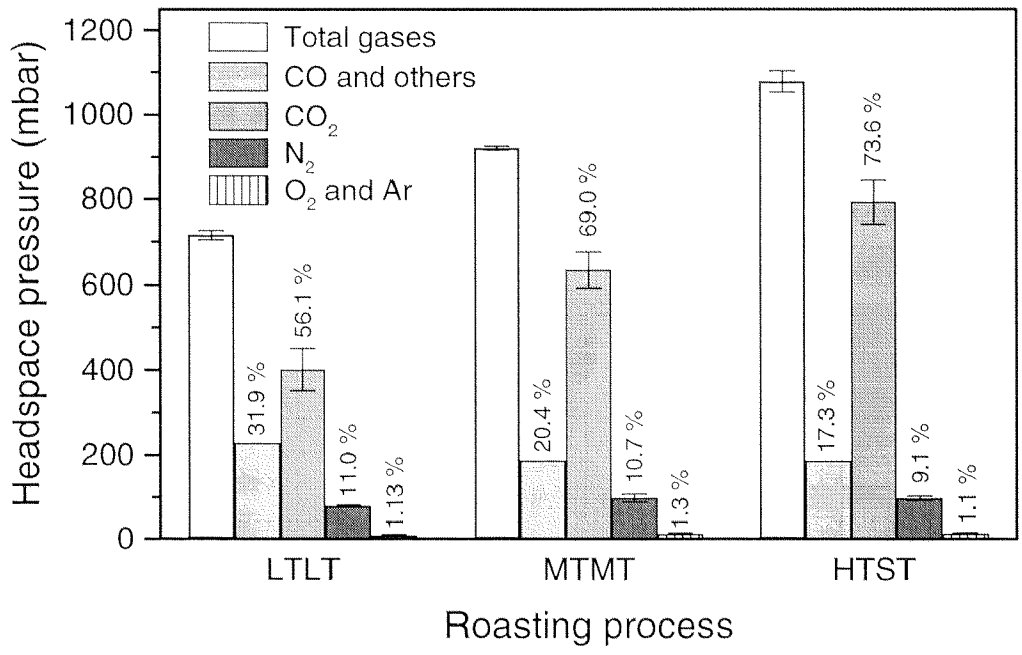

Fig. 18: *Quantities of major gases (expressed as headspace pressure) formed during LTLT, MTMT and HTST laboratory roasting to the identical roast color. Percent distribution (mean and standard deviation s, n=4) as calculated from headspace partial pressures. Data represent gases released during 4 months storage. Gas losses during roasting are unconsidered. O_2 and Ar were not separated.*

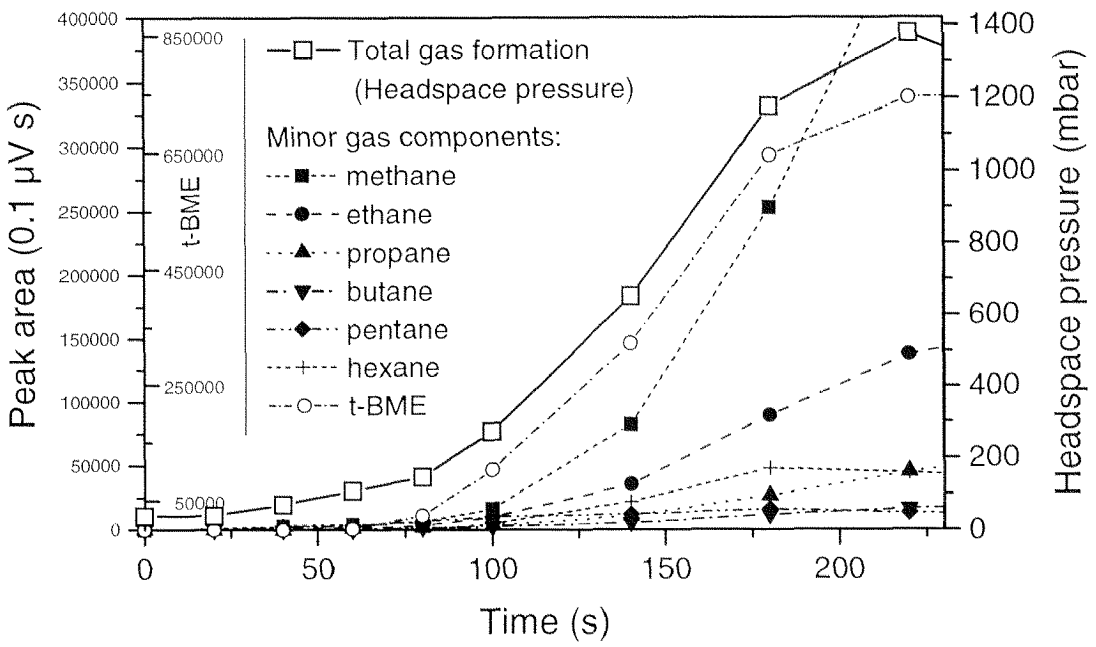

Fig. 19: *Development of minor components gas formation during high temperature laboratory roasting (HTST). Headspace concentrations expressed as GC peak areas. The development of total gas formation (headspace pressure) is given for comparison. Gas losses during roasting are not included.*

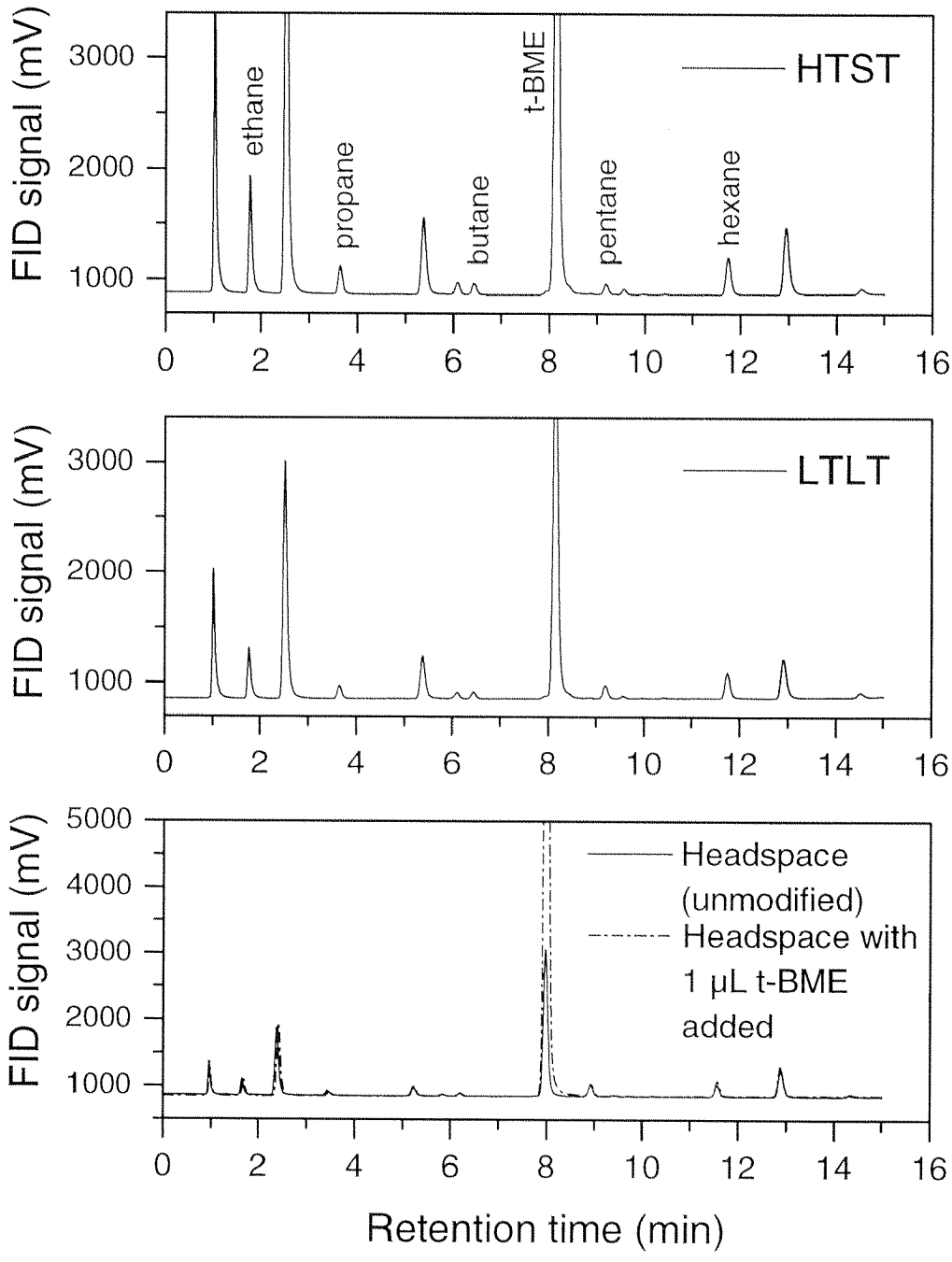

Fig. 20: *FID-chromatograms of headspace samples from HTST (top) and LTLT (middle) roasted coffee beans of identical degree of roast. One of the major peaks was identified as tertiary butyl methyl ether (t-BME) by GC-MS, by comparison of retention time, and by in-situ adding of reference t-BME (bottom).*

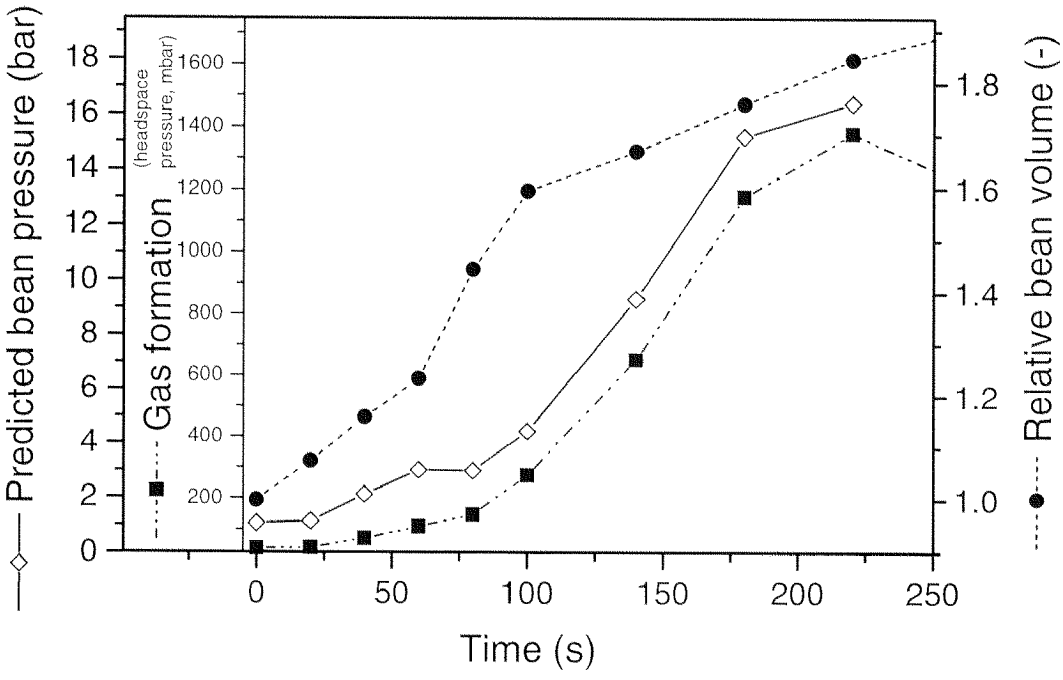

Fig. 21: *Model of gas pressure build-up inside a coffee bean during high temperature roasting (HTST), based on measured gas formation, temperature, volume increase and porosity.*

4.1.5 Extraction yield

Figure 22 shows the development of extraction yield as influenced by HTST and LTLT laboratory roasting. During LTLT roasting the relatively high extraction yield for green beans continuously decreased and reached 23 % for LTLT roasted beans of a medium degree of roast. The development of yield in HTST roasting initially followed more or less the same trend, but started to deviate after a roast loss of 6 %. The extraction yield increased up to 30 %, before it started to fall again during the final roasting stages. The extraction yield of a high temperature roasted coffee of a medium degree of roast was around 29 % and thus, much greater than of the comparable LTLT roasted product. This result confirms earlier reports of greater extraction yields achieved by high temperature roasted low-density coffees (e.g. Dalla Rosa et al., 1980, Kazi and Clifford, 1985, Maier, 1985, Small and Horrell, 1993).

Thaler and Arneth (1968a) and Thaler (1975) reported that a substantial part of green bean polysaccharides are water soluble. Moreover, since the applied method for the determination of yield includes all types of dry matter, other soluble constituents of the green bean (oligosaccharides, sucrose, various sugars, minerals, acids, etc.) result in considerably high extraction yields of green and moderately roasted beans. Most of these non-polysaccharide soluble green bean constituents enter chemical reactions during roasting and are converted into volatile or insoluble compounds. In turn, roasting induces major changes on the polysaccharide fraction and a substantial part of the initially insoluble cell wall polysaccharides is transformed into soluble matter and contributes increasingly to the extraction yield. Apparently, the net result of these two counter-current developments is a general trend to lower yield with the continuation of roasting. This trend was clearly observed during LTLT roasting. However, it may only reflect the *potential* of extractable solids. The extraction yield is also affected by structural properties of the roasted coffee bean tissue. A more porous microstructure and greater surface area for mass transfer in HTST roasted samples may super-compensate the general trend of decreasing extraction yield.

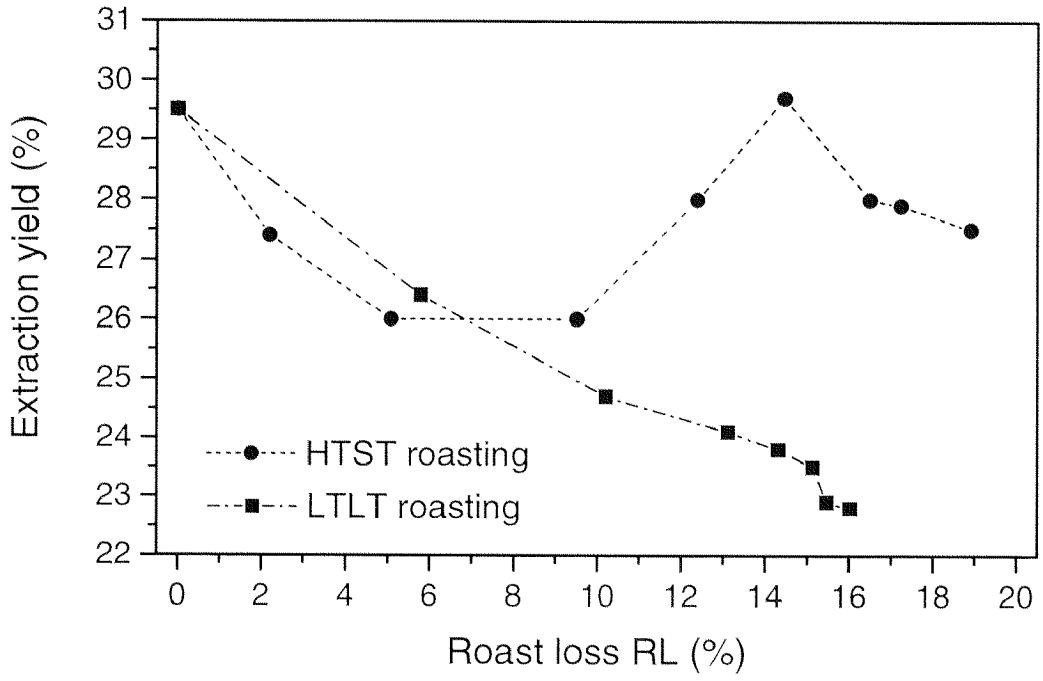

Fig. 22: *Development of extraction yield during high and low temperature laboratory roasting of C. arabica beans from Costa Rica. A medium degree of roast is achieved at a roast loss of 15 %.*

4.2 Changes of bean structure

4.2.1 Tissue structure of the green coffee bean

Figures 23, 24 and 25 show the tissue structure of the green coffee bean. The cells present a compact and dense structure with no intercellular spaces. In general, they are of spherical shape or radially stretched to ellipsoids depending on the location within the bean, but also vary considerably. The cell walls of coffee beans are unusually thick as compared to tissues of other plant seeds. Reinforcement rings give them the typical nodular appearance in the cross sectional view (Figure 25). The cell wall material causes the exceptional hardness and toughness of the seed. Moreover, it complicates and limitates all microscopic specimen preparations involving embedding techniques.

A single large gas-filled bubble was found in the cytoplasm of numerous cells (Figures 23 and 24). Most probably, they originate from the severe dehydration procedures during post-harvest processing of the coffee cherries. Dentan (1985) described similar structures visible in light micrographs of chemically fixed and stained specimens as vacuoles. However, in the present freeze-fracture SEM analysis they do not seem to be bound by a biomembrane or include any deposits of dry matter due to dehydration of a solids-containing cell liquor. Cryo-SEM very often presents a superior technique to preserve and monitor native cell structures. However, cryo-SEM micrographs did not show any other details of the cytoplasm. The structural organization of the cytoplasm was only revealed by TEM-analysis. Coffee oil was found to be organized in numerous oleosomes (oil bodies), that also occur in other oil containing seeds such as nuts (Perren, 1995). In coffee beans these spherical organelles were found to be of about 0.5 µm diameter and to be located in a layer alongside of the cell wall (Figure 26). In general, the subcellular arrangement in all examined samples was very similar to the structures described by Dentan (1985), Wilson et al. (1997) and other authors.

The cell wall polysaccharide microfibrils seem to be arranged in a complex three-dimensional network (Figure 27). Regardless of the different kinds of polysaccharides involved in coffee beans, the structure and complexity of this microfibril network in principle does compare to the situation in the primary cell wall of onions

as shown by McCann et al. (1990). As stated by Dentan (1985), the cell walls are crossed by plasmodesmatae channels in certain areas, providing cell-to-cell connections between protoplasts (Figure 26). No directly visual evidence was found for the existence of additional channels within the walls.

The cell compartmentalization, the storage of lipids within oleosomes and the thick cell walls do not only have a physiological function in nature, but also explain the excellent stability properties during storage of the green coffee bean.

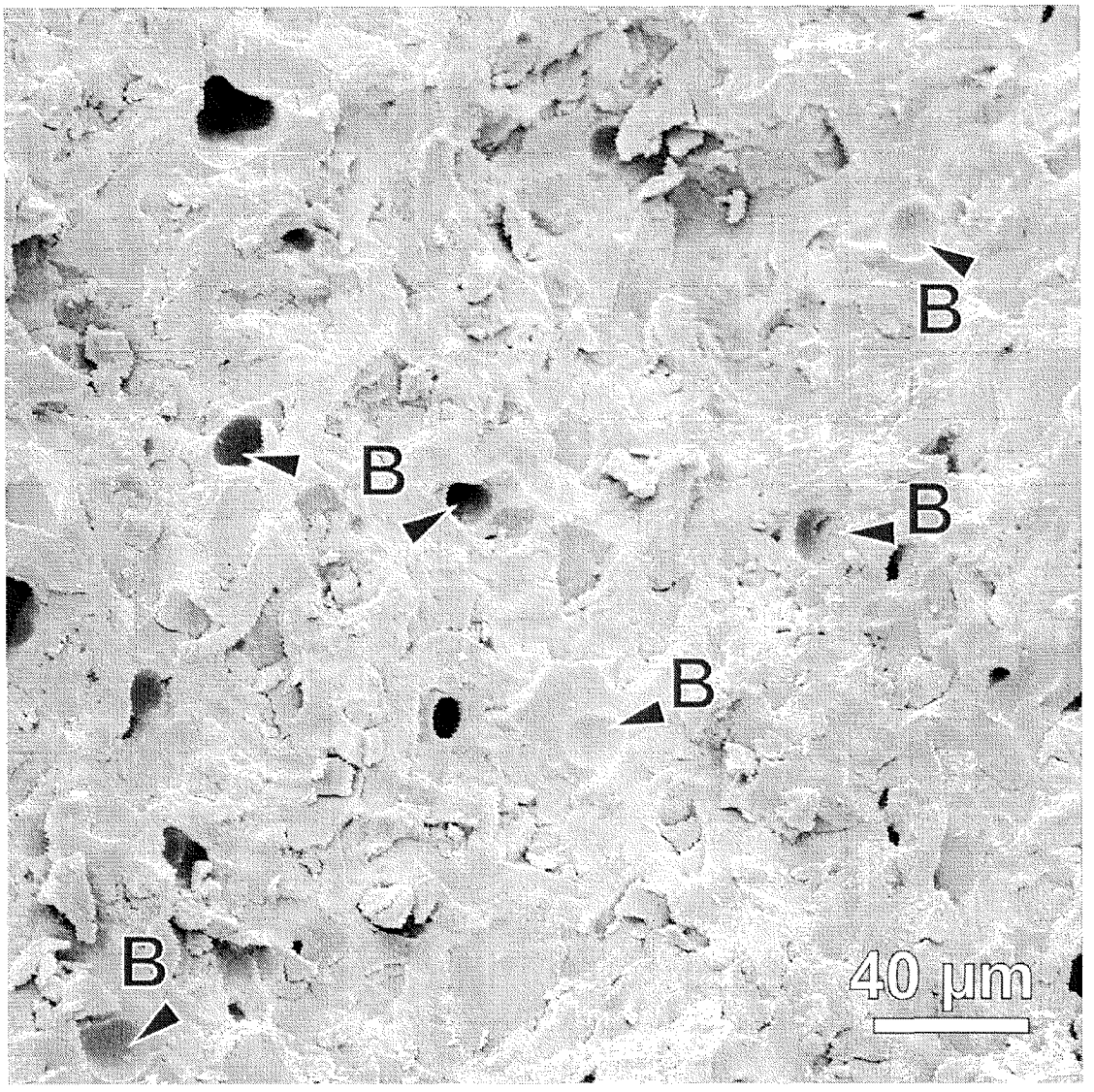

Fig. 23: *Cryo-SEM micrograph of the green coffee bean tissue structure. It clearly illustrates the dense and compact structure in the green bean. Numerous cells show a single large bubble (B) in the cytoplasm. Most probably they stem from the dehydration procedures during the post-harvest processing of coffee cherries. (Image: B. Frey, S. Handschin).*

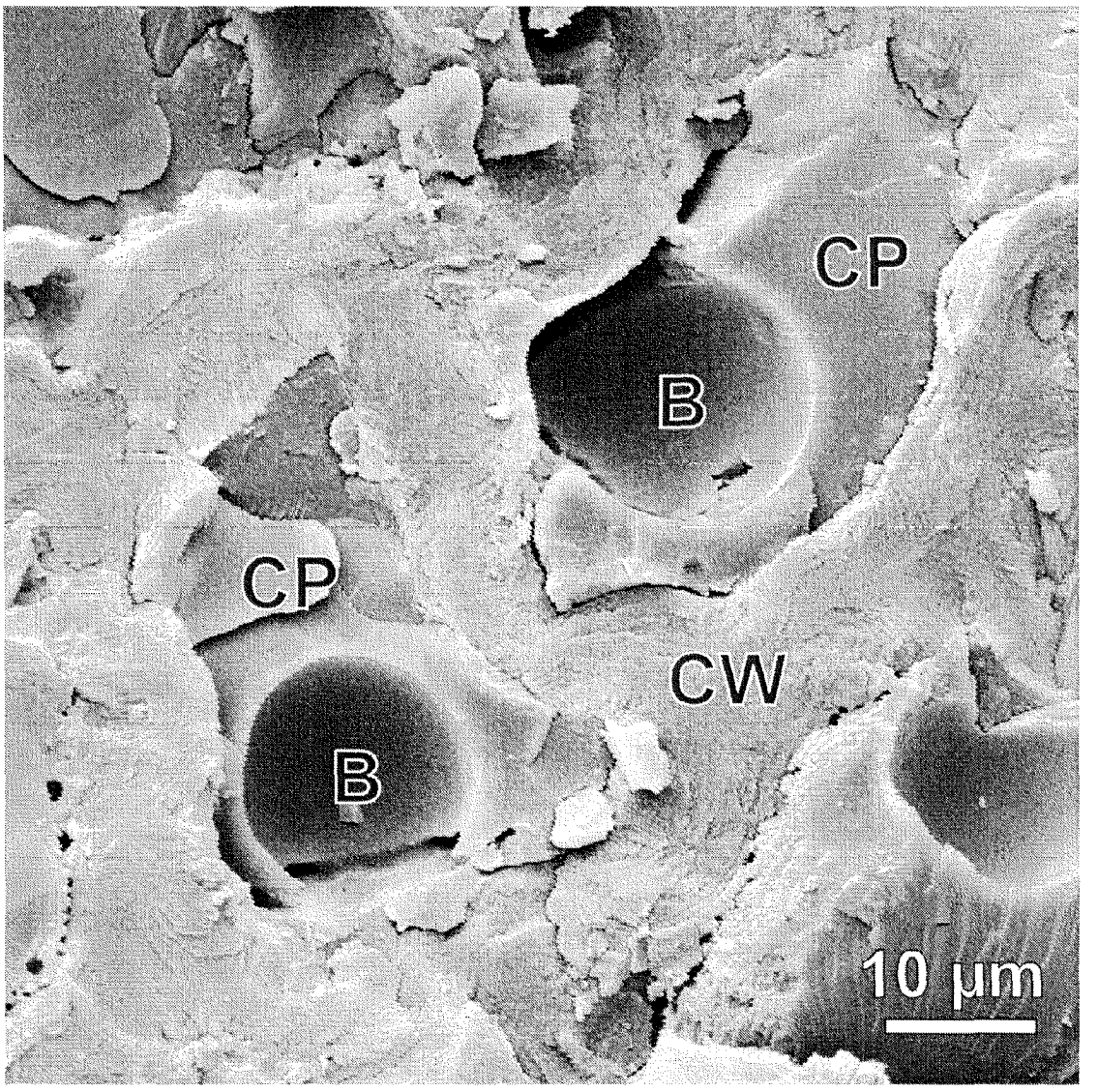

Fig. 24: *Cryo-SEM micrograph of 3 or 4 adjacent cells in the green coffee bean. The cytoplasm of each cell (CP) is surrounded by strong frames of cell wall material (CW). Bubbles (B) in the cytoplasm have no membrane and seem to be gas-filled. They display changes during severe dehydration in post-harvest processing of coffee cherries. (Image: B. Frey, S. Handschin).*

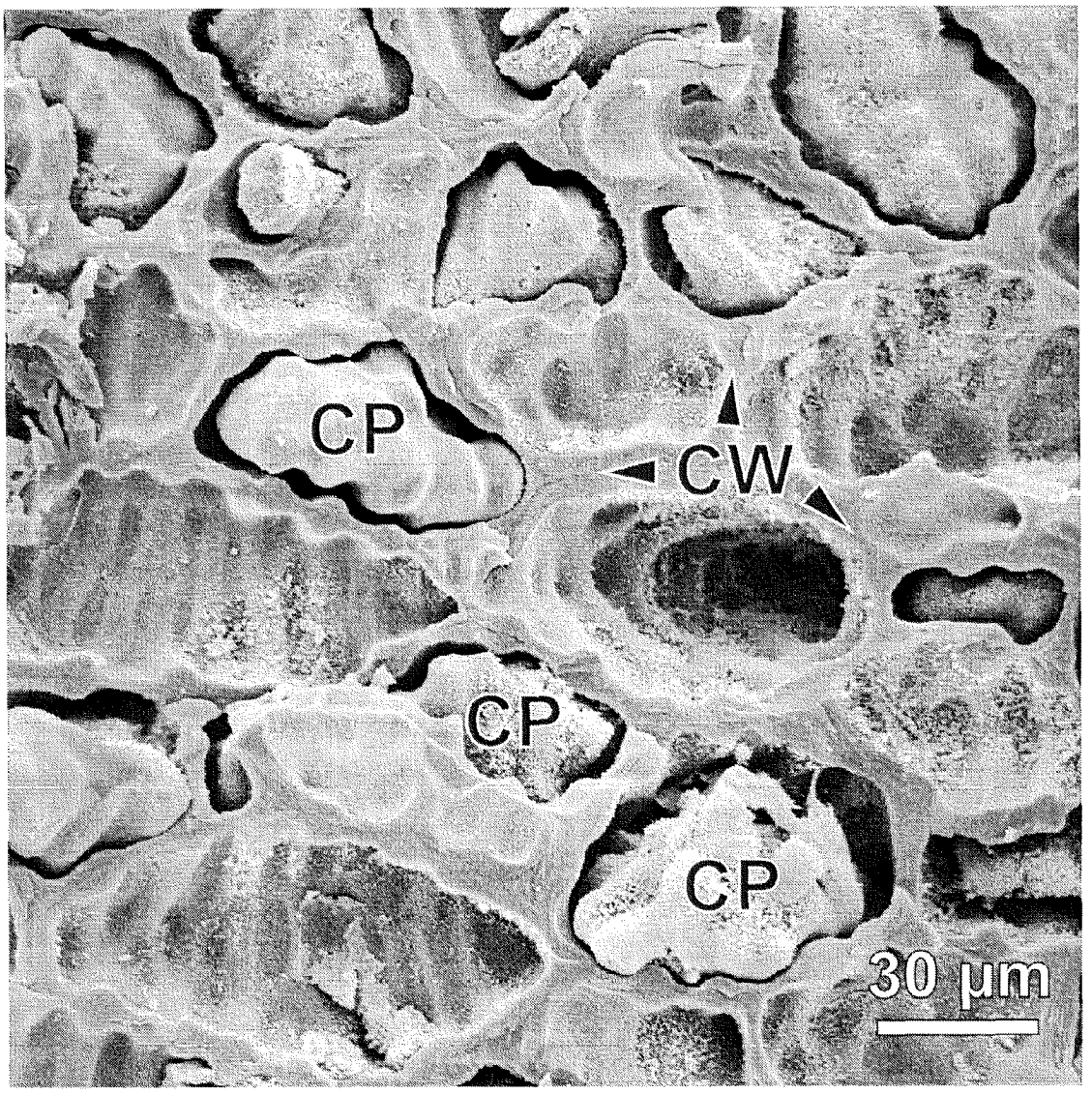

Fig. 25: *SEM micrograph of the green coffee bean tissue structure from a chemically fixed specimen. The cytoplasm (CP) is visible in some cells, whereas it is removed in others due to fractioning during specimen preparation. Surrounding cell walls (CW) are of remarkable thickness and show a striking and typical structuring with characteristic reinforcement rings. The detachment of the cytoplasm from the cell walls displays an artefact caused by the fixation procedures. (Image: S. Handschin).*

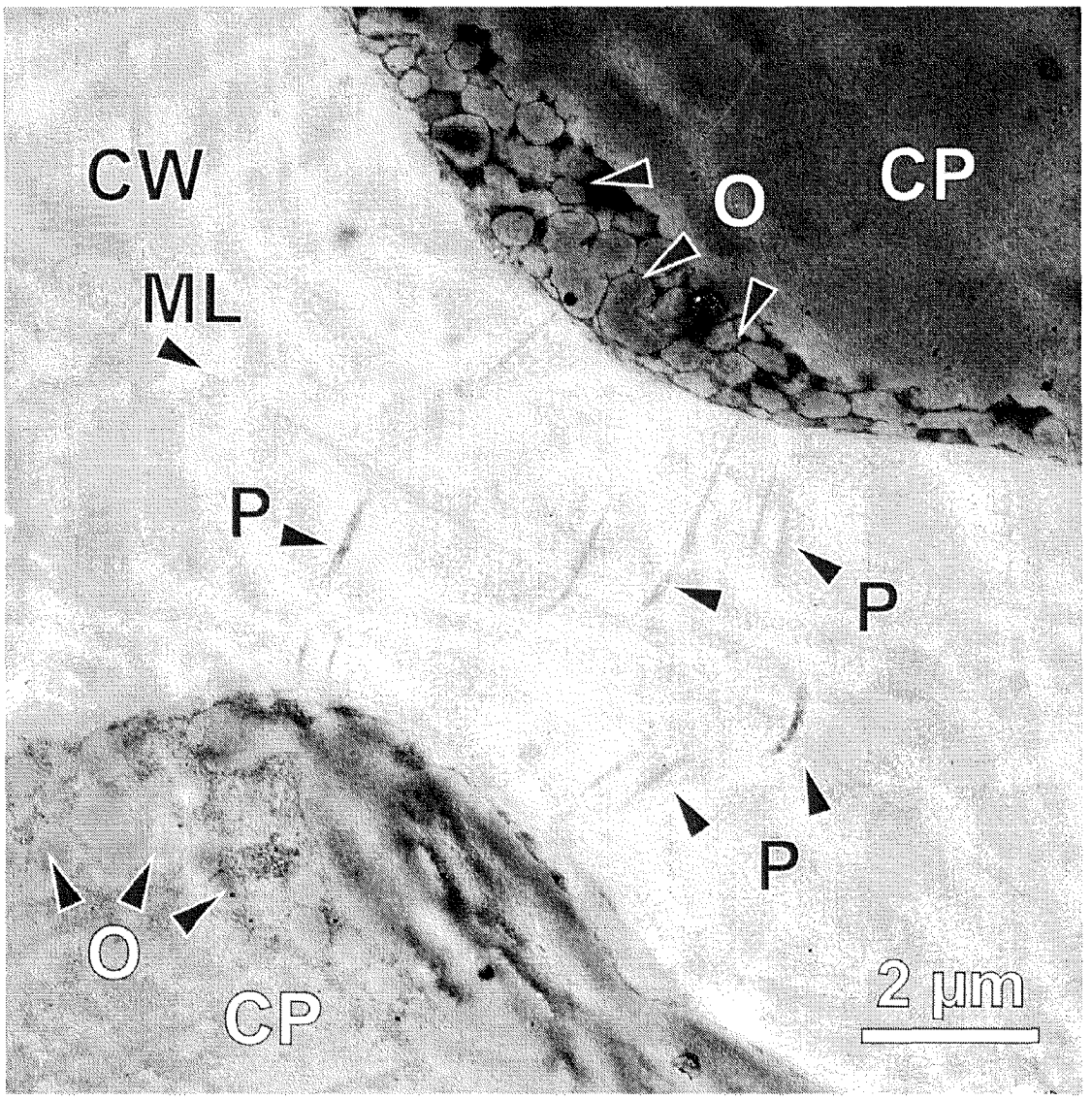

Fig. 26: *TEM micrograph of a cell wall in a green coffee bean. The continuous dark line is formed by the middle lamella (ML), that lies between the thick cell walls (CW) and the cytoplasm (CP) of two adjacent cells. Dark lines perpendicular to the middle lamella are parts of plasmodesmatae channels (P) through the wall. Coffee oil is organized in oleosomes (O) within the cytoplasm and located along the cell wall. (Image: S. Handschin).*

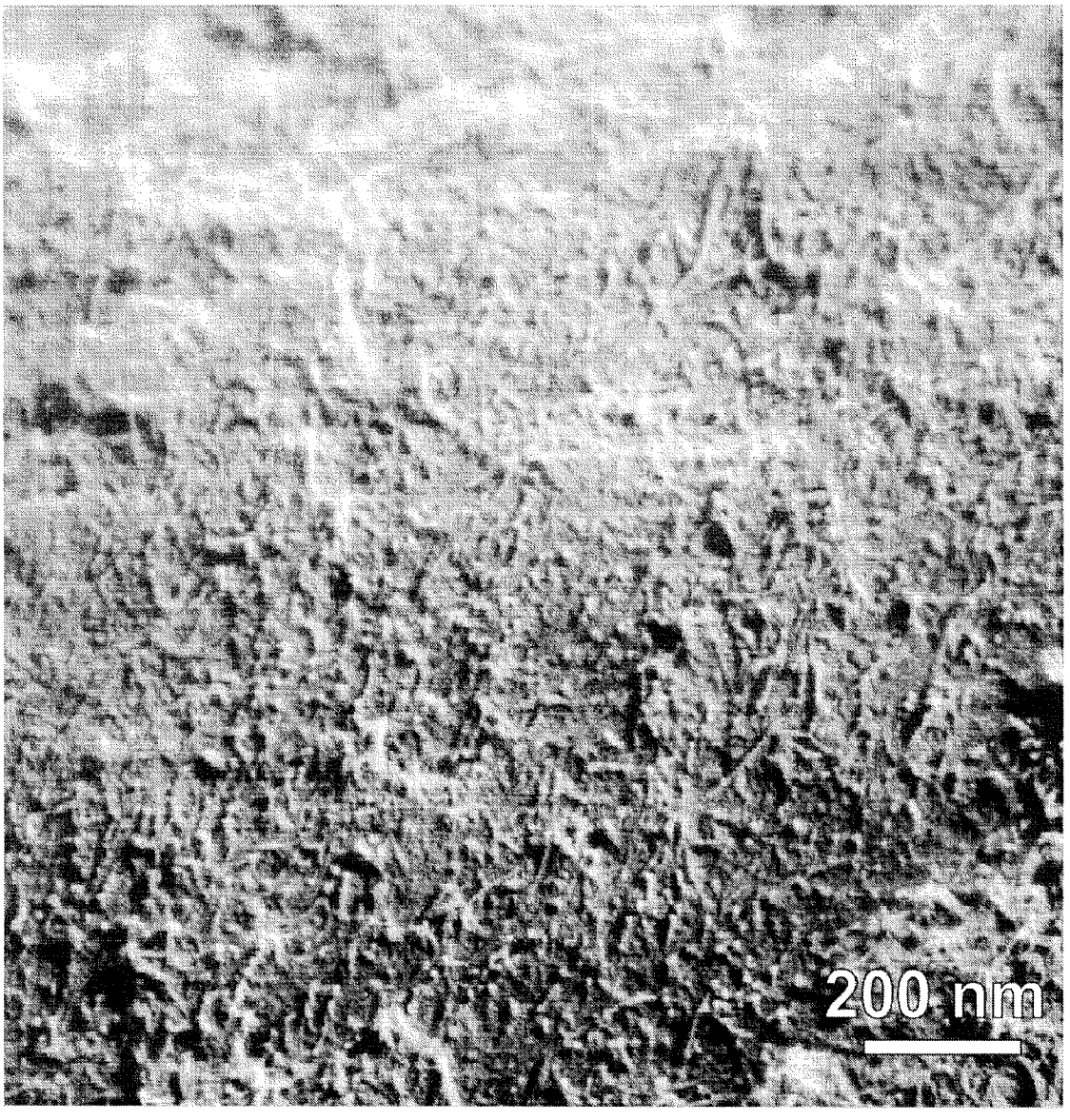

Fig. 27: *SEM micrograph of a cell wall cross section of a chemically fixed, de-oiled and fractured specimen from a green coffee bean. The structure of the fracture surface indicates the presence of a complex three-dimensional network of polysaccharide microfibrils. (Image: S. Handschin).*

4.2.2 Volume increase during roasting

Influence of time temperature profile and initial water content

The decrease of bean density during high and low temperature laboratory roasting is presented in Figure 28. As a result of the fast heat transfer in the laboratory roaster the highest rates of density decrease were found in the first half of processing. From a certain residence time onwards, the curves would continuously level off. Depending on time and temperature, a high or low density coffee was obtained. However, density decrease was limited by temperature, and the potential to achieve a low-density coffee was much higher in HTST processes than in LTLT processing.

Figures 29 and 30 show the development of bean volume in laboratory scale processes. Although volume increase not necessarily has to go inversely in parallel with the density decrease, a corresponding pattern was found for coffee beans. Density decrease as well as volume increase present a steady change in all processes, as no instantaneous expansion was observed that would lead to a discontinuity in the curves. This kind of expansion was confirmed by optical online observation of coffee beans during roasting at various temperatures. High temperature conditions resulted in much higher expansion rates as compared to low temperature conditions (Figure 29). Figure 30 compares the relative bean volume as a function of roast loss and clearly shows the large difference between high and low temperature roasting at a medium degree of roast.

In industrial scale roasting, the volume increase as well as the dehydration were delayed due to much slower heat transfer because of large batches of beans (Figure 31). Since the highest bean temperatures are generally found at the end of an industrial roasting process and the water content of beans may still be at sufficiently high levels, a major part of the overall bean expansion is produced only during the second half of processing.

As different initial water contents of the green beans result in a different development of bean temperature, water content also has a major impact on bean expansion. The influence of initial water content during laboratory roasting is shown in Figure 32. Lower initial water contents result in an accelerated and greater volume increase. Products with identical ORL exhibited different volumes. Small

and Horrell (1993) reported similar findings and suggested pre-drying of the green beans in order to produce low-density coffees.

A general relationship between the time temperature program and the density and volume produced in the beans was found to apply for both the laboratory as well as industrial scale roasting processes. Beans roasted at higher temperatures exhibited greater bean volume and lower density than beans roasted at lower temperatures with longer roasting times. Therefore, the total roasting time to achieve a given degree of roast with a given raw material is a reliable indicator to predict the density and volume properties of a roasted product. This relationship has been described in a series of investigations with different objectives by various authors (Dalla Rosa et al., 1980, Guyot et al. 1985, Kazi and Clifford, 1985, Severini et al., 1991, Small and Horrell, 1993). Like for loss of dry matter or browning, the roasting temperature seems to impose a limit of maximum expansion that cannot be overcome by residence time. Similar to the statements by Dalla Rosa et al. (1980), higher temperatures led to a greater potential of bean expansion. However, as outlined above, not the final temperature achieved in a process, but the total thermal energy transferred during the entire process presents the critical factor. Finally, different bean volumes are obviously related to different average cell sizes (Kazi and Clifford, 1985).

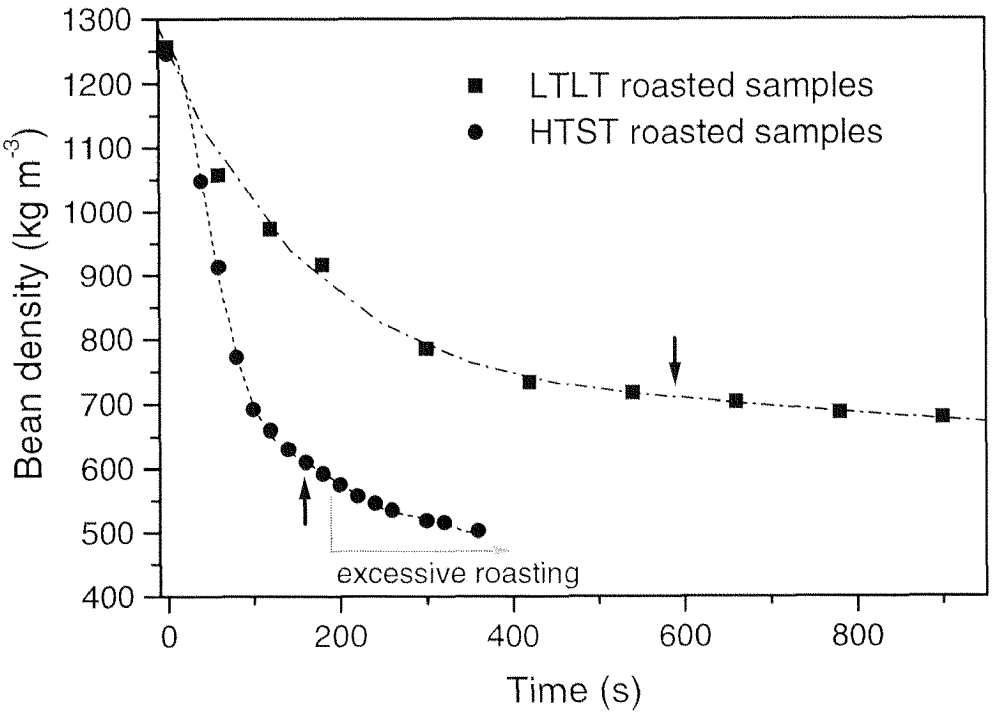

Fig. 28: *Decrease of bean density during high- and low-temperature laboratory roasting. Dotted lines represent trend curves and arrows indicate a medium degree of roast.*

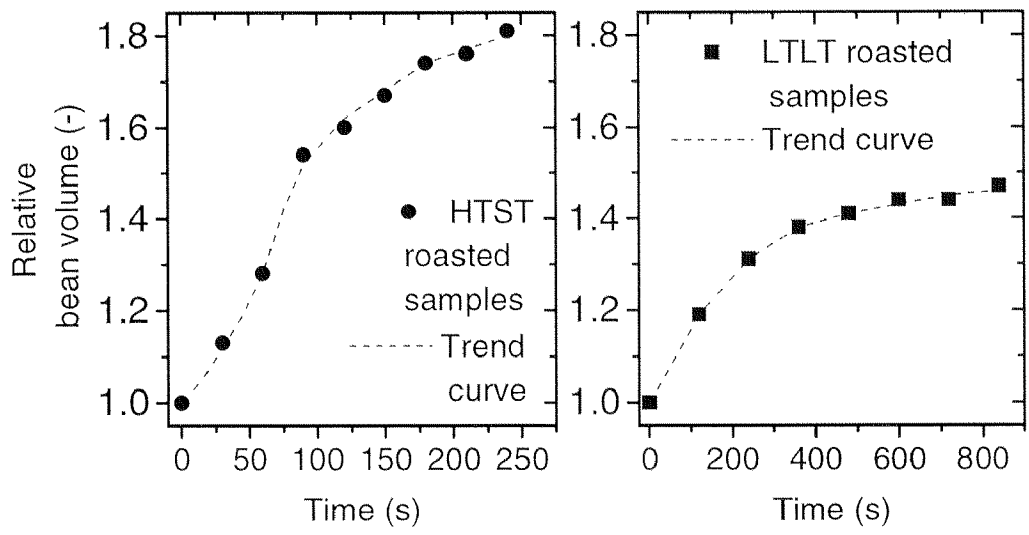

Fig. 29: *Development of bean volume increase during high (left) and low temperature (right) laboratory roasting (C. arabica, Costa Rica).*

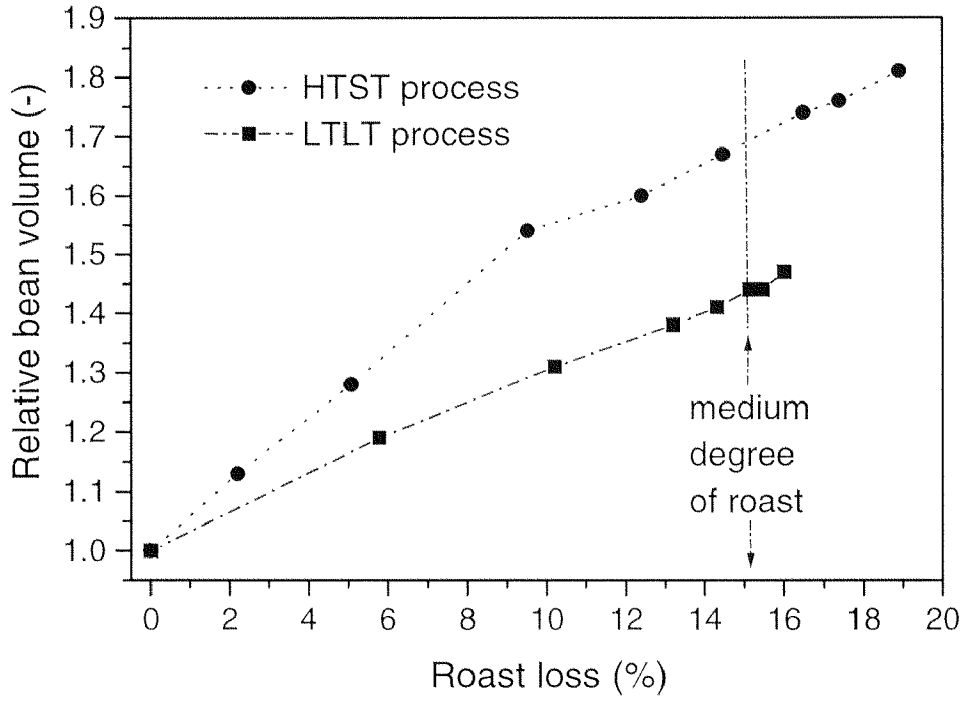

Fig. 30: *Characteristic development of bean volume increase as a function of the degree of roast (roast loss) during high and low temperature laboratory roasting (C. arabica, Costa Rica, identical with raw material in Figure 29).*

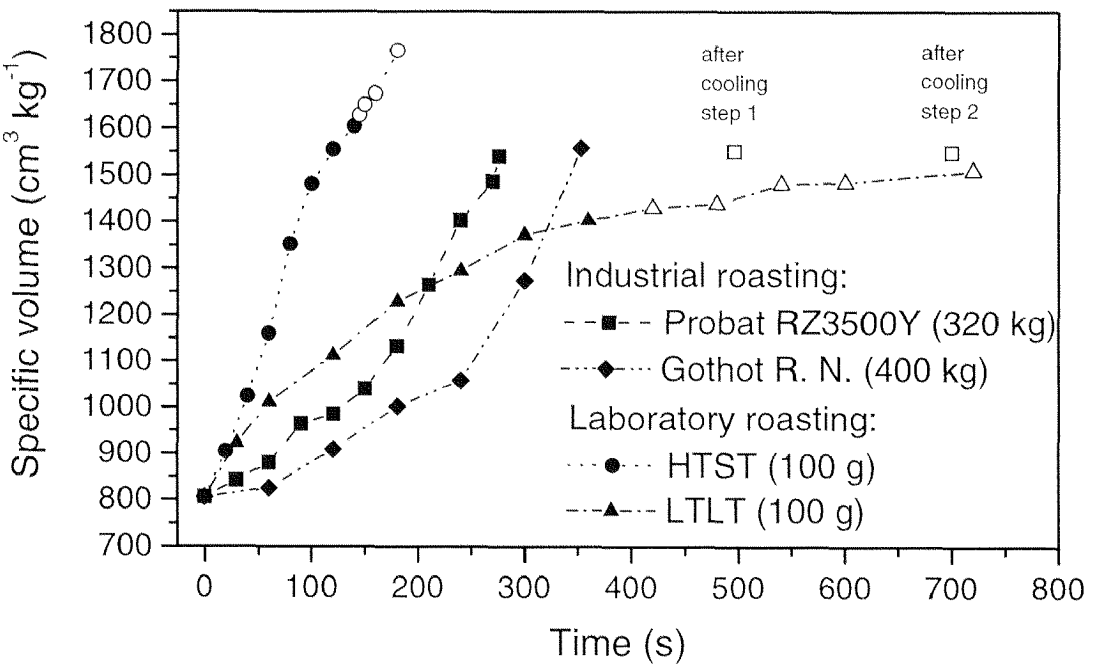

Fig. 31: *Increase of specific bean volume during laboratory and industrial scale roasting. Open symbols indicate samples of a higher degree of roast as compared to the industrial end products. An identical commercial blend of 100 % C. arabica beans was used for each trial.*

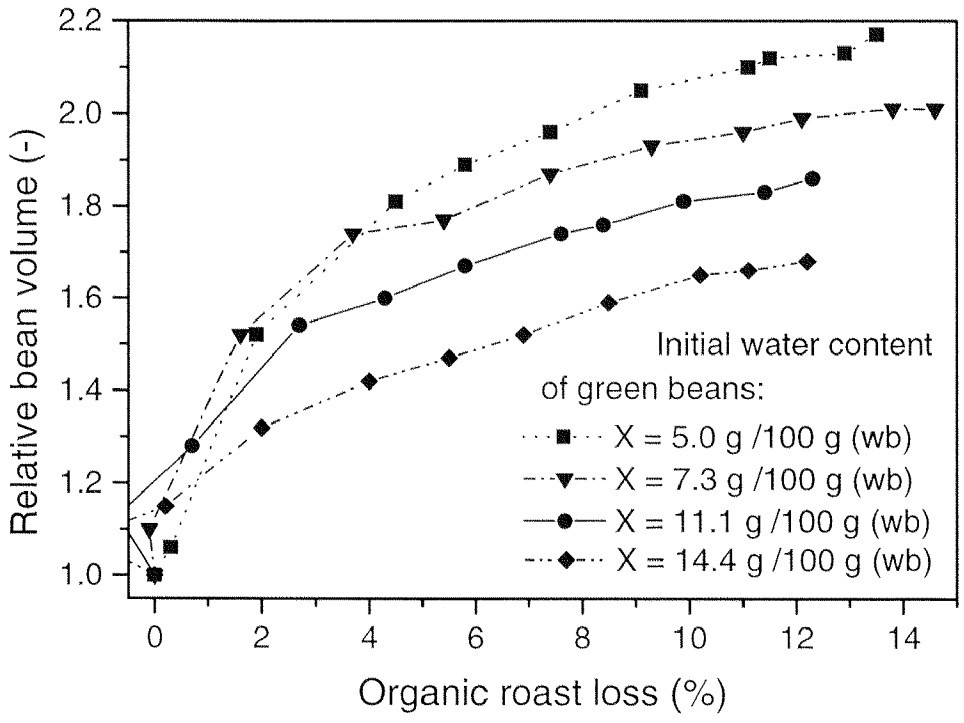

Fig. 32: *Influence of initial water content on bean expansion during HTST laboratory roasting. An organic roast loss of ORL = 7.0 corresponds to a medium degree of roast (C. arabica, Costa Rica).*

Model of coffee bean expansion

Bearing in mind that the gas pressure in the bean reaches its highest level during the final stage of roasting, it is not obvious why the highest expansion rates are found in an early stage of roasting in the case of laboratory roasting processes or an early stage of dehydration in the case of industrial roasting. Likewise it is not clear why bean expansion is limited to low expansion rates in the final roasting stages and beyond usual degrees of roast. Finally the question needs to be answered why much higher expansion rates are found during high temperature roasting as compared to low temperature processes.

The volume increase of coffee beans during roasting is promoted by development of gas and water vapor as the driving force, but limited by structural resistance opposed to it due to the hard and tough cell wall material in coffee beans. Furthermore, polysaccharides in an amorphous or semi-crystalline state in foodstuffs may undergo glass transitions, depending on temperature and water content, which in turn change the physical properties completely (Slade and Levine, 1991). Glass transition phenomena may play an important role in structural resistance of coffee tissue.

Figure 33 shows the assumed principle state diagram of coffee bean polysaccharides linking the glass transition temperature T_g to the water content of the beans. Since T_g is a material property attributed to a particular polysaccharide, there is no sharp transition from one state into the other in foodstuffs with a composition as complex as in coffee beans. Hence, several different glass transitions at different temperatures are to be expected and softening phenomena in foods may be of a more fuzzy characteristic. Roasting implies a large rise in temperature as well as extensive dehydration of the bean. In Figure 33 the roasting curves may cross T_g twice, changing the bean from a hard and glassy initial state into a more rubbery state and finally back into a more glassy state. The more the bean temperature T_{bean} will exceed T_g in stage 2, the more pronounced the rubbery state will be, allowing for bean expansion.

The heating stage during laboratory roasting is passed quickly, which leads to a rubbery state of the bean with high expansion rates in a early stage of roasting. The

rubbery state may be more pronounced with HTST roasting, resulting in greater volume increase than in LTLT roasting. The return to the glassy state during the final roasting stage may cause high structure resistance and hinder further volume increase. The heating stage before exceeding T_g is considerably prolonged in industrial processes. The rubbery state of the bean will be reached only during the second half of industrial roasting, as the water content is still on a sufficiently high level.

The hypothesis of bean expansion outlined above was supported by experimental data obtained from dynamic mechanical thermal analysis (DMTA) measurements, simulating a slow roasting process (Figure 34). At least two softening events could be related to glass transitions in the temperature ranges of around 130 °C (Tg_1) and 210 °C (Tg_2), respectively. As the heating rate in these experiments was as low as 5 °C min^{-1}, dehydration and temperature development differed considerably from real roasting conditions. Hence, Tg_1 and Tg_2 must be interpreted with due care. Nevertheless, 130 °C was also reported to be a critical temperature in nut roasting by Perren (1995).

Small and Horrell (1993) suggested an instantaneous decomposition of chlorogenic acids with subsequent CO_2 formation in high temperature processes to be responsible for extensive bean expansion. This theory cannot be upheld in view of analytical data that show a steady and continuous decrease of these acids and no connection between initial content of chlorogenic acids and bean expansion.

In conclusion, gas formation, dehydration, bean temperature and roasting time present the most important parameters affecting the volume increase of coffee beans during roasting. The shift in the balance between force and resistance due to these parameters controls the steady and continuous increase of bean volume. It is influenced by the roasting conditions in general, and by the roasting temperature in particular.

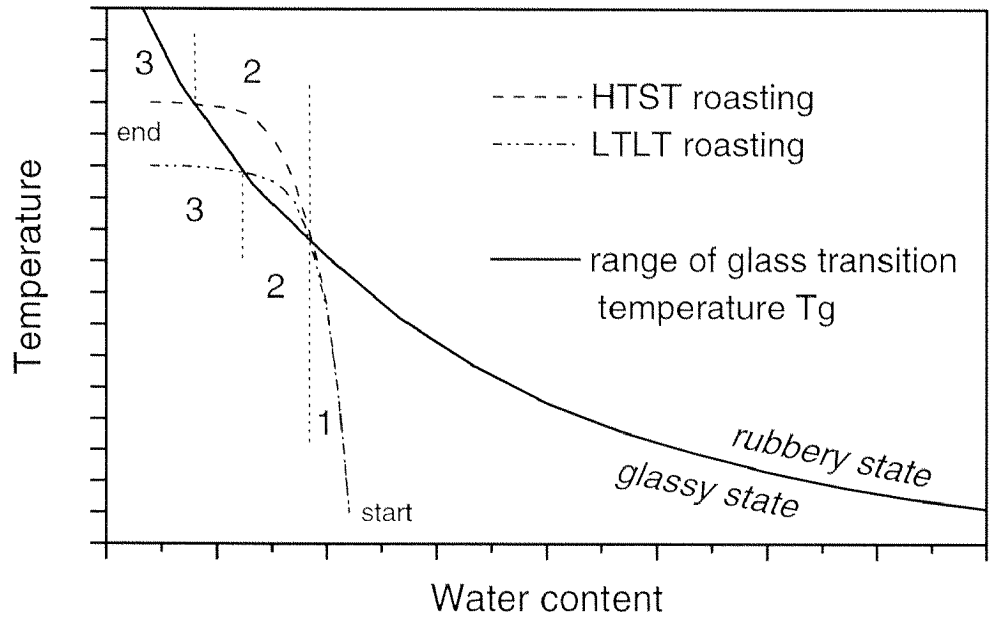

Fig. 33: *Hypothetical state diagram of coffee bean cell wall polysaccharides with T_g range (strictly qualitative assumption) and temperature-moisture development for HTST and LTLT roasting. 1: Heating stage, $T_{bean} < T_g$, glassy state of the bean. 2: $T_{bean} > T_g$, more rubbery state allowing for volume increase, stage of greatest expansion rates. 3: $T_{bean} < T_g$, again more glassy state with high structure resistance.*

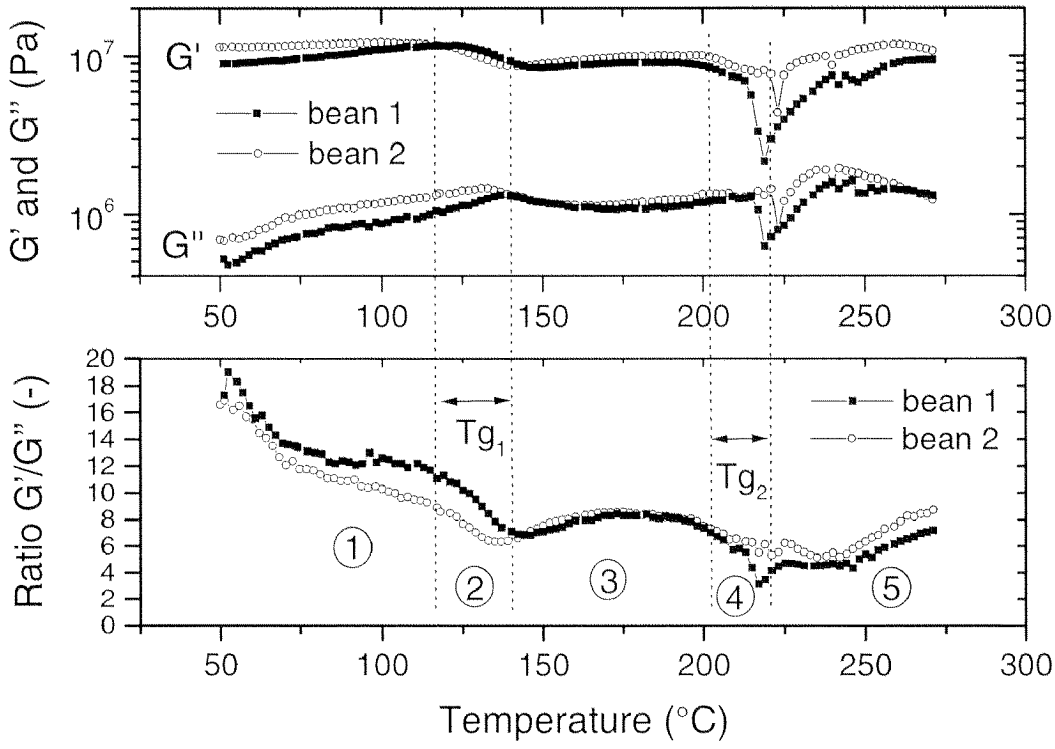

Fig. 34: *Dynamic mechanical thermal analysis (DMTA) of coffee bean slices clamped between a plate-plate measuring geometry. Dynamic testing (oscillation) with a heating rate of 5 °C min^{-1}. G': Storage modulus. G'': Loss modulus. The ratio G'/G'' is a suitable mean to monitor softening phenomena during heating. 1: Moderate general softening due to heating. 2: First glass transition (Tg_1). 3: Trend to moderate hardening due to dehydration. 4: Second glass transition (Tg_2). 5: Trend to hardening due to progressive dehydration and subsequent increase of T_g.*

4.2.3 Structural changes during roasting

Hot air roasting of coffee beans involves a series of substantial macroscopic and microstructural changes. As a result of bean expansion, remainings of silver skins come off and some cracks appear on the bean surface. In HTST and LTLT laboratory roasting most silver skins came off within the first or the first two minutes, respectively, without producing any sounds. For this reason, this event is not related in any way with popping sounds, but with increasing shear stress on the bean surface. Major surface cracks are created preferably on the flat side of the bean, and near to the poles in particular. Optical online observations of beans during roasting revealed, that the generation of a major crack starts with a crack as fine as a hair, probably accompanied by a sharp popping sound. The crack is then continuously enlarged as bean expansion proceeds. The typical popping sounds in coffee roasting may be caused by escaping gas. The sounds become remarkably frequent during the final roasting stage.

Volume increase, dehydration and chemical reactions during roasting lead to a profound microstructural change of both the cell wall and the cytoplasm of the green bean. Figures 35-45 illustrate this dynamic process of structural change. The most striking appearance is the formation of excavated cells with the cytoplasm pressed towards the walls and a large void occupying the cell centre. This state is entered immediately after subjecting the bean to high temperature (Figure 35). Most probably it is caused by built up pressure due to water vapor and gas formation.

The layer of modified cytoplasm becomes thinner on continuation of roasting, since more and more cell mass is converted into gases and water vapors and cell sizes are increased. It also seems to undergo a viscosity increase during roasting, leading to a more irregular surface (Figure 38) and to filament-like structures stretching from one cell wall side to the opposite (Figure 39). Occurrence of filament-like cytoplasm structures in large numbers (Figure 40) was observed in some tissue regions and was found to be more frequent and typical with higher degrees of roast. The numerous voids in the shape of burst bubbles embedded in the cytoplasm layer (Figure 38) are most likely connected with the break up of oleosomes and the subsequent mobilization of coffee oil. In general, the structure of high temperature roasted beans (Figure 41) was comparable to the one in low temperature roasted coffee. It may

appear slightly more disorganized. However, since inhomogenities from cell to cell within the same bean were far more pronounced than possible variations of differently roasted beans, a distinction on the basis of different roasting conditions would be unreasonable.

The TEM micrographs in Figures 44 and 45 demonstrate that the well-organized original cytoplasm structure in green beans is subject to profound changes during roasting too. Although oleosomes are reported to be very stable (Huang, 1996), they are completely or partially destroyed in the roasting process, allowing the mobilized oil to fuse and form new coalesced oil droplets. Numerous oil droplets were observed within as well as upon the cytoplasm layer (Figure 45). The average droplet diameter falling in the range of 0.5 to 1.0 µm, much larger droplets of more than 6 µm diameter were found in some cases and also reported by Wilson et al. (1997). In contrast, numerous smaller droplets but no droplets larger than 1.0 µm were found in SEM analysis of chemically fixed specimens (Figures 42 and 43). The findings indicate the presence of a disorganized, rearranged and highly mobilized lipid phase in a matrix of other denatured cytoplasmic constituents.

The cell wall frame work appears as the most stable structure part during roasting. Nevertheless, closer investigations by SEM analysis suggest fundamental changes in the microfibril network of cell walls in roasted beans (Figure 46). The fraction surface points to a more muddled three-dimensional network made of denatured microfibrils with shorter chain lengths as compared to green bean cell walls. Similar microscopic findings have been described by Wilson et al. (1997). Moreover, this visual impression is supported by analytical data on polysaccharides reported by Thaler and Arneth (1968a, 1968b, 1969), Thaler (1975), Bradbury and Halliday (1990), Navarini et al. (1999), and Leloup and Liardon (1993). These authors stated fundamental changes in chemical composition of the polysaccharide fraction during roasting. Leloup and Liardon found that roasting considerably reduces the molecular weight range of arabinogalactans and galactomannans in cell walls.

Considering the fact of coffee oil and gas transport across the bean tissue during storage, the existence of a cell wall micropore network allowing for mass transfer must be assumed. Plasmodesmatae channels present in the green bean were also found in the roasted state in some spots of the cell walls (Figures 44 and 45).

However, these channels are cell-to-cell connections and do not provide access to the bean surface. Moreover, it is unclear, whether these channels are free for mass transfer or congested by denatured proteins. Thus, they do contribute but do not seem to play a key role in mass transfer. On the other hand, several authors assume that the roasting process alters the porosity of the cell wall (Gutiérrez et al., 1993; Illy and Viani, 1995; Massini et al., 1990; Puhlmann et al., 1986; Saleeb, 1975; Wilson et al., 1997). The microscopic investigations favor a model concept where the cell wall microchannels are embodied by the individual meshes of the microfibril network.

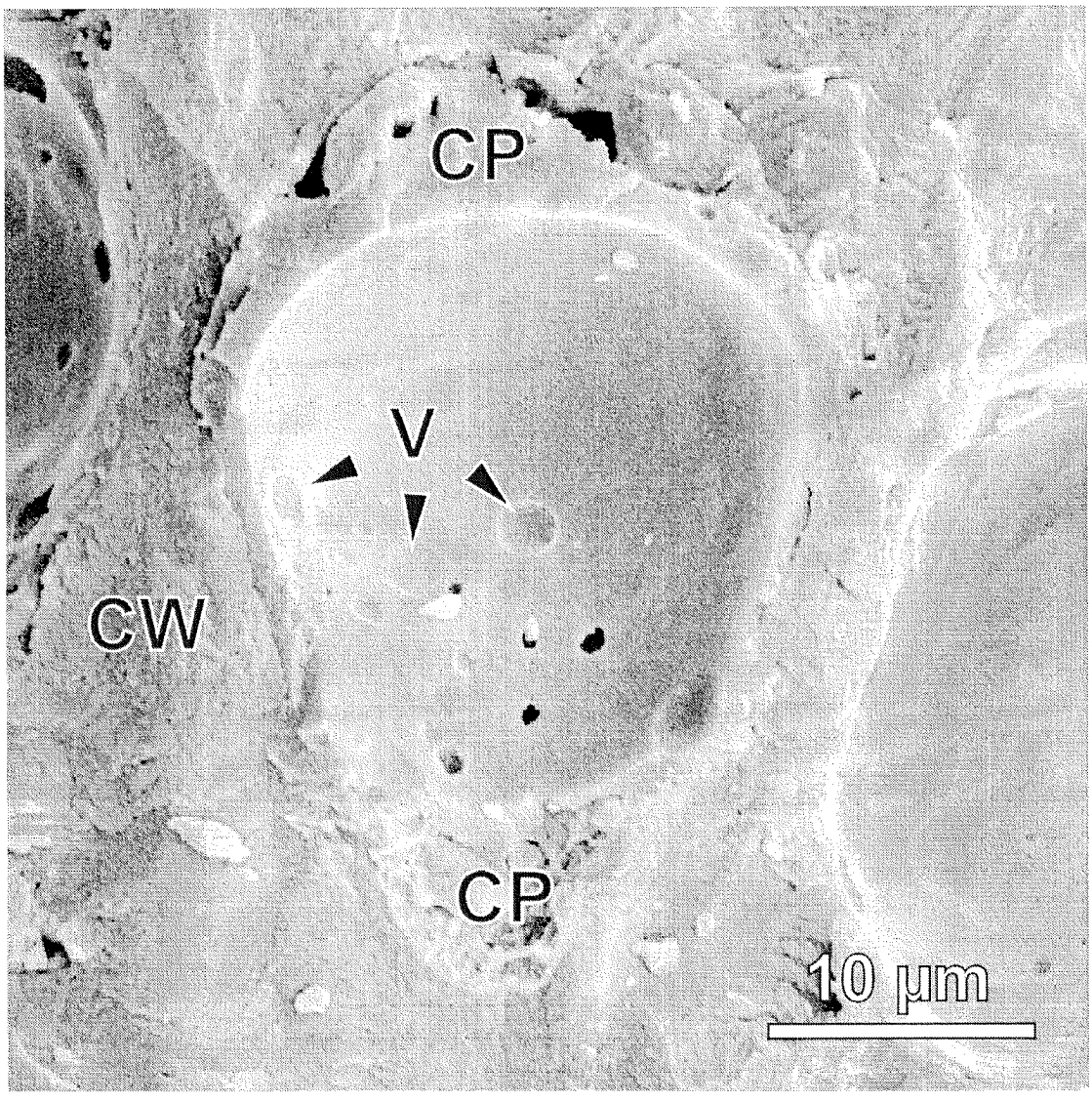

Fig. 35: *Cryo-SEM micrograph of a coffee cell in an early stage of roasting after 60 s of low temperature roasting (LTLT-process). The cytoplasm (CP) is already rearranged and forms a thick layer along the cell walls (CW). A large void occupies the cell centre. Smaller voids (V) of a burst-bubble structure appear in the cytoplasmic layer. (Image: B. Frey, S. Handschin).*

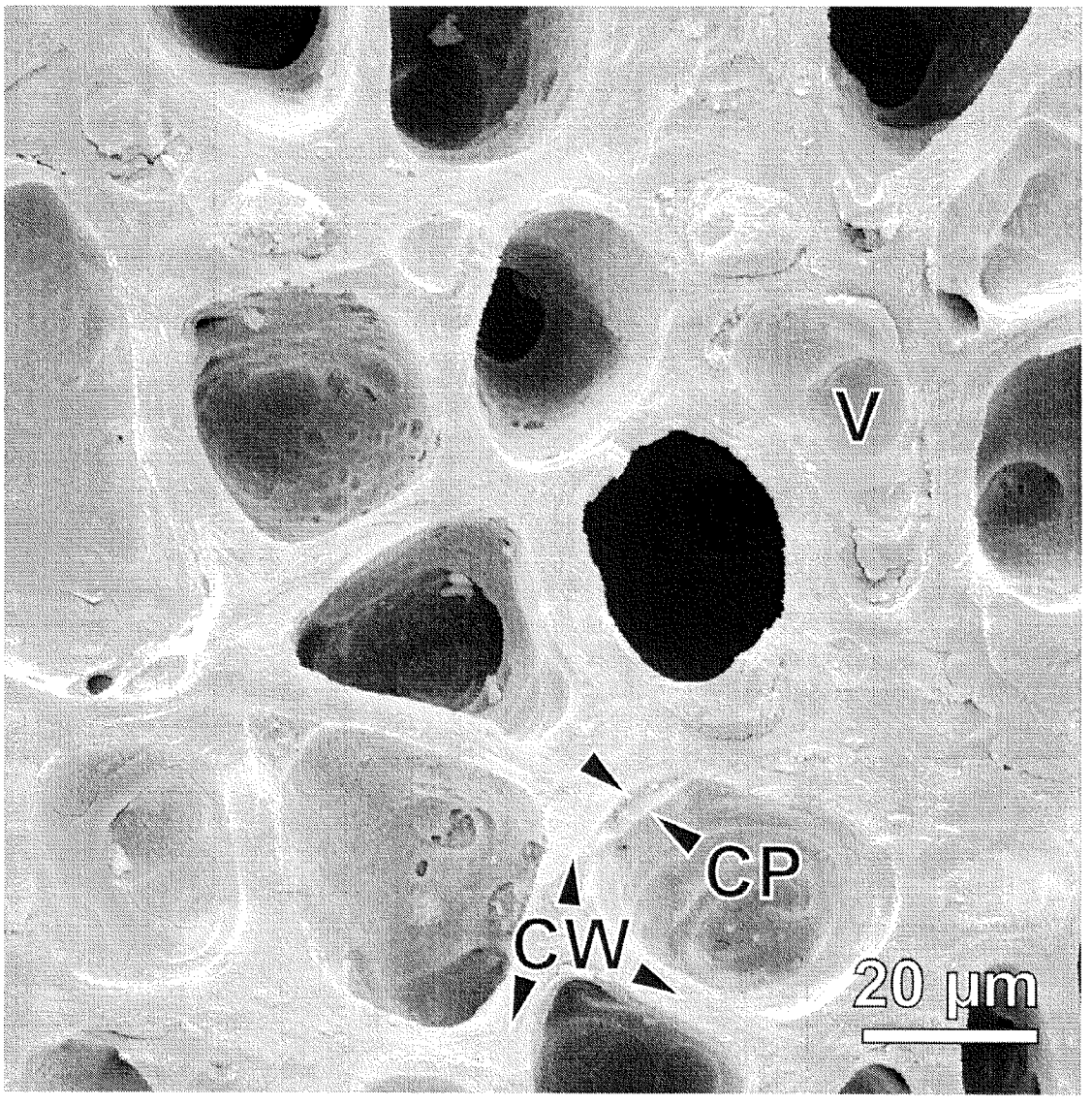

Fig. 36: *Cryo-SEM micrograph of the tissue structure of a coffee bean roasted for 180 s at 220 °C (LTLT). Each cell exhibits changes of the cytoplasm. Irregular layers of modified cytoplasm (CP) stretch along the cell walls (CW). A number of smaller voids (V), but of various sizes, are embedded within these layers. (Image: B. Frey, S. Handschin).*

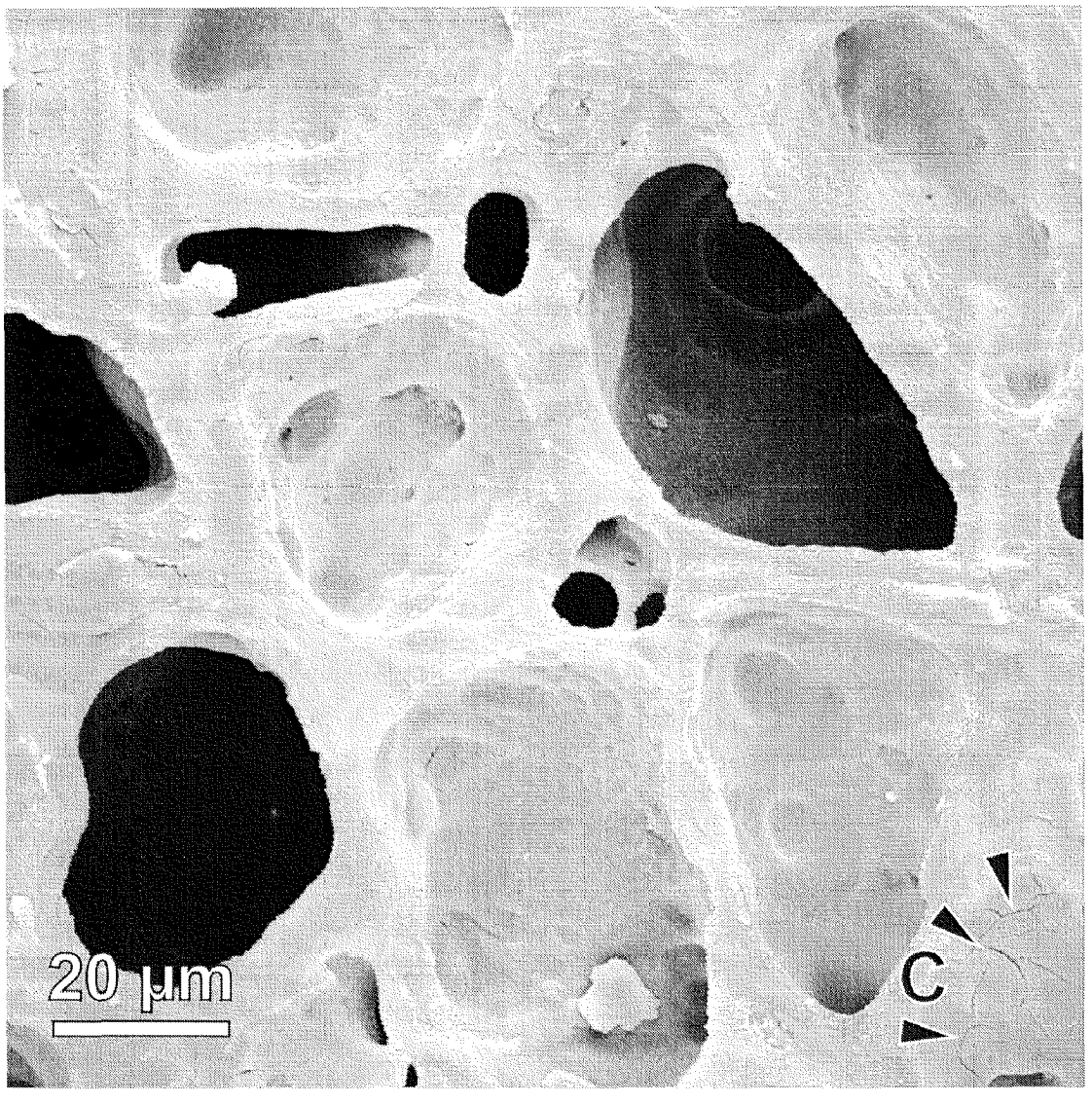

Fig. 37: *Cryo-SEM micrograph of the tissue structure of a LTLT roasted coffee bean after 360 s of roasting. With the proceeding of roasting the microstructural changes developed further. The layer of modified cytoplasm appears somewhat thinner and more irregular. Cracks (C) are preparation artefacts and may indicate a high content of oil in the cytoplasmic layer. (Image: B. Frey, S. Handschin).*

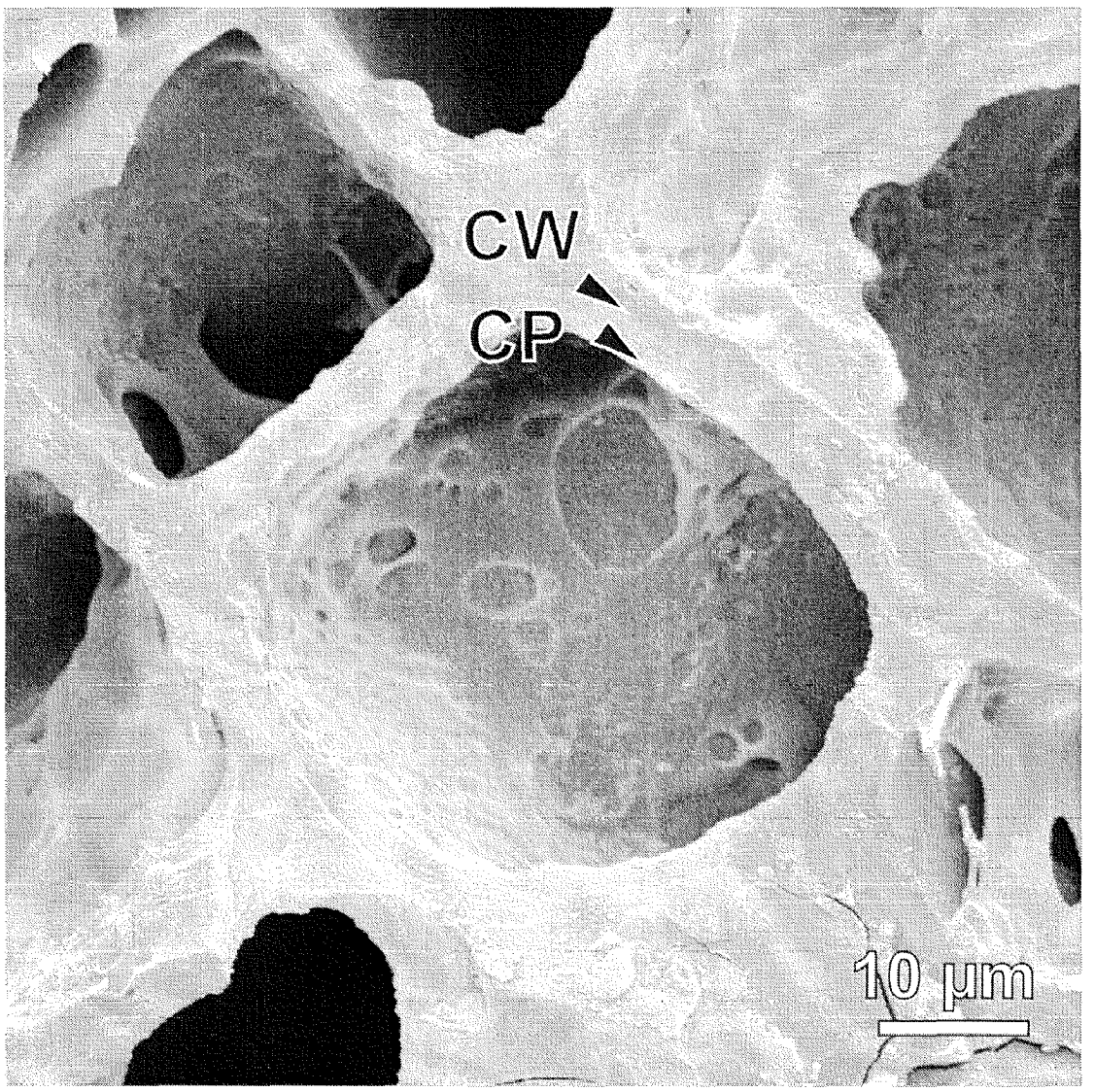

Fig. 38: *Cryo-SEM micrograph of a cell in a fully roasted coffee bean at a medium degree of roast (600 s, LTLT processed). The remaining layer of modified cytoplasm (CP) along the cell wall (CW) is only thin. It exhibits a marked burst-bubble structure with numerous embedded voids. (Image: B. Frey, S. Handschin).*

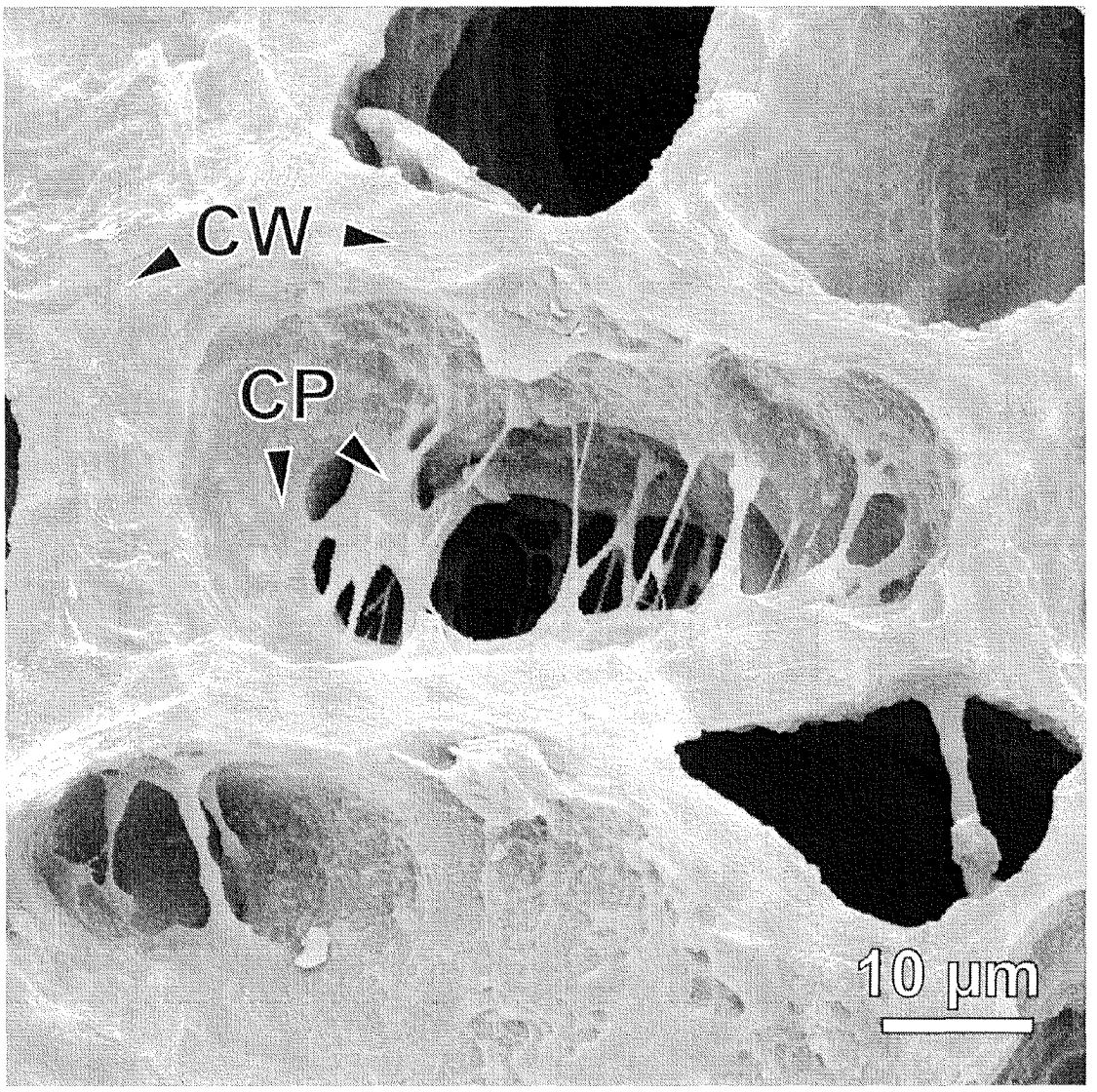

Fig. 39: *Cryo-SEM micrograph of a cell in a fully roasted coffee bean, LTLT roasted for 600 s. It was obtained from the same specimen as micrograph 38 and illustrates the large discrepancies of appearance between different neighboring cells from the same sample. Filament-like cytoplasmic structures (CP) stretching from one cell wall (CW) side to the opposite were found in numerous cells. (Image: B. Frey, S. Handschin).*

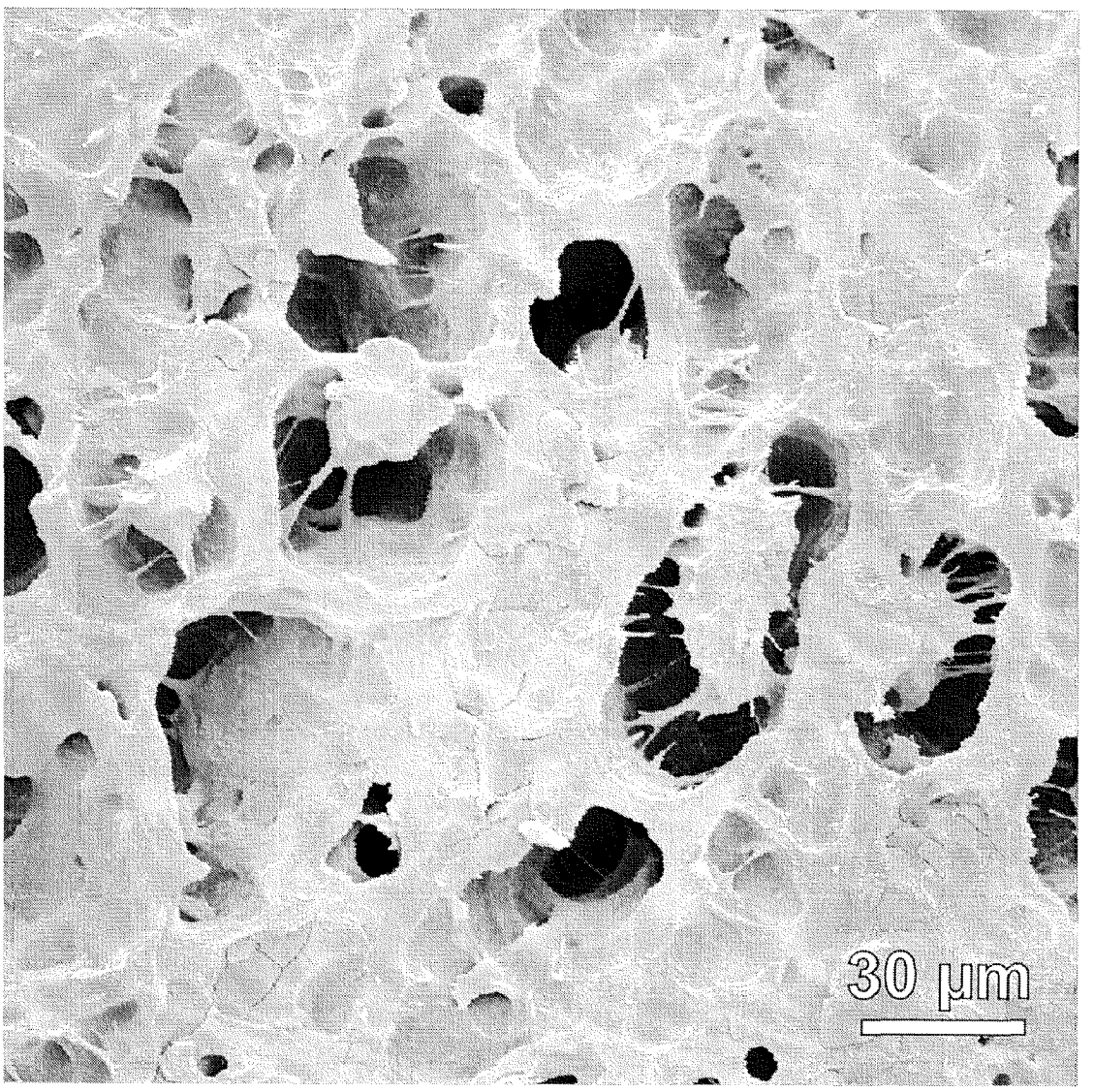

Fig. 40: *Cryo-SEM micrograph of the cell structure in a bean excessively roasted for 780 s (LTLT process). It shows a tissue region with cumulated occurrence of filament-like cytoplasmic structures. The presence of such regions was found to be more frequent and typical with higher degrees of roast. (Image: B. Frey, S. Handschin).*

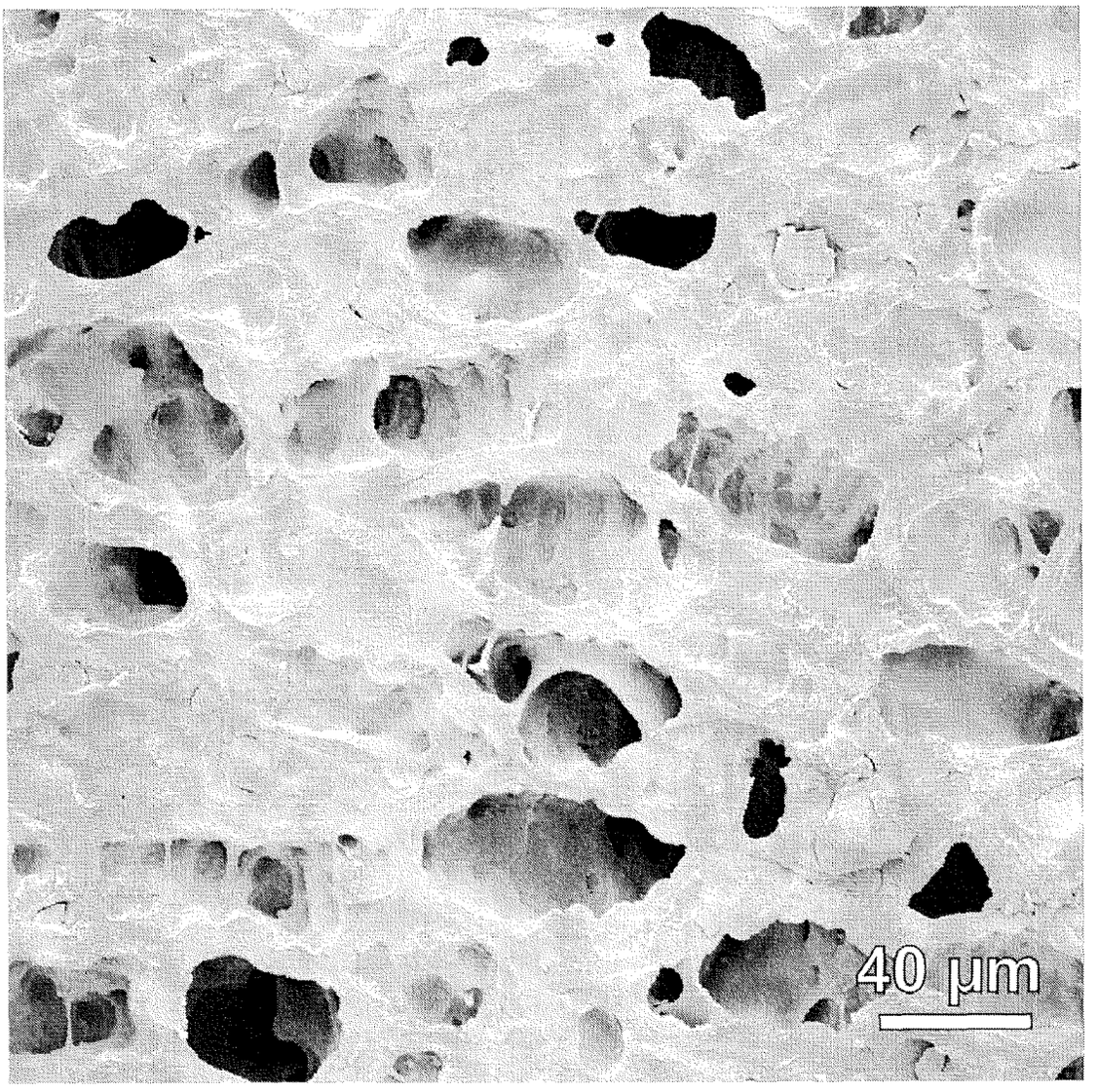

Fig. 41: *Cryo-SEM micrograph of the tissue structure in a high temperature roasted coffee bean (120 s, HTST process). In general, the structure is comparable to the one in LTLT roasted beans. Inhomogenities from cell to cell within the same bean were found to be much more pronounced than possible variations due to different roasting conditions. (Image: B. Frey, S. Handschin).*

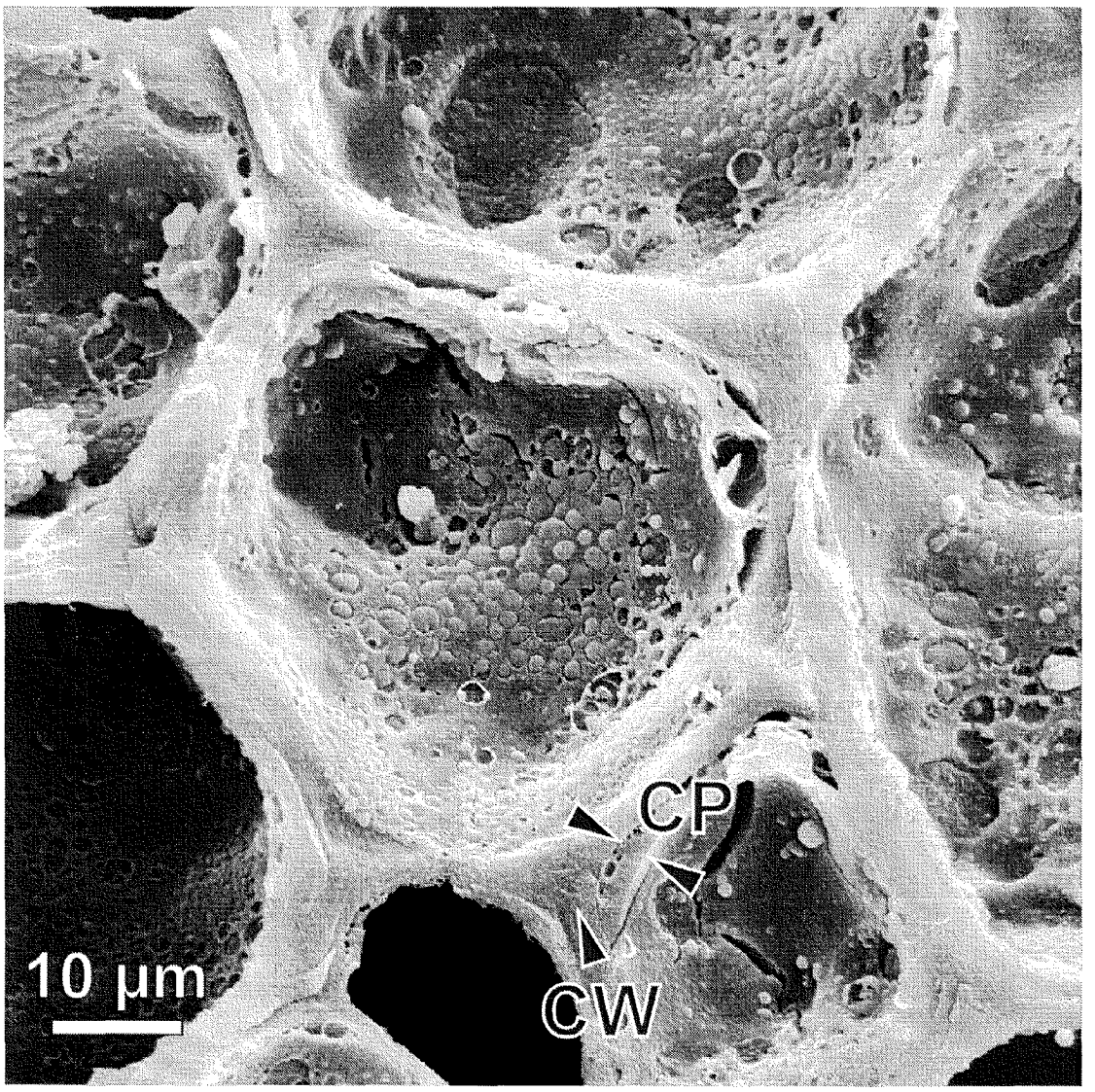

Fig. 42: *SEM micrograph of a chemically fixed specimen from an excessively roasted coffee bean (220 s, HTST process). Layers of modified cytoplasm (CP) spread along the cell wall (CW) framework. The applied preparation technique provides a different image of the layer structure, showing numerous embedded droplets. (Image: S. Handschin).*

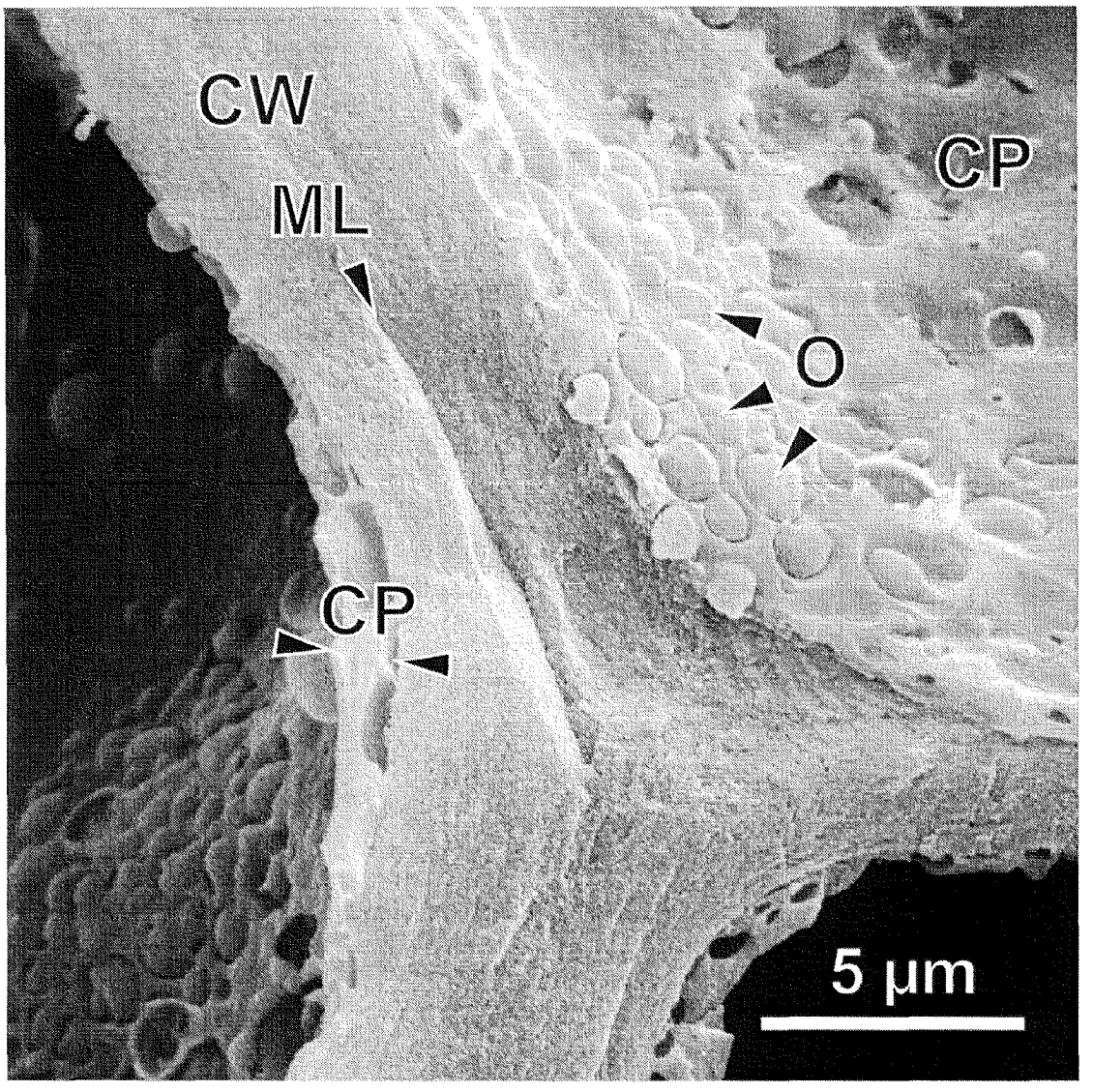

Fig. 43: *SEM micrograph of a chemically fixed specimen from an excessively roasted bean (identical specimen as in micrograph 42). It shows parts from 3 cells, separated by a cell wall (CW) junction. Different fraction behavior of the middle lamella (ML) caused a marked stair within the cell wall. Modified cytoplasm (CP) with numerous embedded droplets (O) lies along the walls. The droplets may be either more or less intact oil bodies or mobilized and coalesced oil droplets. (Image: S. Handschin).*

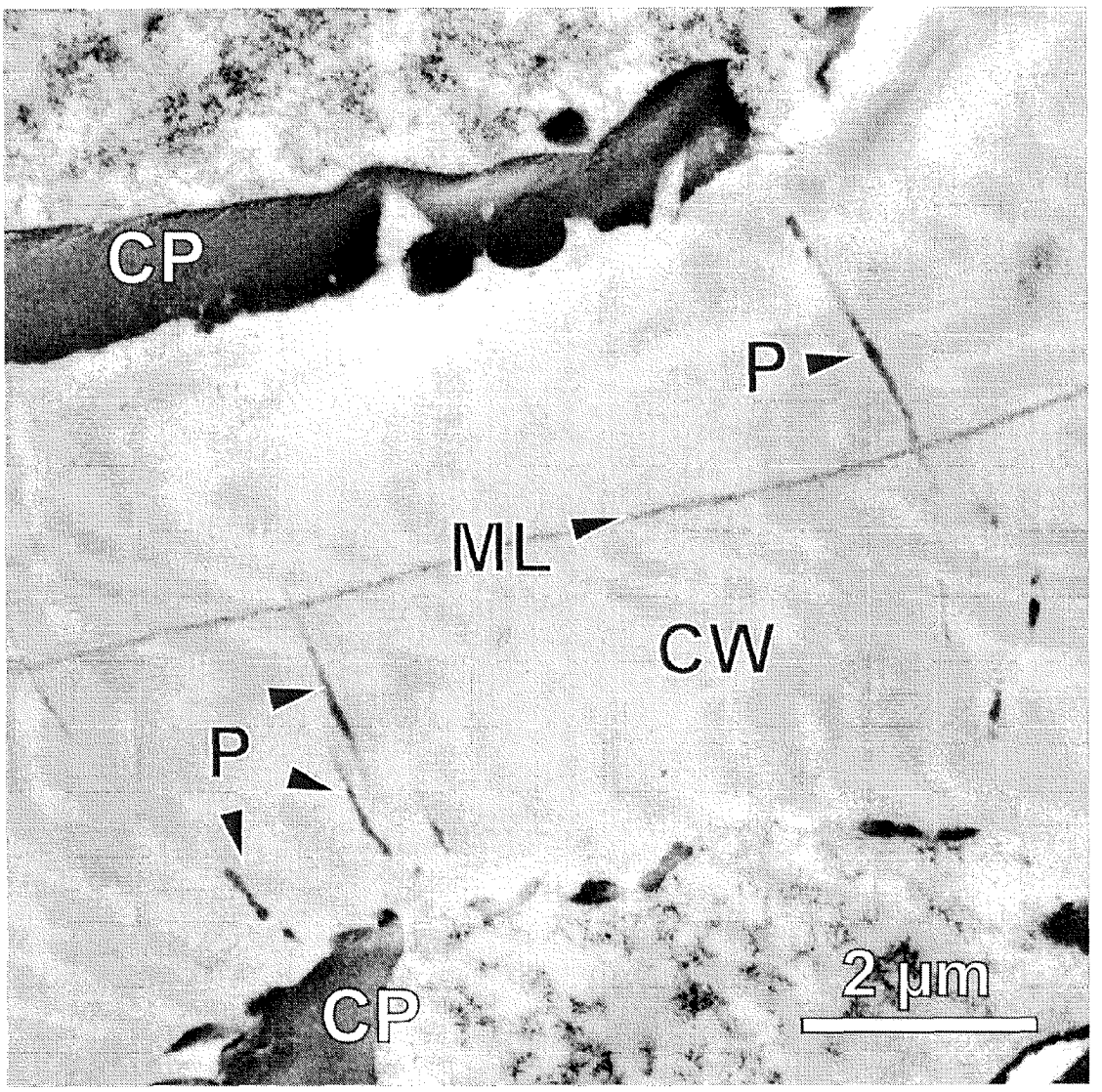

Fig. 44: *TEM micrograph of a cell wall in a partially roasted coffee bean (80 s, HTST process). The middle lamella (ML) forms a continuous black line and separates the cell walls (CW) and the layers of modified cytoplasm (CP) of the two adjacent cells. Parts of modified plasmodesmatae channels (P) are visible perpendicular to the middle lamella. (Image: S. Handschin).*

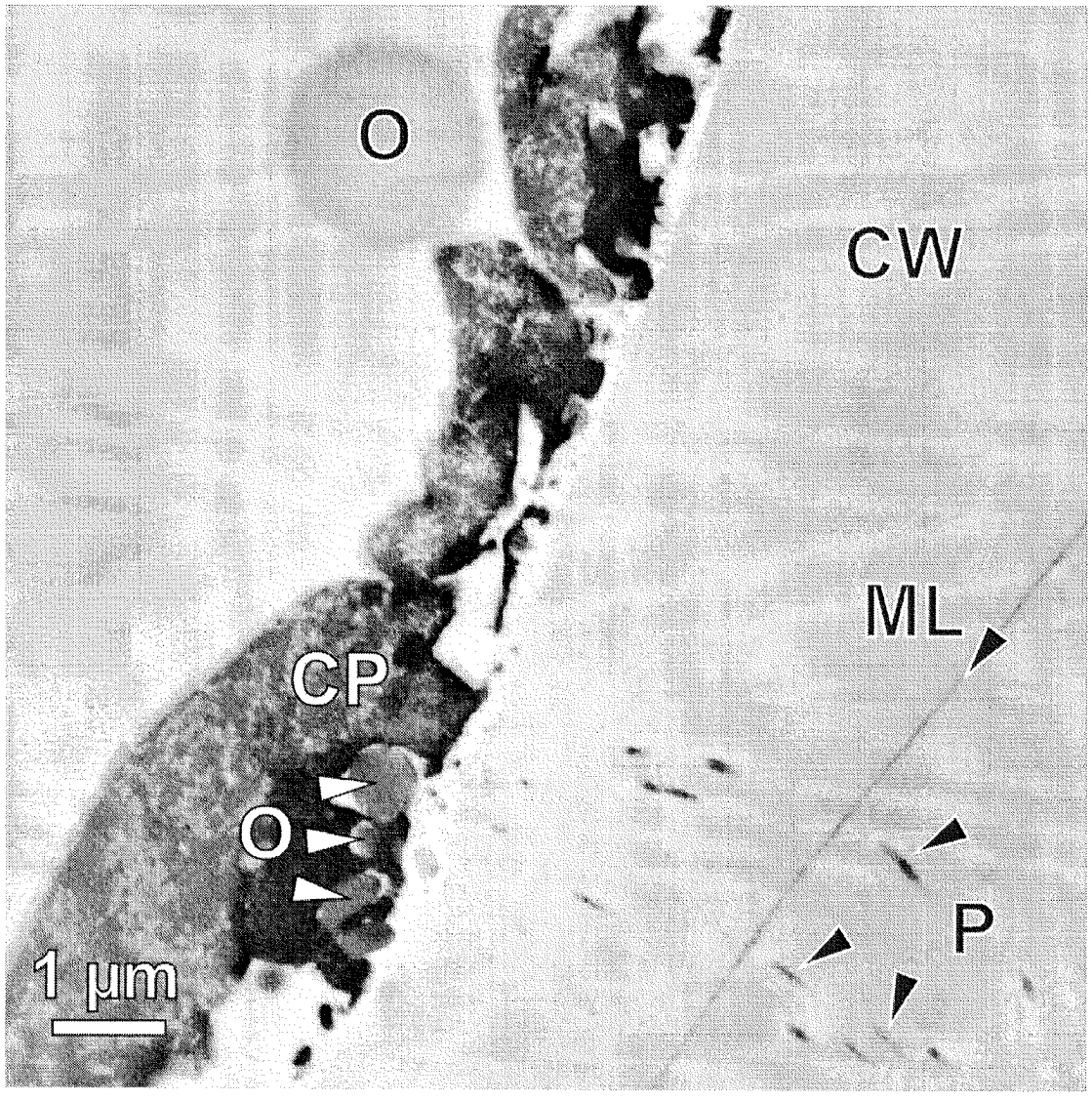

Fig. 45: *TEM micrograph of a cell wall in a partially roasted coffee bean (identical specimen as in micrograph 44). The middle lamella (ML) and parts of presumably modified plasmodesmatae channels (P) are clearly visible. Oil droplets (O) of various sizes lie embedded in the layer of modified cytoplasm (CP) or alongside to it. (Image: S. Handschin).*

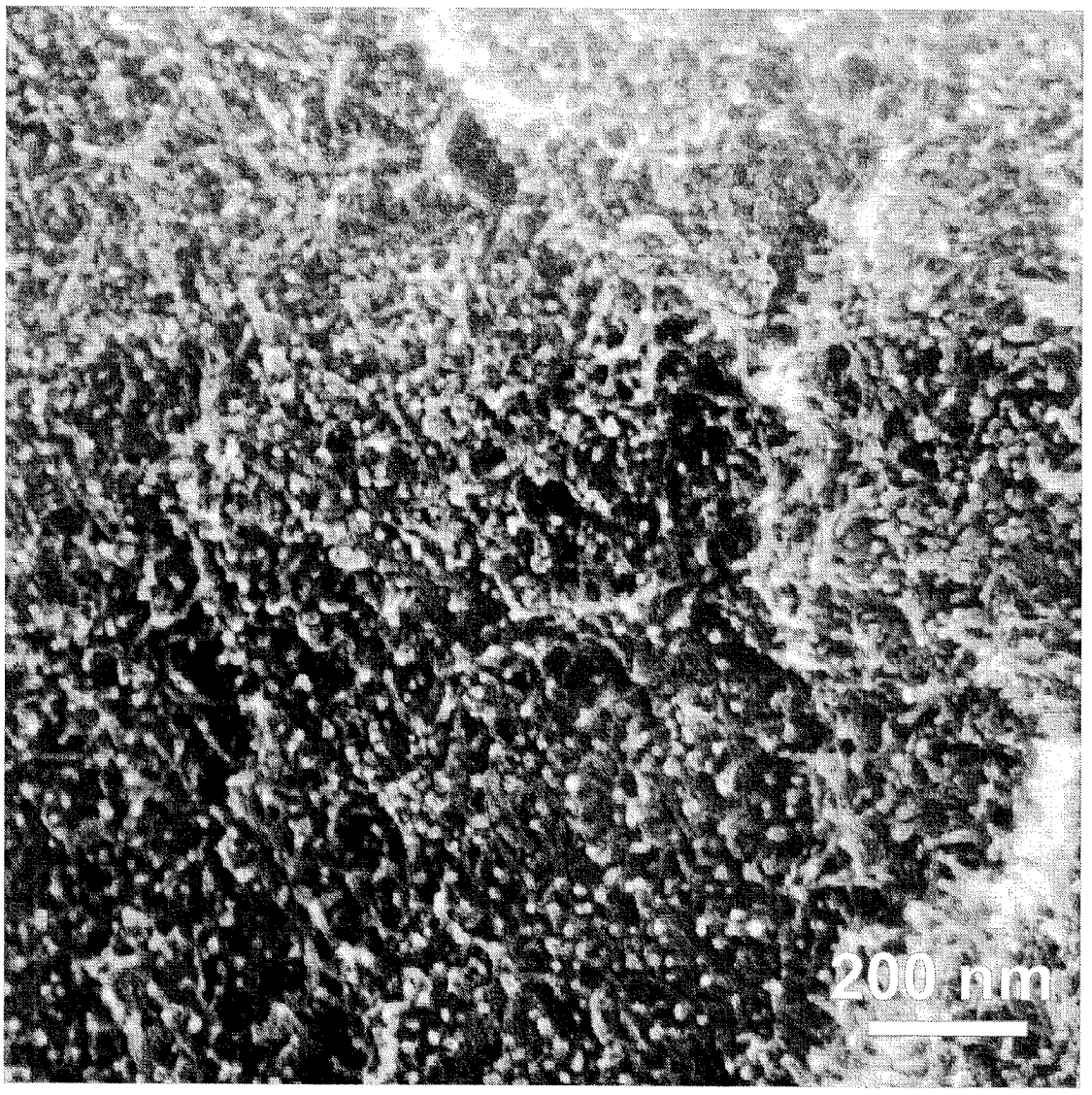

Fig. 46: *SEM micrograph of a cell wall cross section of a chemically fixed, de-oiled and fractured specimen from a fully roasted coffee bean. The structure of the fraction surface suggests fundamental changes in the microfibril network of roasted cell walls as compared to the green bean. (Image: S. Handschin).*

4.2.4 Changes in porosity

Characteristics of porosimetric curves and model of pore structure and mercury intrusion

The pore structure of green and roasted coffee beans was investigated by mercury porosimetry. Figure 47 shows typical porosimetric curves from roasted coffee beans. The intruded pore volume is related to the micropore sizes from 10 µm down to 2 nm radius. In general, curves obtained from coffee were of consistently characteristic shape. They exhibited only minor mercury intrusion over a wide range of possible pore sizes and were then dominated by a sharp increase in a narrow diameter range of 20 to 50 nm. This pattern of narrow-ranged pore sizes resulted in a single peak in the pore size distribution function.

The model in Figure 48 explains the origin and generation of this shape of curve. Access for mercury to the excavated cell lumina is provided by small micropores in the cell walls, forming a so-called "ink bottle" pore system. Therefore, only a high pressure corresponding to the small size of the entrance pores allows for mercury penetration of the cell lumina. Consequently, high values for apparent pore volume for the micropores of the cell wall were obtained, while this corresponded to the filling of the cell lumina. Hence, the pore size at the maximum of the distribution function (r_{main}) represents the size of the cell wall micropores. The value for cumulated pore volume at the end of analysis (2 nm pore radius) corresponds to the overall bean porosity.

The model is supported by SEM analysis of mercury intruded coffee beans after porosimetric analysis (Schenker et al., 1998). The micrographs in Figures 49 and 50 revealed a picture of still intact cell wall structure and mercury-filled cell lumina. No artefacts such as structure collapse due to high pressure during porosimetry were observed. Cell lumina were filled with spheres. The elemental mapping of mercury in a freeze fracture across the cells clearly confirms, that mercury does enter to full extent during porosimetry (Figure 50). A weak signal was even detected in the cell walls, indicating that mercury must have passed a cell wall micropore network to intrude the cell lumina. Mercury was then partially withdrawn during the depressurization procedure after porosimetric analysis. This, together with the contamination

of mercury with cell constituents, resulted in the formation of stabilized small spheres.

As has already been mentioned in the experimental part, there may be limitations in applying mercury porosimetry due to pressure sensitivity of some foods. Examination for potential artefacts and careful interpretation of the results are necessary. Moreover, it must always be kept in mind that the concept of mercury porosimetry is based on a series of idealizing assumptions, such as cylindrical shape of the intruded pore. The rate of mercury intrusion in coffee beans is low and requires a low rate of pressure increase during analysis. Nevertheless, the present results show that the method is suitable for roasted coffee beans and successful in describing the bean pore structure. The stability of coffee bean tissue exposed to mercury porosimetry can be attributed mainly to the unusually thick cell walls.

The model concept of an "ink-bottle" pore structure with large cavities of different shapes and sizes, but with a unique type of pore opening of a very narrow size is consistent with findings made by Saleeb (1975). From the shape of gas adsorption isotherms he concluded a very narrow pore size distribution in coffee beans. He suggested multilayer adsorption and capillary condensation in micropores in the range of 2 nm radius being responsible for the ability of massive CO_2 uptake in roast coffee. For various types of wheat cells Chesson et al. (1997) reported cell wall micropores in the size of 3 to 6 nm diameter. These data were also obtained by gas adsorption measurements.

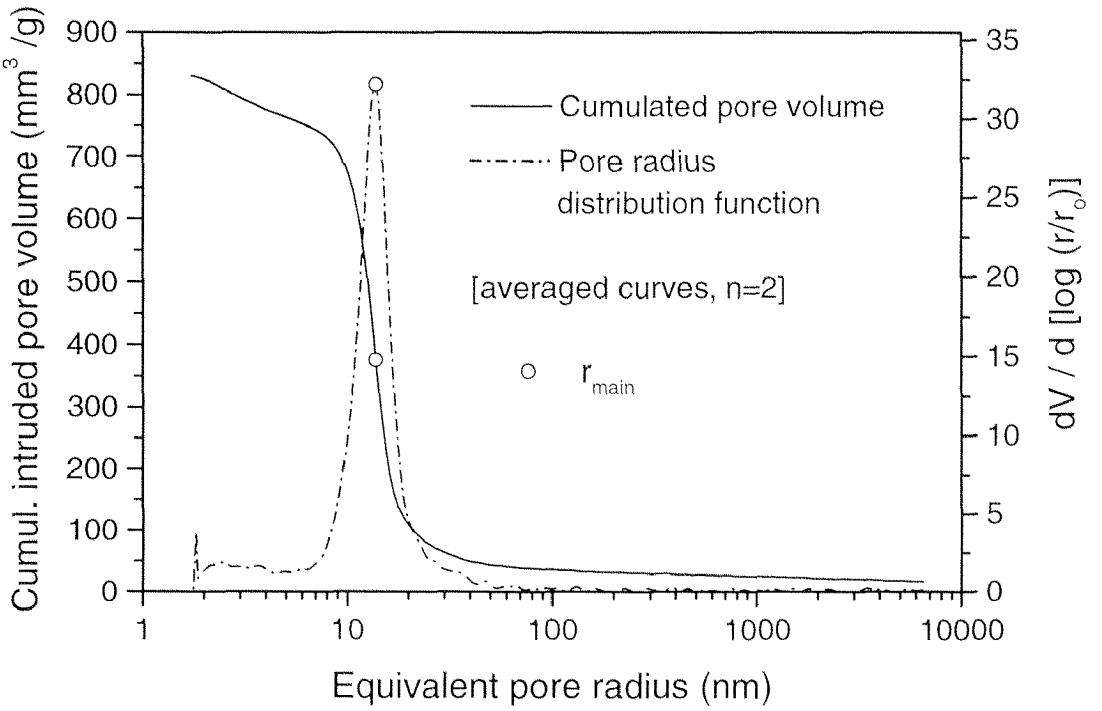

Fig. 47: *Typical porosimetric data obtained from roasted coffee beans (HTST processed sample, 160 s).*

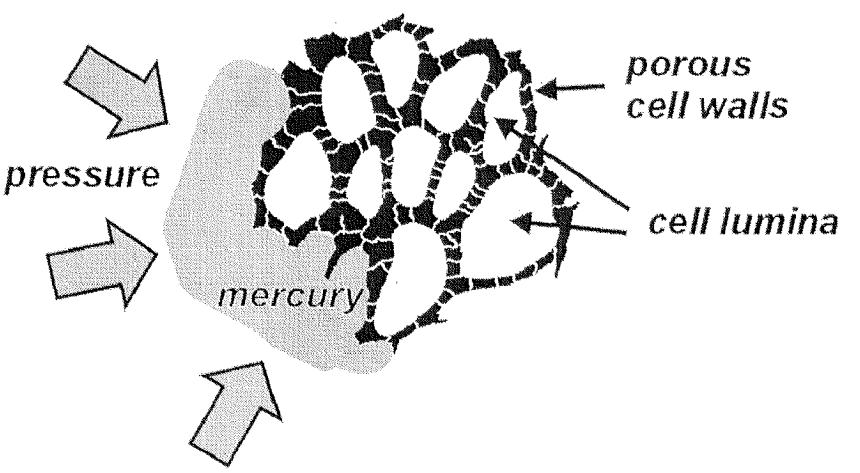

Fig. 48: *Model coffee bean pore system surrounded by pressurized liquid mercury during porosimetric analysis. Access to the cell lumina is provided by small micropores in the cell walls. Only a high pressure corresponding to the small size of these entrance pores will allow for mercury penetration of the large cell lumina.*

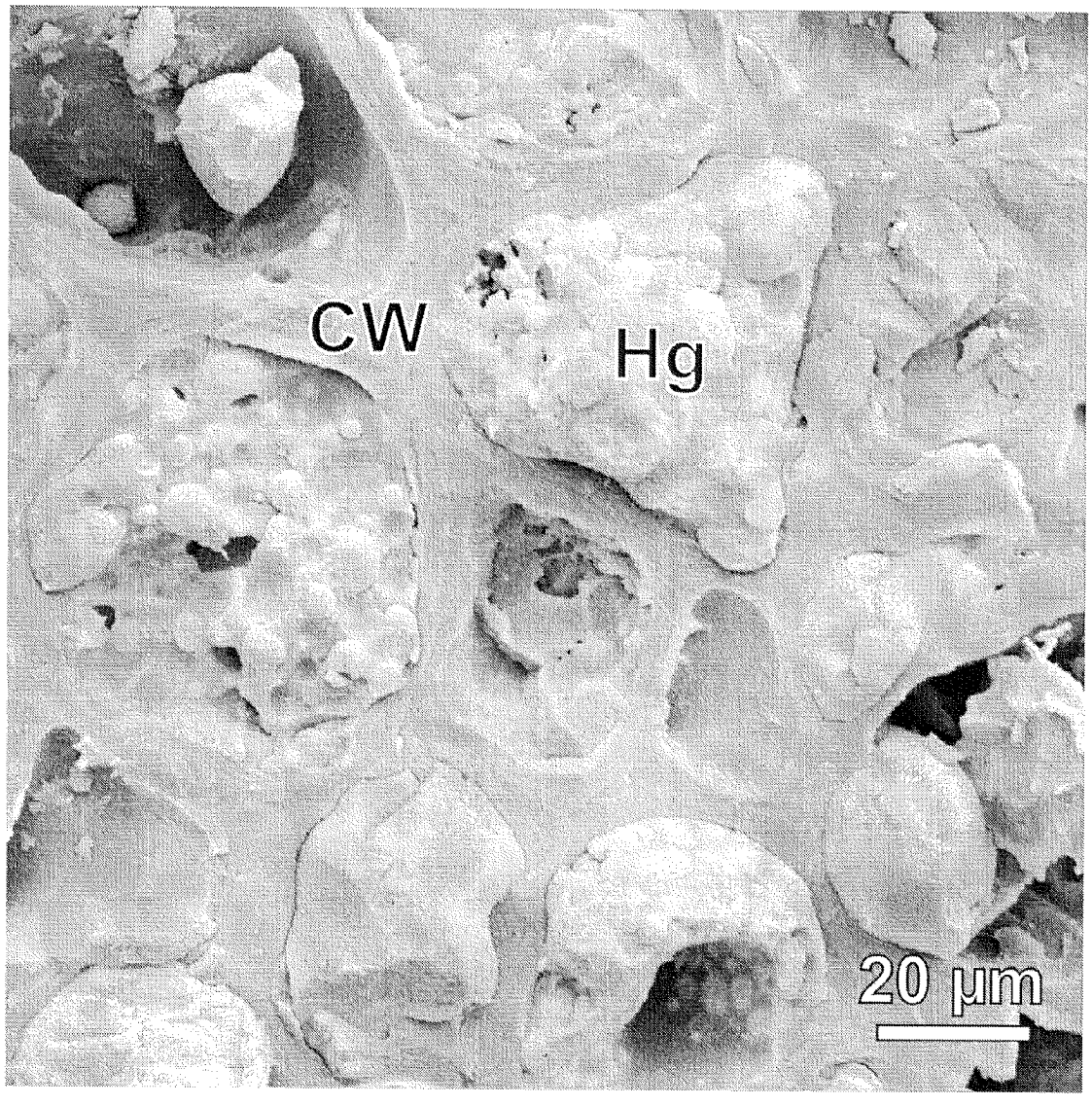

Fig. 49: *Cryo-SEM micrograph of cells in a roasted bean intruded with mercury during porosimetric analysis. The tissue shows an intact cell wall (CW) structure with mercury-filled cell lumina. Mercury (Hg) must have penetrated a cell wall micropore system before intruding the cell lumina. It was then partially withdrawn during the depressurization procedure after the porosimetric analysis. (Image: B. Frey, S. Handschin).*

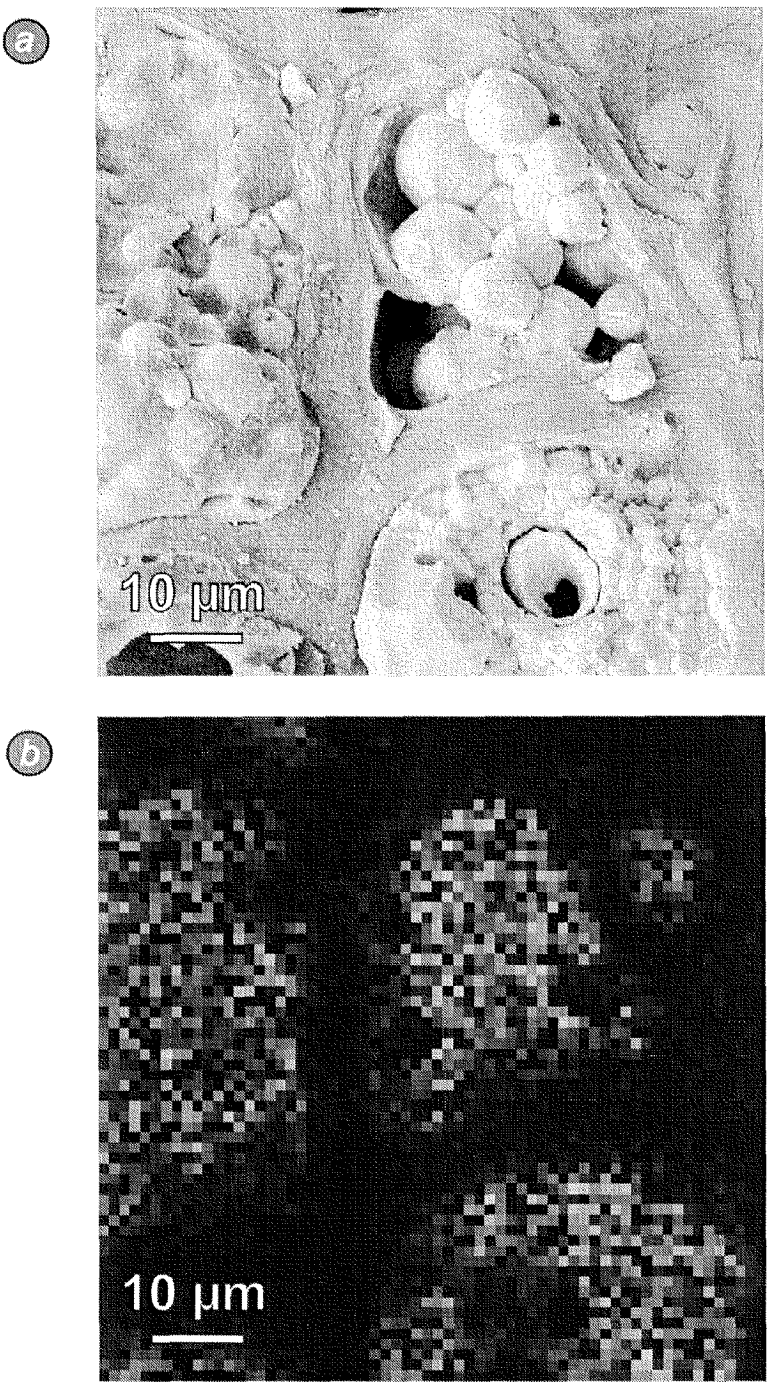

Fig. 50: *Cells of a roasted coffee bean intruded with mercury during porosimetric analysis. 50a: Cryo-SEM micrograph of 3 adjacent cells with integer cell walls. 50b: Mercury mapping obtained by X-ray microanalysis from the same location as in 50a. Bright spots are generated by great mercury net counts and indicate the presence of mercury. (B. Frey, S. Handschin).*

Influence of roasting on pore structure

Figure 51 shows the development of cumulated intruded pore volume for green coffee and beans of various degrees of roast. It documents the influence of HTST roasting on porosimetric curves. A slight but continuous increase of cumulated pore volume to a final value of 100 mm^3g^{-1} was observed for green beans. It may be caused partially by micropores and partially represent an artefact due to compression of coffee oil at high pressures. Since roasting involves substantial volume increase, bean porosity gradually increases as well. Greater values for final cumulated pore volume are observed with progressing roasting. Moreover, a slight shift to greater r_{main} and r_{50} values with increasing degree of roast was observed (Figure 52). These data indicate that cell wall micropores are formed and/or enlarged during roasting.

At equal degree of roast, curves of cumulated pore volume were influenced by the roasting conditions (Figure 53). As expected from greater volume increase, high temperature roasted samples showed substantially greater overall porosity as compared to low temperature roasted beans. Further, they exhibited significantly greater r_{main} values, meaning that HTST roasted samples developed wider cell wall micropores than LTLT roasted beans. A survey of volumetric and porosimetric data of HTST and LTLT roasted beans is given in Table 10.

Overall porosity values were in the same order as found by Radtke (1975). Values for r_{main} fall between the two cell wall micropore sizes obtained from electron microscopy by Wilson et al. (1997). They are considerably higher than the gas porosimetric values proposed by Saleeb (1975), but coincide with porosimetric data reported by Chesson et al. (1997) for wheat cell walls. The findings on the relationship between overall porosity and process temperature are in agreement with Ortolà et al. (1998), Kazi and Clifford (1985) and Puhlmann et al. (1986), but contrast with conclusions of Gutiérrez et al. (1993), who did not find a significant influence of roasting conditions on bean porosity. So far, no other study has shown the size of cell wall micropores to be dependent on the roasting conditions. These micropores are assumed to be of great importance since they control mass transfer phenomena during storage.

In conclusion, mercury porosimetry showed the existence of a cell wall micropore network that is enlarged during roasting and dependent on the process conditions. Origin and structure of this system are not yet elucidated satisfactorily. It is still unclear, whether it consists of countable microchannels rather than of a complex network. However, microscopic and porosimetric results support a model of a three-dimensional permeable wad-like network of polysaccharide microfibrils. In this case, increased polysaccharide degradation at higher temperatures may cause the larger cell wall micropores found in high temperature roasted coffee beans.

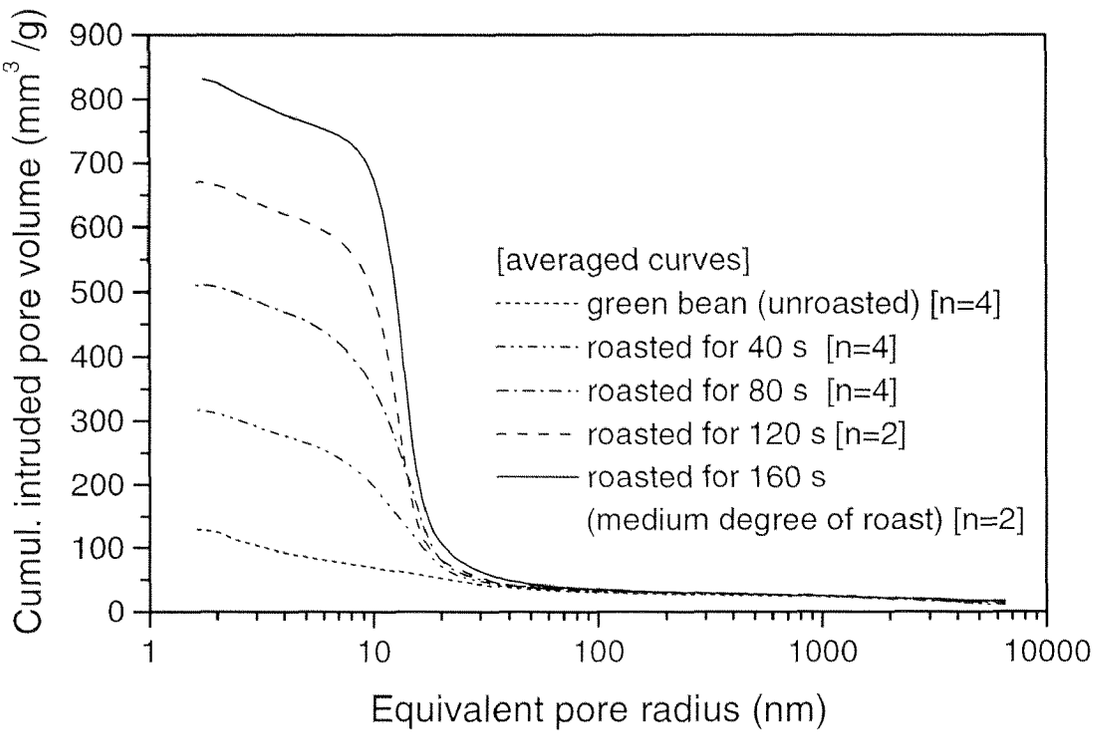

Fig. 51: *Influence of HTST roasting on porosimetric curves of coffee beans with increasing degrees of roast.*

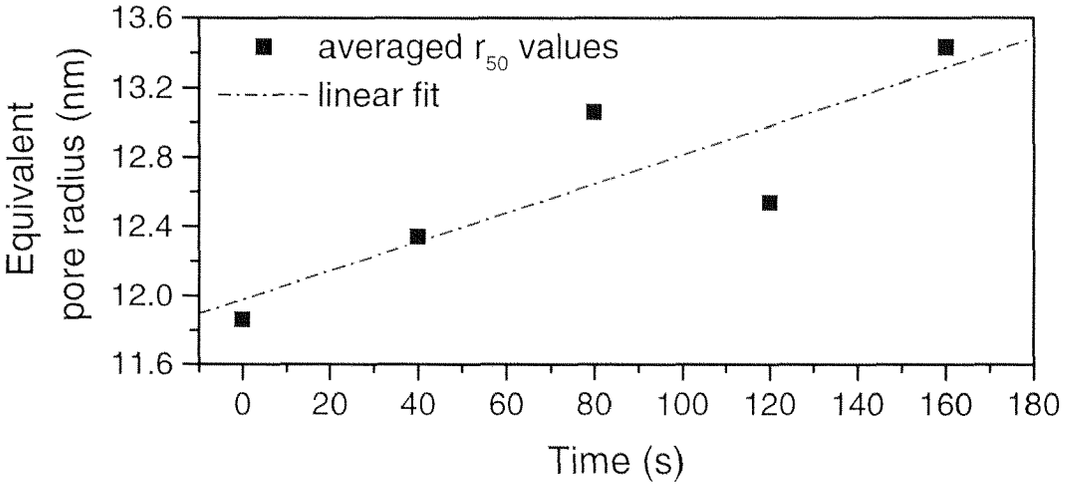

Fig. 52: *Relationship between degree of roast (roasting time) and the averaged pore size at which 50 % of total pore volume is mercury penetrated (r_{50}).*

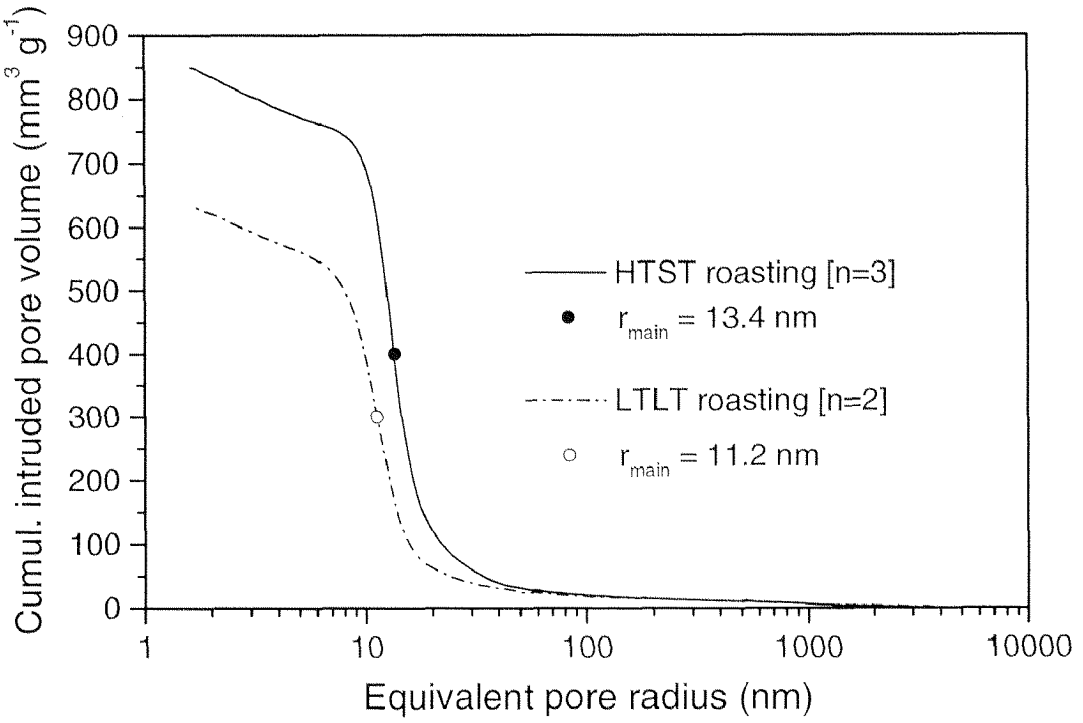

Fig. 53: *Influence of HTST and LTLT roasting on porosimetric curves of beans with identical degree of roast and on r_{main}.*

Tab. 10: *Influence of roasting conditions on volume and pore characteristics of coffee beans at equal degree of roast.*

	HTST roasting	*LTLT roasting*
Roast loss (%)	14.95	15.01
Bean density (kg m^{-3})	622	747
Bean volume V_B (mm^3 g^{-1})	1609	1350
Hg-intruded volume V_{Hg} (mm^3 g^{-1})	850	640
Bean porosity $\varepsilon = V_{Hg}/V_B$ (-)	0.528	0.474
r_{main} (nm)	13.4	11.2

4.3 Development of aroma compounds profile and flavor

4.3.1 Aspects of methodology

The isolation technique in aroma analysis is critical for the result of a particular investigation. Figure 54 shows the differences in aroma compounds profiles from isolates obtained by two different methods. Isolates obtained from simultaneous distillation/extraction (SDE) were generally of higher concentration and displayed, for example, considerably more 2,3-butanedione, 2,3-pentanedione and guaiacol than isolates from vacuum distillation (VD). 4-vinylguaiacol exhibited the largest discrepancy. It was not found in VD-isolates of LTLT roasted samples, but present in substantial amount in SDE-isolates. In general, greater artefacts due to greater heat influence with the SDE technique may be assumed. On the other hand, the group of pyrazines seems to be widely unaffected by the type of isolation technique. In contrast, polar and hydrophil compounds are likely to be retained in the water phase during SDE-isolation and are therefore under-represented in the respective isolate. Acetic acid is an extreme representative of this group because it was found to have a 10-fold higher content in VD than in SDE-isolates, relative to the internal standard.

Isolation by VD imposes lower heat influence on the sample, but is more troublesome to handle than the SDE technique. SDE proved to be a convenient and suitable method for coffee, but may cause some artefacts. In consequence, the sensory relevance of an aroma compound within the profile must be assessed on the bases of at least two isolation techniques. Nevertheless, the SDE technique is advantageous and may be sufficient for purely relative (semi-quantitative) evaluation of aroma compounds.

Aroma isolates were exposed to further heat strain during conventional instead of "on column" GC injection. They were subjected to GC-FID analysis without pre-fractionation, accepting incomplete separation of compounds. Therefore, a high separation performance of the capillary column was essential. Figure 55 shows the superior separation performance of the 60 m polar column (Supelcowax 10) in use as compared to a 30 m unpolar column (DB 5). With the polar column peaks were

evenly distributed over the entire analysis time, whereas with the unpolar column peaks were overlaid within a compressed time/temperature window in the first part of the analysis. However, regardless of high separation performance, co-elution of compounds had to be accepted in some cases, with subsequent restrictions for identification and quantification.

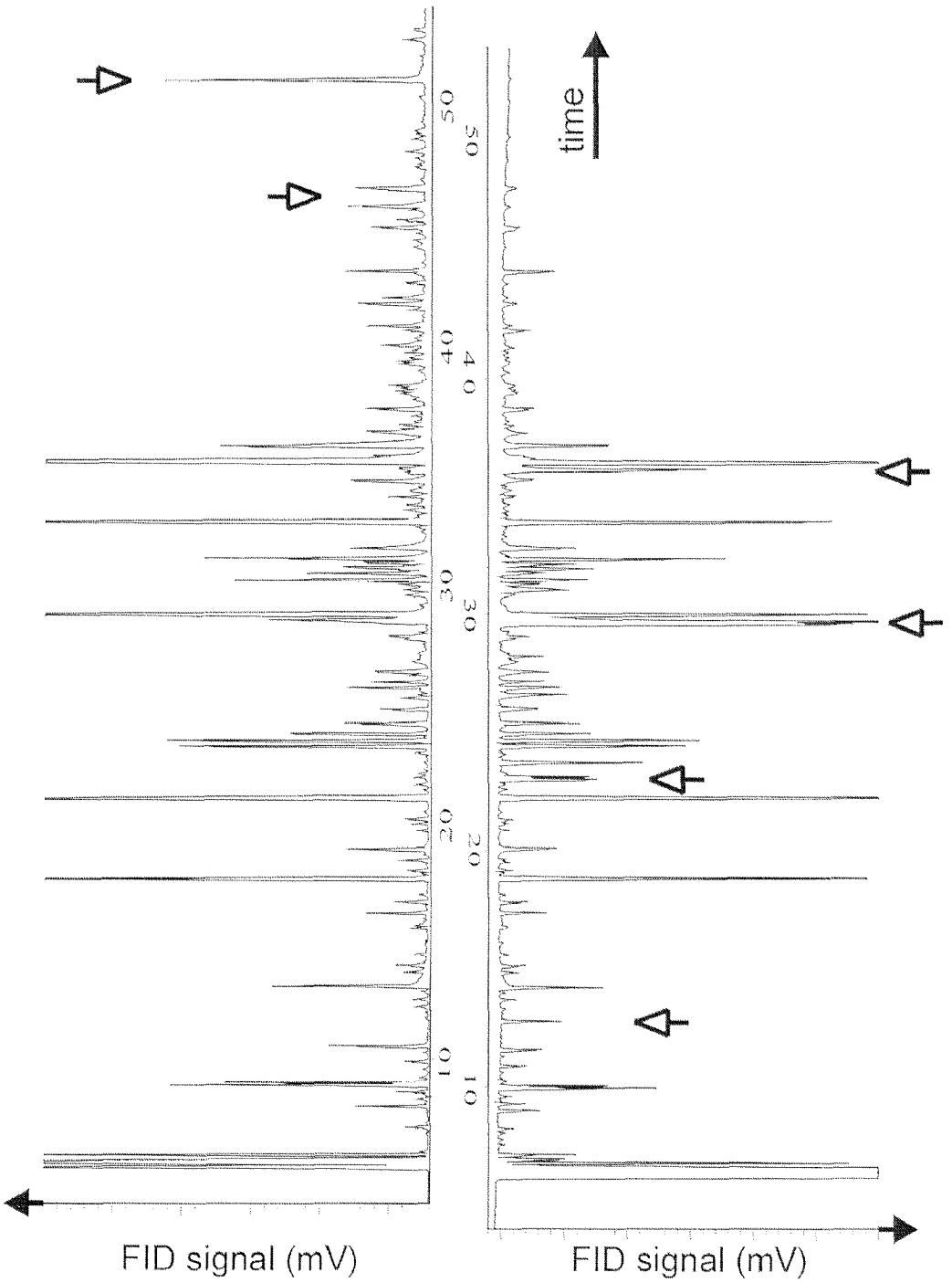

Fig. 54: *GC-FID chromatograms from aroma isolates of LTLT roasted coffee beans. Isolates were obtained by simultaneous distillation/extraction according to Likens and Nickerson, 1964 (left) and by vacuum distillation (right). Open arrows point to examples of inconsistencies between the two chromatograms.*

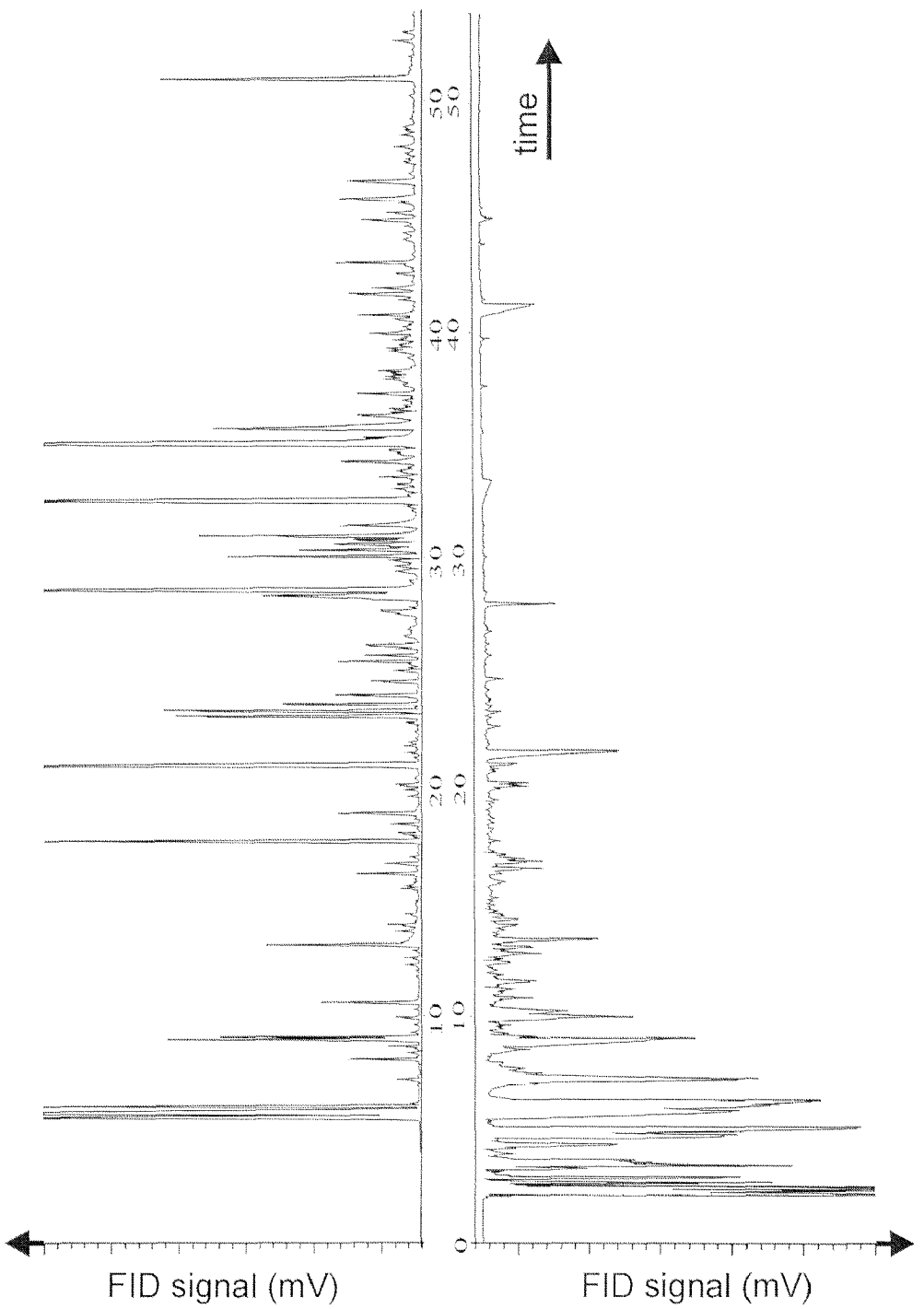

Fig. 55: *GC-FID chromatograms of a SDE aroma isolate from roasted coffee beans. Chromatographic separation of compounds was performed using a 60 m polar capillary column Supelcowax 10 (left) and a 30 m unpolar capillary column DB 5 (right).*

4.3.2 Character impact compounds

Table 11 gives a survey on selected identified aroma compounds, their aroma qualities and sensory relevance as analyzed by GC-olfactometry. FD-factors show, that the degree of contribution to the overall aroma perception varies widely from compound to compound. So far, more than 800 compounds have been identified in the volatile fraction of roast coffee, but the aroma may be dominated only by a small number of so-called *aroma impact compounds* (Holscher et al., 1990). A widely used synonym for the latter is *character impact odorants*. In the present investigation, listed compounds with an FD-factor 512 or 1024 are considered as aroma impact compounds (AIC) with high sensory relevance.

A group of 11 AIC was identified for high temperature laboratory roasted Colombian coffee, whereas 6 AIC out of it made up the respective group for low temperature roasted coffee. The majority of these compounds is well-known in literature to contribute to the group of AIC (Blank et al., 1991, Blank et al., 1992, Czerny et al., 1999, Grosch, 1995, Grosch et al., 1996, Holscher et al., 1990, Semmelroch and Grosch, 1995a, Semmelroch and Grosch, 1996, and others). 2,3-butanedione, 2-furfurylthiol, methional, 2-ethyl-3,5-dimethyl pyrazine, methyl butyrate, guaiacol and 4-hydroxy-2,5-dimethyl-3[2H]-furanone belong to this category. However, 3 compounds have not yet been described in literature as AIC of coffee. 2-hydroxy-3-methyl-2-cyclopenten-1-one, 3-methyl-mercapto-3-methyl butylformiate and propyl pyrazine appeared to be exclusively characteristic for the specific coffee provenience in use. In the case of propyl pyrazine a similar compound, namely dimethyl-propyl pyrazine, is described in literature. 2,3-butanedione, propyl pyrazine, 2-hydroxy-3-methyl-2-cyclopenten-1-one, 4-hydroxy-2,5-dimethyl-3[2H]- furanone and the unknown compound with RI = 2329 did not reach an FD-factor 512 or greater in LTLT roasted products. Hence, they were exclusive AIC of HTST roasted beans. In turn, guaiacol (AIC) and ß-damascenone were important aroma contributors characteristic for low temperature roasted beans.

2-furfurylthiol is generally regarded as one of the most important AIC in roast coffee. However, in high concentrations it may be more considered as an off-flavor than as an AIC, since it is reported to change its aroma quality depending on the concentration (Tressl and Silwar, 1981).

Aroma compounds with highest sensitivity to the roasting conditions exhibited large FD-factor deviations between HTST and LTLT roasting. They may serve as "process indicator" aroma compounds. Most typical representatives of this group are 2,3-butanedione, 2,3-pentanedione, propyl pyrazine, linalool, 2-hydroxy-3-methyl-2-cyclopenten-1-one and again the unknown compound with RI = 2329.

AIC are considered as the most important aroma contributors. However, evaluation of sensory relevance concluded from FD-factors imply methodological limitations. For reasons outlined above, aroma isolates are only partially representative for the roast coffee they were obtained from. In addition, odor perceptions in GC effluents may considerably differ from real conditions, as aroma compounds can change their aroma qualities depending on their concentration (Tressl et al., 1981). Moreover, the perceived profile in the final coffee beverage is different from analytical aroma profiles of roasted beans, as the extraction procedure, the different matrix (water) and the complexity of human odor perception mechanisms have a major impact on aroma compounds. Recent investigations have shown large discrepancies between aroma impact compounds profile in roast coffee and the sensory relevant profile in the beverage (Czerny et al., 1999).

In conclusion, the spectrum of aroma impact compounds is assumed to be determined by the raw material, whereas the degree of expression of each AIC within the whole aroma compounds profile is subject to roasting conditions. In other words, the quality of the green bean determines the aroma profile potential, whereas roasting technology determines the specific part of this potential that is brought to realization. Some AIC are found ubiquitous in coffee and therefore seem to be essential to produce the general odor perception "coffee", whereas others do more embody the different potential due to different origin.

Tab. 11: *Alphabetical listing of selected identified aroma compounds from high and low temperature laboratory roasted Colombian coffee beans and their sensory relevance.*

No.	Compound	RI[a]	Aroma quality[b] present study / (literature)	FD factor[c] HTST roasting	FD factor[c] LTLT roasting
1	Acetic acid	1461	(pungent)	-	-
2	p-Anis aldehyde (= 4-Methoxy-benzaldehyde	2070	grass, hay (sweet, mint)	-	-
3	2,3-Butanedione (= Diacetyl)	908	butter (butter)	1024	256
4	ß-Damascenone (= 2,6,6-Trimethyl-1,3-cyclohexadienyl) (= (E)-2-buten-1-one)	1851	fruits, flowers, (honey, fruity, tea)	16	128
5	2,3-Diethyl-5-methyl pyrazine	1505	(earthy, roasty)	n.a.[d]	n.a.
6	2,3-Dimethyl pyrazine	1334		-	-
7	2,5-Dimethyl pyrazine	1304	roasty, nuts	4	4
8	2,6-Dimethyl pyrazine	1311	sulfur-like, nuts	4	4
9	2-Ethenyl-5-methyl pyrazine	1493	musty, burnt	64	4
10	2-Ethyl-3,5-dimethyl pyrazine	1468	(earthy, roasty, potatoes)	1024	1024
11	3-Ethyl-2,5-dimethyl pyrazine	1443		-	-
12	4-Ethyl guaiacol	2025	flowers (spicy)	4	-
13	2-Ethyl-3-methyl pyrazine	1403	roasty, nuts	4	16
14	2-Ethyl-5-methyl pyrazine	1388	caraway	4	32
15	2-Ethyl-6-methyl pyrazine	1380	cheese, caraway	4	1
16	Ethyl pyrazine	1320		-	-
17	2-Furfurylthiol (= Furfuryl-mercaptan) (= 2-Furanmethanthiol)	1440	bouillon, potatoes (roasty, sulfur-like, coffee-like)	1024	1024
18	Guaiacol	1889	medical, adhesive (smoky, phenolic, aromatic, spicy)	512	1024
19	Hexanal	1016	grass	1	-
20	4-Hydroxy-2,5-dimethyl-3[2H]-furanone (= Furaneol[e]) (= 2,5-dimethyl-4-hydroxy-3[2H]-furanone)	2058	roasty, sweet, (caramel)	1024	256
21	2-Hydroxy-3-methyl-2-cyclopenten-1-one (= 3-Methyl-1,2-cyclo pentanedione	1851	(spices, celeriac)	1024	32
22	2-Isobutyl-3-methoxy pyrazine	1525	herbes, smoky (earthy, paprika)	64	4

Tab. 11: *Alphabetical listing of selected identified aroma compounds from high and low temperature laboratory roasted Colombian coffee beans and their sensory relevance.*

No.	Compound	RI[a]	Aroma quality[b] present study / (literature)	FD factor[c] HTST roasting	FD factor[c] LTLT roasting
23	Kahweofuran	1769	coffee-like, smoky	4	1
24	Linalool	1555	grass, vegetables (flowers)	256	4
25	Methional (= 3-Methylthio-1-propanal) (= 3-Methyl-mercapto-propionaldehyde)	1462	cooked potatoes (sweet)	1024	1024
26	2-Methyl butanal	857	caramel, nuts (malt)	128	16
27	3-Methyl-2-buten-1-thiol	1042	vegetables, green (sulfur-like, foxy, amin-like)	256	64
28	3-Methyl butyric acid	1680	sweaty, pungent (fermented)	1024	1024
29	Methyl dihydro cyclopenta pyrazine		(roasty, sweet)	n.a.	n.a.
30	2-Methyl-3-furanthiol (= 3-Mercapto-2-methylfuran	1304	sulfur-like (roasty, meat-like)	32	32
31	3-Methyl mercapto-3-methyl butyl formiate	1525	herbes	1024	1024
32	1-Octen-3-one	1274	fungi, hay	16	32
33	2,3-Pentanedione	989	butter (butter)	128	4
34	Propyl pyrazine	1418	potatoes, vegetables	1024	64
35	2,3,5-Trimethyl pyrazine	1402	herbes, bouillon (roasty, earthy)	16	32
36	unknown	1625	roasty, nuts		
37	unknown	1667	spicy, bouillon	512	256
38	unknown	2093	muck		
39	unknown	2139	herbes, smoky		
40	unknown	2329	sweet, medicine	1024	4
41	Vanillin		(sweet, vanilla)	-	-
42	4-Vinyl guaiacol (= 4-Vinyl-2-methoxy phenol)	2245	sweet, flowers (spicy-phenolic)	256	256

a. RI on Supelcowax10, 60m
b. Perception at sniffing port
c. Flavor dilution factor
d. n.a.: Not analyzed
e. Tradename of Firmenich SA

4.3.3 Formation of aroma compounds during roasting

Figures 56 to 59 show the formation of selected important aroma compounds during different roasting stages. Since chemical pathways in the bean are very complex, the characteristics of formation can vary considerably from compound to compound. However, the three selected AIC in Figures 56 and 57 may give a typical picture of development of important compounds. It was similar for the HTST and LTLT isothermal laboratory processes and is characterized by low formation rates in the first third of roasting time, followed by rapid formation in the second third. During the final roasting stage the concentrations of 2-ethyl-3,5-dimethylpyrazine, propylpyrazine and 3-methylbutyrate were found to decrease again, indicating that aroma formation was already superimposed by an accelerated decay of compounds due to the high temperatures. A group of pyrazines as shown in Figure 58 as well as 2,3-pentanedione as shown in Figure 59 exhibited remarkably consistent behavior of this kind. In contrast, a group of other important compounds did not follow the above described pattern of superimposed decay in the final process stage. For example the smoky, aromatic and spicy smelling AIC guaiacol, the buttery AIC 2,3-butanedione, the spicy and roasty AIC 2-furfurylthiol (Figure 59) as well as the spicy AIC 2-hydroxy-3-methyl-2-cyclopenten-1-one continuously increased even during excessive roasting at high final temperatures.

It is clear from Figure 57 that with both laboratory processes aroma quantities of a number of important compounds already decreased when the process was terminated at a medium degree of roast. This fact may require to stop roasting in time, in order to achieve a high aroma level. But other flavor compounds, such as organic acids and bitter components, must be considered as well. Guaiacol and 2-furfurylthiol may greatly contribute to the aroma of dark roasted coffees. The present results cannot be compared directly to those presented by Mayer et al. (1999). The part of their study on the influence of the degree of roast is limited to a narrow range (light, medium and dark), whereas the present results cover the development from the green to roasted beans beyond usual degrees of roast. Nevertheless, some consistent formation trends can be found. 2,3-butanedione, 2,3-pentanedione, guaiacol and 2-furfurylthiol in Colombia coffee and also 2-ethyl-3,5-dimethyl pyrazine in Kenya coffee exhibit similar developments.

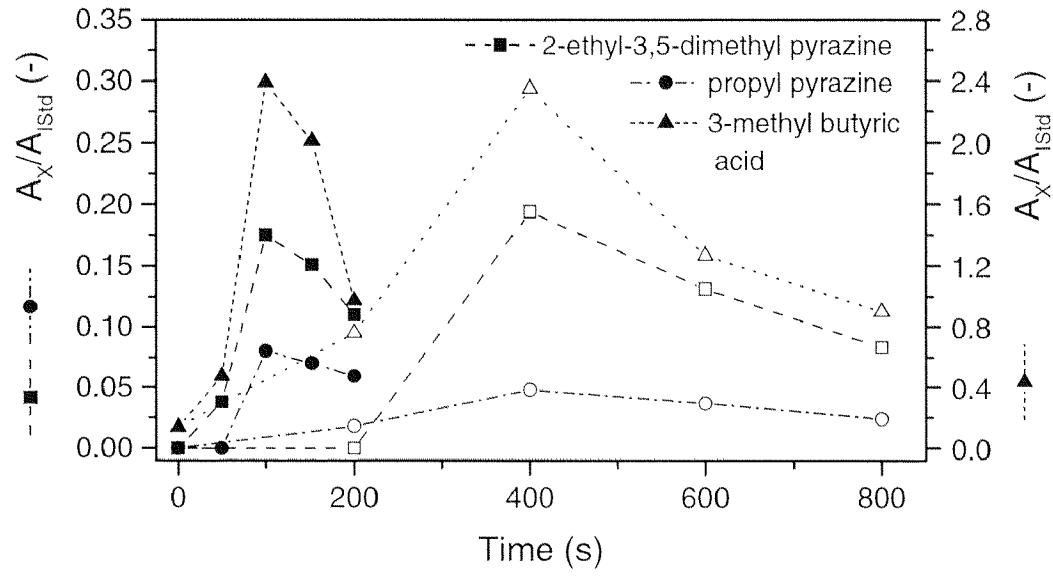

Fig. 56: *Quantitative development of three selected aroma impact compounds during HTST (solid symbols) and LTLT (open symbols) laboratory roasting. Sampling took place at 1/3, 2/3, 3/3 and 4/3 of the normal roasting time to achieve a medium degree of roast.*

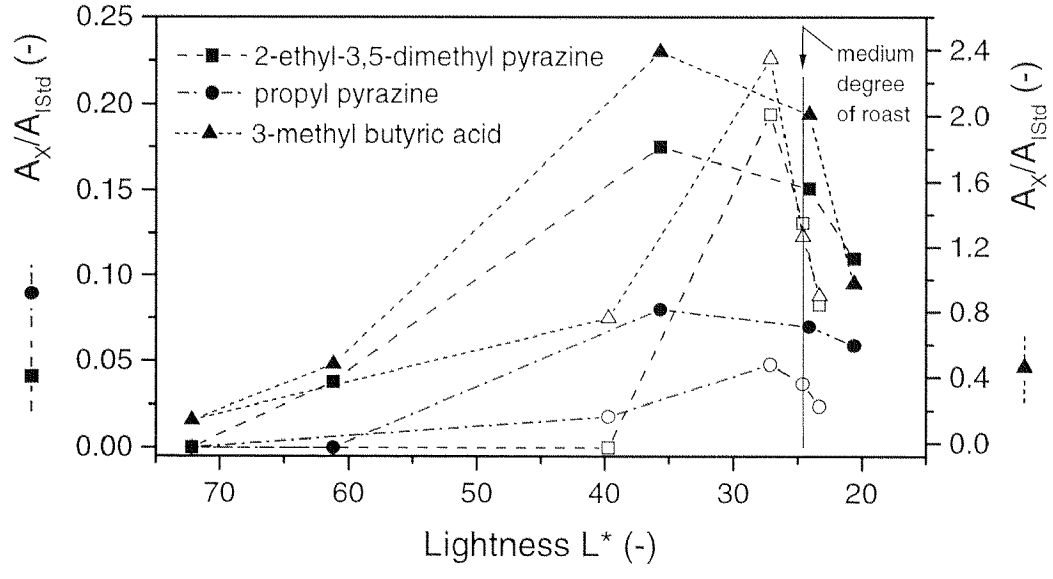

Fig. 57: *Quantitative development of three selected aroma impact compounds in relation to the degree of roast (color). Solid symbols: HTST roasting, open symbols: LTLT roasting. Medium degree of roast is marked by a perpendicular line.*

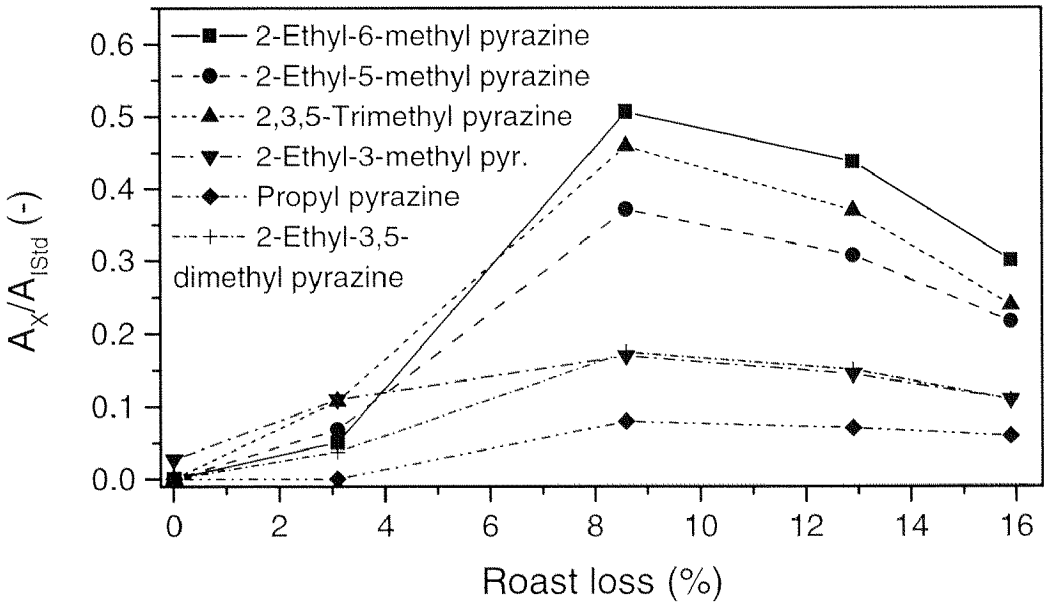

Fig. 58: *Quantitative development of pyrazines during high temperature laboratory roasting related to roast loss. A roast loss of 13 % corresponds to a medium degree of roast.*

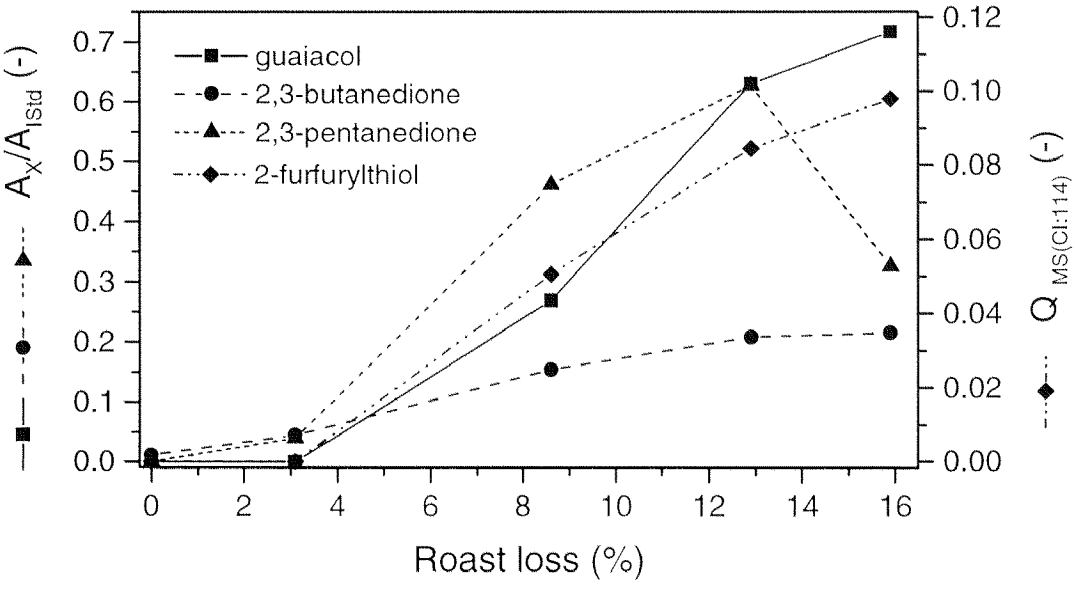

Fig. 59: *Development of relative quantities of various important aroma compounds during HTST laboratory roasting. A roast loss of 13 % corresponds to a medium degree of roast.*

In summary, the first roasting stage at a still high water content of the beans does not result in large aroma quantities, but may be important to develop aroma precursors. The greatest aroma increase rates are found as soon as dehydration proceeds to a water content below 5 g /100 g (wb). Some aroma compound quantities decrease again during the final roasting stage due to compounds decay caused by high temperatures, whereas other compounds develop unhindered. Hence, there are considerable shifts in the aroma compounds profile during the last roasting stages.

4.3.4 Influence of roasting parameters on aroma profiles

At a given coffee raw material roasting parameters control the conditions of chemical reactions in the coffee bean, which may be considered as a "bioreactor". Roasting trials with ground raw coffee beans revealed that the presence of this intact "bioreactor" is essential in producing an acceptable coffee aroma. Figure 60 compares aroma compound profiles of high and low temperature roasted coffee beans at identical degree of roast. As with AIC, the same aroma compounds were formed during HTST and LTLT laboratory roasting, although the quantities and the relative importance of each compound within the profile are specific for a certain process. Table 12 provides a semi-quantitative survey on the influence of different roasting processes on the generation of aroma compounds relevant to coffee flavor. The formation of most aroma compounds was found to be dependent on the temperature conditions during roasting. With 2-hydroxy-3-methyl-cyclopenten-1-one as one of the few exceptions, the response of the formation of a compound to a process is not necessarily bond to chemical classes. Neither the sulfur containing compounds nor the pyrazines showed a common trend and aroma compounds responded rather individually to varying roasting processes.

The majority of aroma compounds were formed to a greater extent with greater process heat impact. Roasting temperatures below 220 °C resulted in roast coffee of weak aroma strength. LTLT roasted coffees exhibited lowest values for most of the compounds. As an exception, ß-Damascenone is formed preferentially at low temperature conditions (Table 12). On the other hand, HTST roasting with the most severe temperature profile and the shortest roasting time did not develop the greatest quantities of aroma compounds. The high final bean temperature in this process may

have induced a more extensive decay of aroma compounds than the other processes with lower final bean temperatures. The greatest overall quantities of aroma compounds were achieved with the LHCI temperature profile in which the temperature was continuously increased up to 240 °C and held there for the final roasting stage. However, maximum quantities of aroma compounds must not necessarily be positively related to superior sensory quality of a coffee aroma.

A comparison between LHC and PLHC processes revealed that a pre-drying stage was not generally effective in generation of higher concentrations of aroma compounds. Most compounds were even slightly more pronounced without a pre-drying stage. 2,3-butanedione and 2,3-pentanedione were the only important compounds to be significantly increased with the application of a pre-drying stage. Therefore, no general benefit from enhanced formation of aroma-precursors during pre-drying can be expected. Even during short time roasting processes, there is obviously sufficient time for the reactants to form precursors and final aroma compounds.

Including a temperature reduced final stage in the roasting process (PHL versus PLHC) did not affect the overall aroma concentrations, but caused a shift in profile. Reduced final temperatures enhanced 2,3-diethyl-5-methyl pyrazine and 2,3,5-trimethyl pyrazine and lowered 3-methyl-mercapto-3-methyl butyl formiate, 2,3-butanedione, 2,3-pentanedione and ß-damascenon. It may be concluded that a reduced final process temperature is beneficial for temperature sensitive compounds, but disadvantageous to the formation of more stable compounds.

A comparison of HL and LHC roasting shows that high temperature exclusively during the initial roasting stage was not efficient in producing aroma strength. Therefore, a sufficiently high temperature during the medium or final roasting stages is required. HL and LTLT processes did not follow this requirement and consequently yielded only weak aroma strength.

Distinct temperature profiles resulted in coffee products of individual aroma compounds profile and may therefore influence the sensory aroma perception. Figure 61 shows an attempt to visualize sensory qualities on the bases of relative comparison of aroma compounds quantities and their related sensory aroma quality. HTST roasted coffee appears superior to LTLT roasted beans in all sensory groups.

Processes with or without a final stage of reduced temperature caused marked differences in the group of earthy, roasty, smoky compounds and in the group buttery notes. A pre-drying step resulted in weaker development of all notes, except for the buttery note, which is due to higher concentrations of 2,3-butanedione and 2,3-pentanedione. Figure 61 must not be overinterpreted, as it comprises a number of systematic limitations. It is based only on relative and normalized quantities without statistical treatment. Moreover, the simple grouping of compounds to classes of sensory aroma quality does not take different FD-factors into account.

In conclusion, development of aroma can be controlled mainly by the temperature profile and a wide range of distinct profiles of aroma compounds can be obtained from the same raw material. Of course, not only temperature, but also other process conditions such as the air to bean ratio, air humidity and contact with oxygen may affect the aroma quality. Moreover, the aroma fraction of roast coffee is known to be subjected to changes and staling mechanisms immediately after roasting (Vitzthum and Werkhoff, 1979, Spadone and Liardon, 1989, Holscher and Steinhart, 1992a and 1992b, Leino et al., 1992)

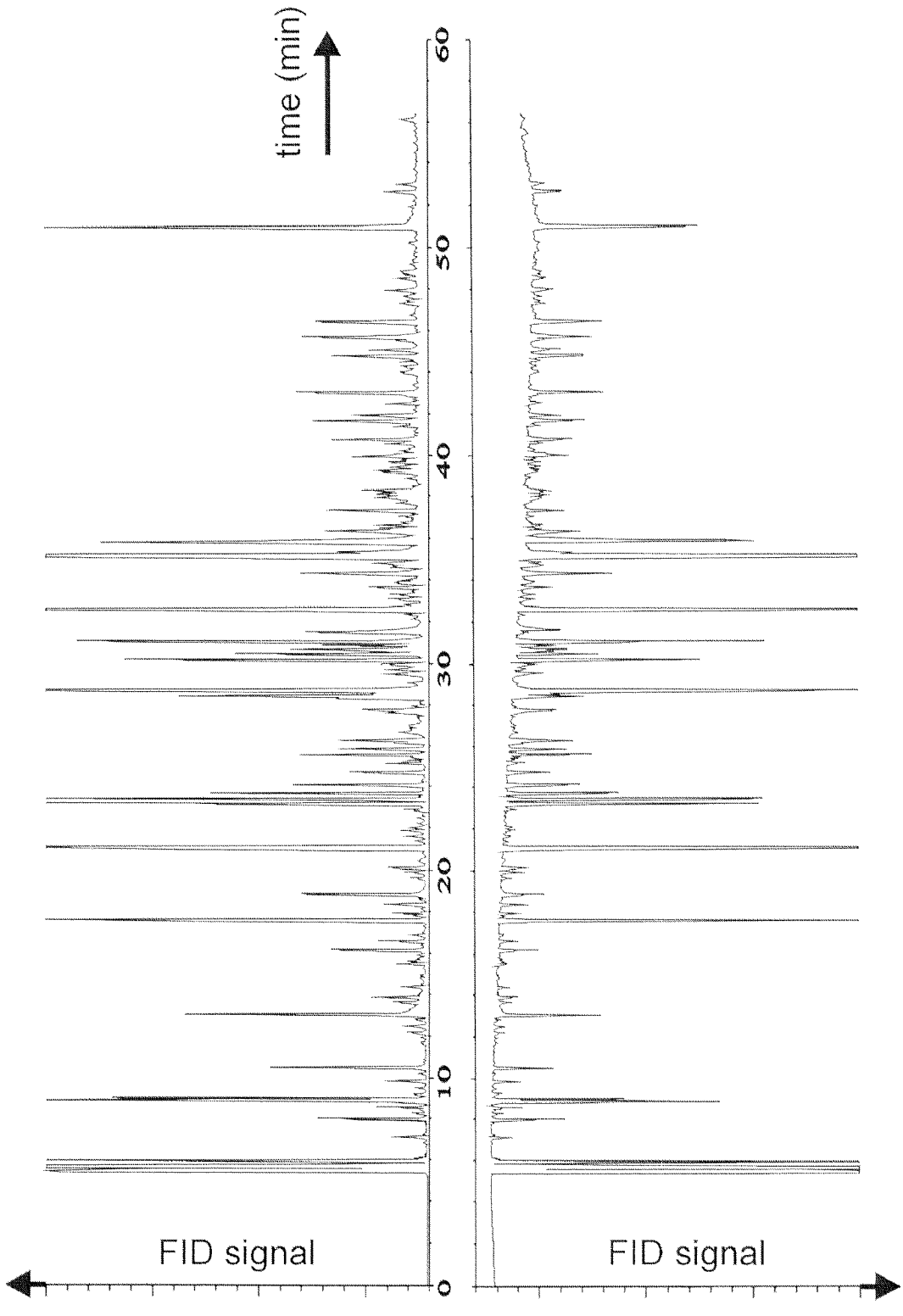

Fig. 60: *GC-FID chromatograms of SDE aroma isolates from HTST roasted (left) and LTLT roasted (right) coffee samples of identical degree of roast.*

Tab. 12: *Influence of different temperature profiles[a] as defined in Tables 4 and 5 on the relative quantities of important aroma compounds in laboratory roasted coffees of identical degree of roast.*

Compound	$A_X/A_{IStd.}$ (-)					
	LTLT	HTST	HL	LHC	PLHC	PHL
2,3-Butanedione	0.130	0.204	0.110	0.171	0.196	0.130
ß-Damascenone	0.019	0.015	0.016	0.016	0.016	0.019
2,3-Diethyl-5-methyl-pyrazine	2.695	2.273	3.308	3.638	3.572	4.033
2-Furfurylthiol	0.019	0.035	0.027	0.029	0.022	0.024
Guaiacol	0.107	0.144	0.131	0.160	0.141	0.148
2-Hydroxy-3-methyl-2-cyclopenten-1-one	0.042	0.041	0.041	0.050	0.042	0.042
Linalool	0.025	0.017	0.023	0.022	0.018	0.022
Methional	0.098	0.154	0.143	0.193	0.178	0.170
3-Methyl butyric acid	0.567	0.653	0.777	1.001	0.750	0.816
Methyl-dihydro cyclopenta pyrazine	0.011	0.015	0.014	0.014	0.013	0.015
3-Methylmercapto-3-methyl butyl formiate	0.125	0.180	0.127	0.183	0.175	0.143
2,3-Pentanedione	0.404	0.512	0.416	0.533	0.551	0.478
Propyl pyrazine	0.015	0.019	0.014	0.020	0.018	0.016
p-Vinyl guaiacol	0.304	0.614	0.445	0.740	0.554	0.446

a.
Temperature profiles: LTLT: Low temperature long time. HTST: High temperature short time. HL: High temperature and temperature reduced final stage. LHC: Continuous temperature increase from low to high. PLHC: Pre-heating with subsequent LHC process. PHL: Pre-heating, high temperature, reduced final stage.

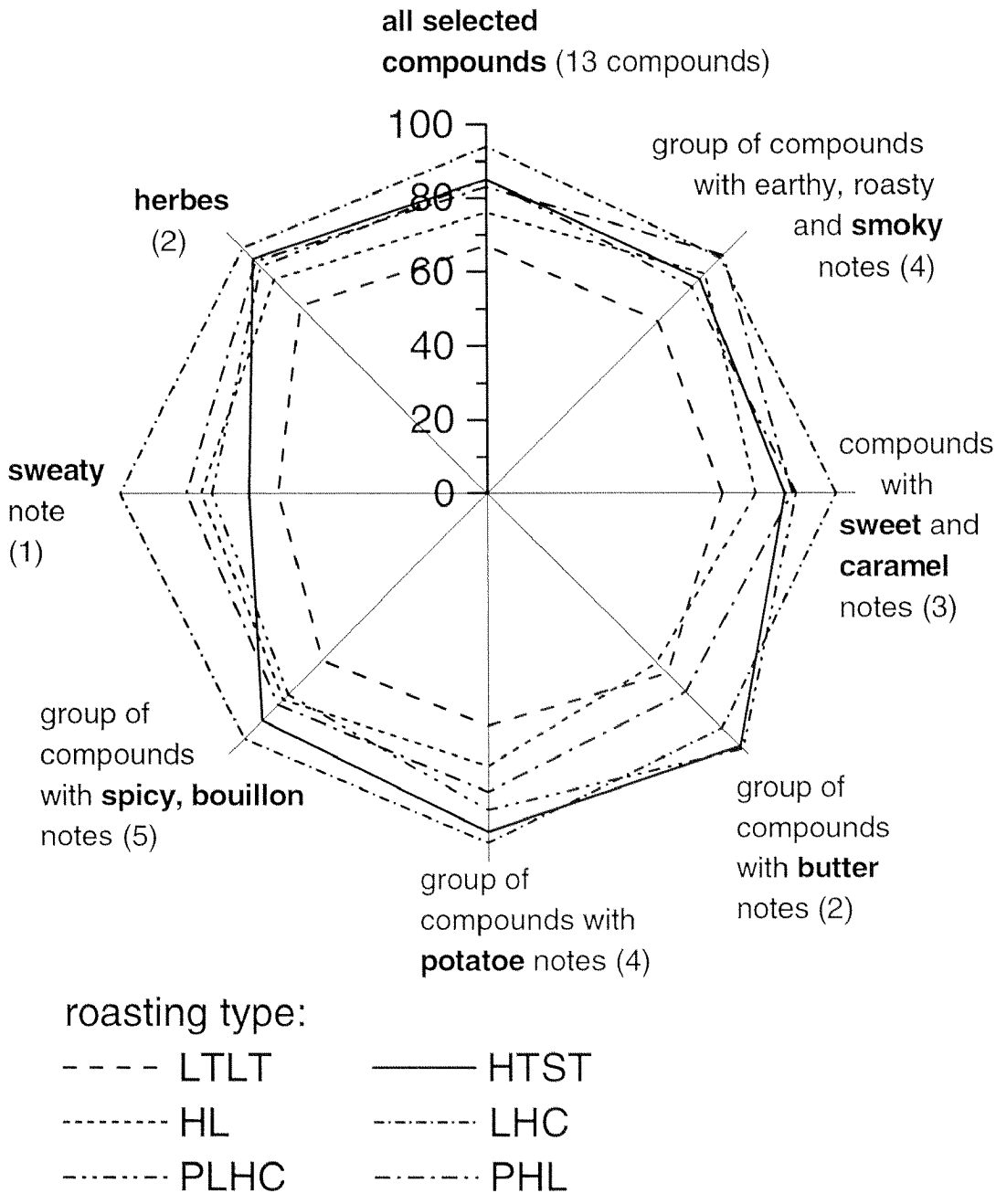

Fig. 61: *Influence of laboratory temperature profiles, leading to identical degree of roast, on aroma compounds grouped according to sensory properties. Normalized presentation with the highest quantity of an aroma compound receiving the value 100, values added up in each group and divided by the number of compounds.*

4.3.5 Influence of roasting time and temperature on sensory quality of the coffee beverage

Figure 62 illustrates the development of the sensory profile during LTLT roasting to a medium degree of roast and beyond and shows how sensory properties are shifted with continuing of roasting. The "green" note decreases in favour of a "roasty" note or even a marked "burnt" note in overroasted products. The bitter taste is increased continuously during roasting, whereas overall acidity is decreased at least in the initial roasting stages. The development of "aroma intensity" coincided with the instrumental analytical data presented in Figure 56. A highly significant and marked increase of aroma strength between samples roasted for 200 s and 400 s is followed by a stagnation in aroma development as formation and decay of aroma compounds compete with each other. The low sensory score of the overroasted product is visible in a number of attributes. For example, it was rated lowest in the pleasant "floral" and "citrus-like" notes and exhibited highly significant a pronounced "burnt" note. The data emphasize again the importance of the appropriate termination point in the roasting process.

Figure 63 provides the sensory flavor properties of isothermally high and low temperature laboratory roasted coffees with identical degree of roast. Deviations were statistically significant for the attributes "bitterness", "green" note, "burnt" note, "roasty" note and "aroma intensity". An apparent contrast in the "floral" note was just not significant, whereas no difference could be seen in the "spicy" note, presumably due to difficulties in defining and distinguishing this note. High temperature roasted coffees turned out to be more powerful in aroma, but also to comprise intensified unpleasant notes, such as "burnt" and "bitter". However, differences in sensory score of these two beverages may also partially be attributed to the marked discrepancy in extraction yield of the respective coffee beans. The influence of different solids content in the beverage may not be restricted to the attribute "body", but also affect flavor components.

Expert panel tasting of a series of coffee beverages from laboratory and industrial roasted beans (results not shown) confirmed the trends concerning the relation between the length of roasting time and the sensory profile. Moreover, it provided insights on additional roasting factors influencing the aroma quality. A marked

general divergence was found between coffees roasted in industrial scale with a low air to bean ratio and coffees roasted in laboratory scale in full fluidized-bed with an air to bean ratio that is several orders of magnitudes greater than in industry. Laboratory roasted beans usually tasted more bland, dull and flat as compared to industrial products roasted under equivalent temperature conditions. Greater oxidation due to intensified contact with oxygen or due to an actual physical aroma stripping by the hot air stream may provide reasonable explanations for this difference. The rather preliminary result suggests that high air to bean ratios are detrimental to the flavor quality of roast coffee. This finding, if confirmed quantitatively, would have relevant consequences on roaster design and process development. It may be necessary to design roasters that operate on low air to bean ratios, allowing for the creation of a bean enclosing "microclimate", and with oxygen contact accurately limited to the required dose. This point will be further discussed in chapter 4.4.3.

The comparison between instrumental and sensory analytical data revealed that there is no proportional or otherwise simple relationship between the quantities of aroma impact compounds and the sensory quality of the beverage. Substantial progress in understanding this relationship has been achieved recently by Czerny et al. (1999) and other authors. Nevertheless, a lot more research is needed on these complex connections between instrumental and sensory data of coffee aroma.

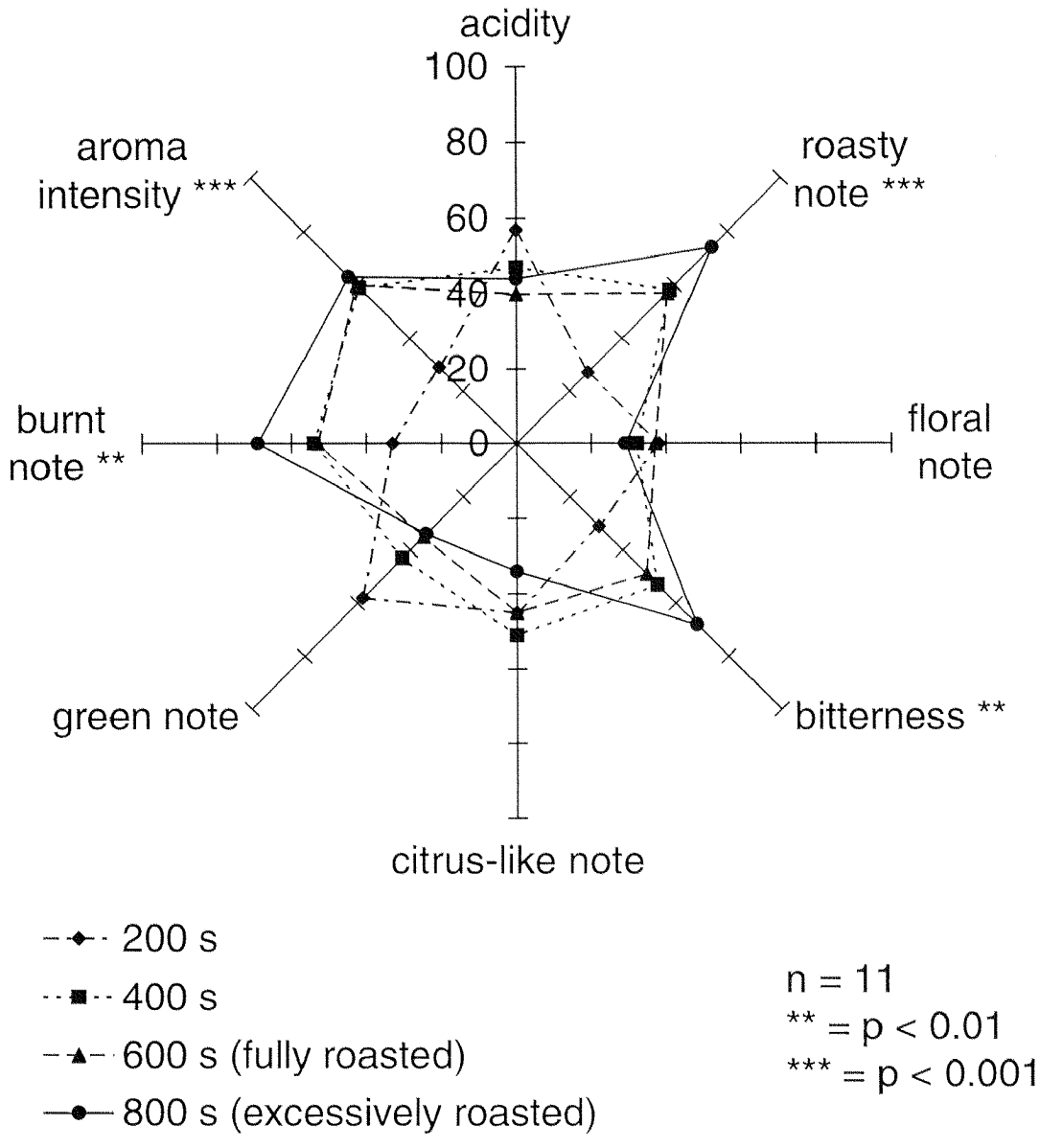

Fig. 62: *Sensory profiles of coffee beverages from LTLT laboratory roasted beans of increasing degree of roast. The product with a roasting time of 600 s corresponded to a medium degree of roast.*

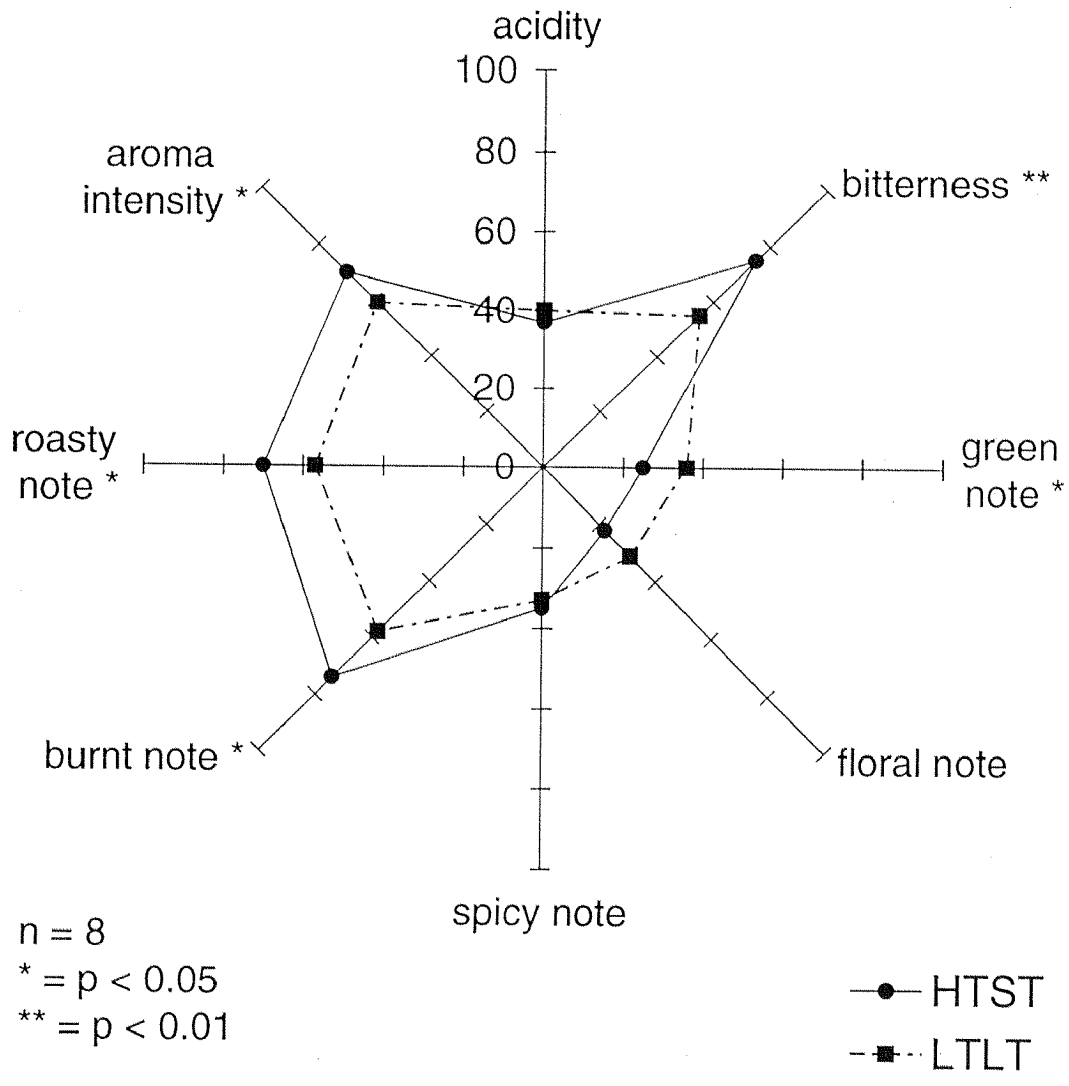

Fig. 63: *Influence of HTST and LTLT laboratory roasting to the same degree of roast on the sensory profiles of the respective coffee beverages.*

4.4 Changes of the roasted product during storage

4.4.1 Gas desorption

At the end of roasting, a major part of this gas is entrapped within the bean and is only released during storage. Gas desorption in whole beans is known to proceed very slowly, yet, it is be greatly accelerated by grinding and storage in the form of ground coffee (Radtke, 1975, Meister and Puhlmann, 1989). Figure 64 demonstrates the gas desorption curves of various whole bean products during a 2 month storage period. Since the amount of gas within a bean is continuously increased during roasting, identical degree of roast is crucial for comparison of the effects of different roasting conditions on gas desorption during storage. This fact is clearly visible when the two desorption curves of LTLT roasted beans with slightly different degrees of roast are compared. However, the process temperature profile had an equally important influence on gas desorption. More extensive gas formation by HTST than by LTLT roasting was expressed once more in greater headspace pressure at the end of storage. Moreover, HTST roasted samples showed much greater desorption rates. Green beans of identical origin, but subjected to decaffeination by ethylacetate, formed roughly equal amounts of gases during HTST roasting. This result must not be generalized, as it depends on the applied decaffeination technique. However, regardless of equal gas quantities, decaffeinated beans exhibited greater initial desorption rates.

Different desorption rates are mainly due to different pressure gradients. In addition, the microstructure may play an important role for desorption properties. The location of entrapped gas in the cells is not yet clear. Cell lumina of roasted beans may be regarded as pressurized gas-filled containers. The fact that a major part of the gas is easily released during grinding supports this theory. On the other hand, a substantial amount of gases can be assumed to be located adsorbed to the modified cytoplasmic layer and in the micropore network of the cell walls. The true nature of gas location most likely is a combination of the two assumptions.

The size of cell wall micropores would have a major influence on resistance opposed to mass transfer. Since high temperature roasted beans develop larger micropores (see 4.2.4), the structural differences may contribute considerably to

greater desorption rates of these products. This theory of structure-related influence is supported by the greater desorption rates of decaffeinated roast coffee. Due to equal gas formation, the pressure gradient and therefore the driving force in decaffeinated beans may be considered equal to that in the untreated sample. Hence, the hysteresis between the two desorption curves is most probably caused to full extent by structural differences. Greater desorption rates may be due to more severe structural changes of the cell walls during both the decaffeination and the roasting step. This assumption concurs with additional observations in industrial practice.

Packaging problems with roast coffee in air tight bags due to gas desorption have been solved long ago by introducing vent packaging materials (Radtke, 1975). However, the gas formation and desorption behavior is not only of technological importance, but may also affect staling. It would not be unreasonable to assume that aroma compounds are partially swept away together with the escaping gases. Moreover, as with major component gases, diffusion of aroma compounds out of the bean is subject to the same conformity of physical laws imposed by microstructure.

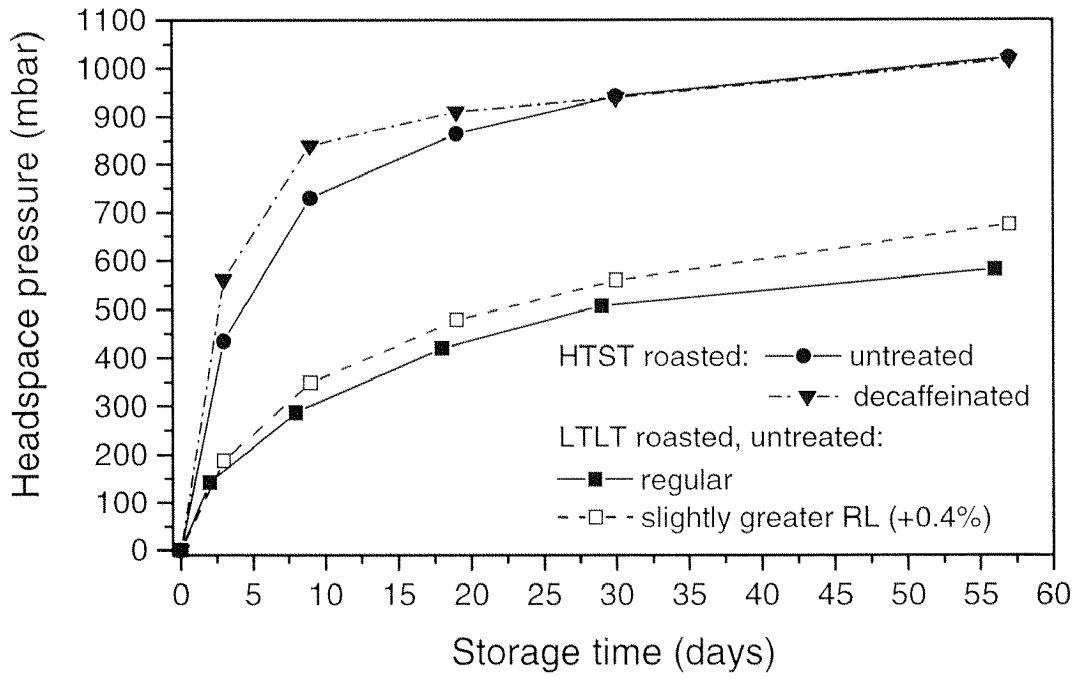

Fig. 64: *Gas desorption during storage of differently roasted coffees with identical degree of roast and of equally roasted coffees with slightly different degree of roast.*

4.4.2 Oil migration

Roasted coffee beans exhibit occasionally a more or less severe "oil sweating". Figure 65 provides a microscopic view of the phenomenon. During the initial stages of the migration process, numerous small oil droplets appeared on the bean surface. The droplet distribution was not restricted to specific surface areas, but spread evenly over the entire surface. Thereafter, they coalesce to larger droplets and become visual by eye. For a given raw material, the extent of this oil migration process is mainly influenced by the degree of roast (Table 13). Darker roasted beans tend to more severe oil migration. Online process observations of coffee beans exposed to roasting revealed that oil migration can even develop to visible extent already in the roaster. With excessive roasting beyond usual degrees of roast large amounts of oil suddenly emerged on the bean surface. Starting from certain spots of the surface it soon covered the whole bean with an oil film. It may have been due to local injury of the bean surface also known as "tipping", where small bits of bean tissue are burst off.

Provided the same degree of roast, roasting conditions govern the subsequent oil migration process (Figure 66). High temperature roasted coffees developed much more surface oil than low temperature roasted products. Migration ended after a storage period of approximately 2 months.

Structural changes in the coffee bean tissue during roasting destroy the native cell organization and mobilize the coffee oil (see 4.2.3). The high gas pressure gradient between the bean core, the outer bean parts and the exterior may drive the oil out of the bean. Additionally, the flow may be assisted by capillarity. As outlined in chapters 4.2.3 and 4.2.4, the oil transport can be assumed to make use of an extensive micropore network developed in the cell walls of beans by roasting. The uniform distribution of oil droplets displayed in Figure 65 supports the model of a generally permeable, three-dimensional, wad-like network of polysaccharides. Accordingly, oil droplets can emerge everywhere on the cell surface and their occurrence is not restricted to the openings of major cracks in the surface. However, the narrow size of free ways for oil to pass, together with a high viscosity of the modified cytoplasmic matrix, may make up for the slowness of the oil migration process.

Similar to gas desorption, the oil migration is determined by gas pressure and micro-structural factors. The gas pressure may act as the driving force for oil migration. Therefore, a greater driving force can be expected for high temperature roasted beans. Also the structural pre-conditions in HTST roasted coffees favor oil migration, since HTST coffees develop larger cell wall micropores. Consequently, minimal oil migration can be achieved employing low temperature roasting profiles and light degrees of roast.

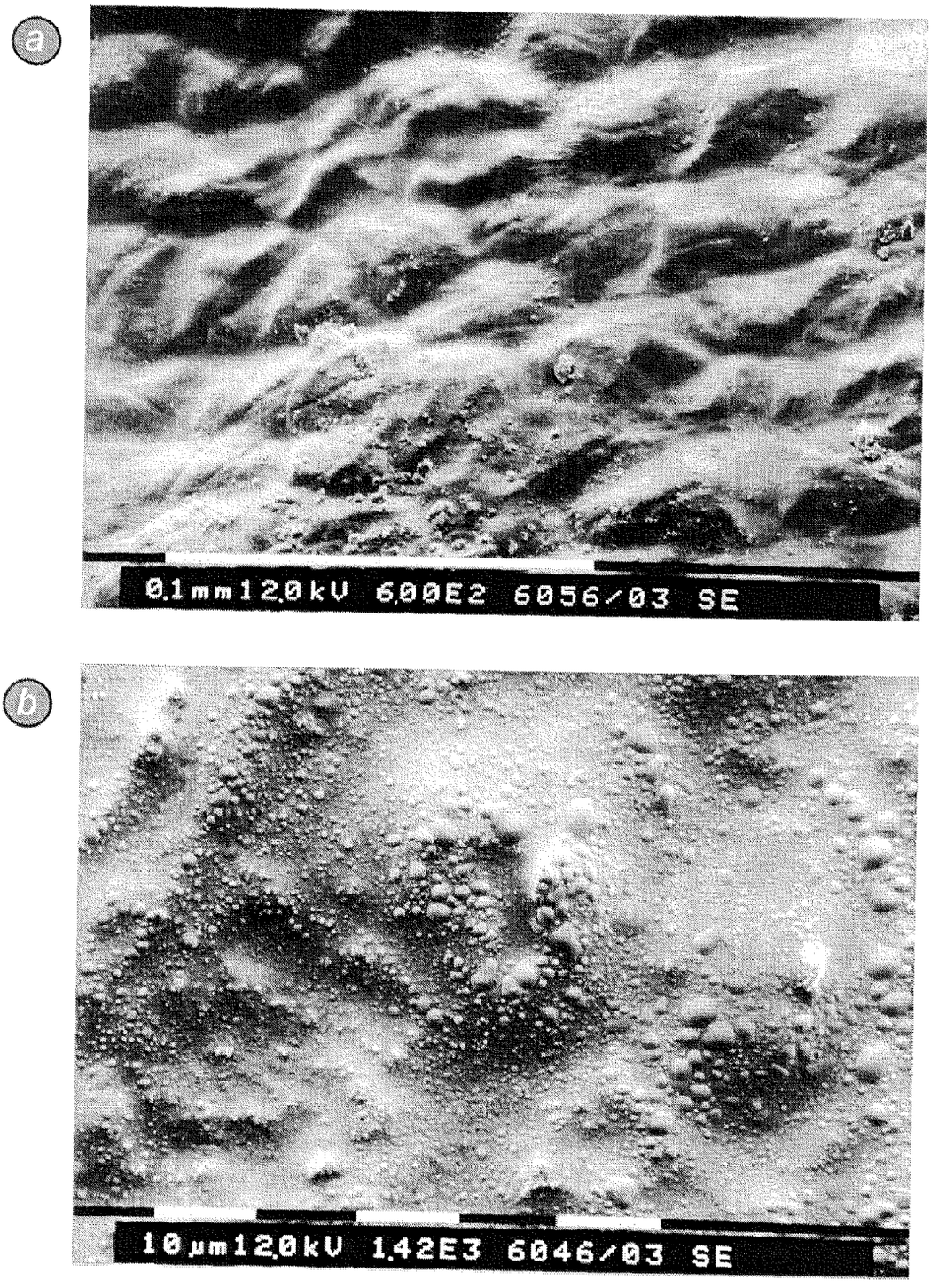

Fig. 65: *Cryo-SEM micrographs of the surface of a high temperature dark roasted coffee bean, illustrating the initial stage of the oil migration process. 65a: Immediately after roasting. Smooth epidermal cell surfaces. 65b: After 1 day of storage. Numerous very small oil droplets cover the surface. (Images: B. Frey, S. Handschin).*

Tab. 13: *Influence of the degree of roast on the extent of oil migration during storage of high temperature roasted coffee beans.*

Roast loss (%)	Surface oil after 33 d storage (g oil / 100 g bean)	Linear regression
14.28	0.064	regression coefficient
15.45	0.325	r = 0.992
16.17	0.441	
16.86	0.628	
17.35	0.646	

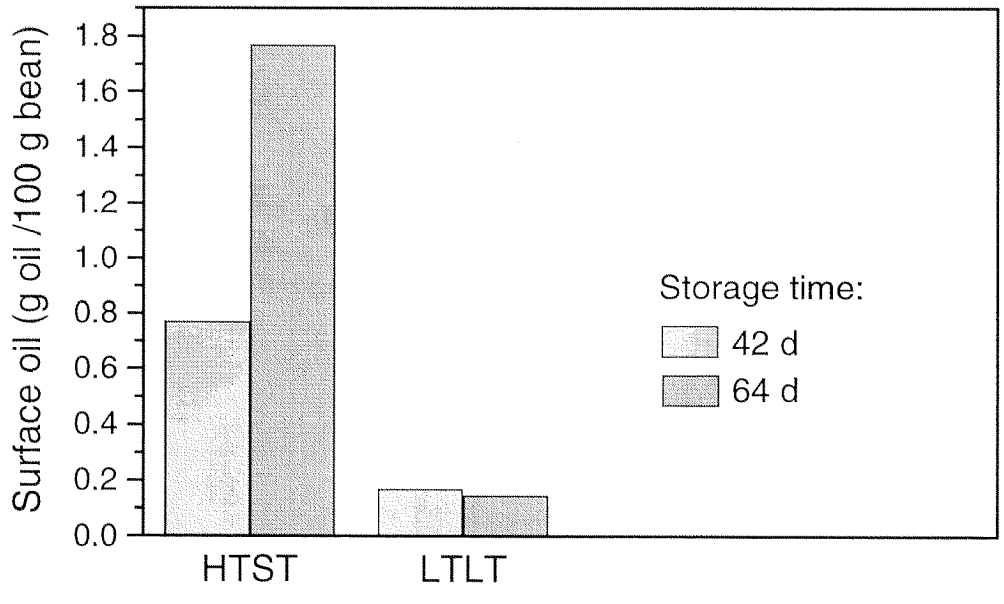

Fig. 66: *Surface oil on HTST and LTLT laboratory roasted coffee beans with identical degree of roast after storage.*

4.4.3 Staling

The unprotected aroma of fresh roast coffee starts to deteriorate soon after roasting. Oxidation is assumed to play an important role in this staling process. The green bean is apparently well protected against oxidation by the native cell organization (4.2.3) and by antioxidative constituents, such as chlorogenic acids (Morishita and Kido, 1995). However, these protective capacities are destroyed to large extent during roasting. On the other hand, some Maillard-products of thermally processed foods are well-known to exert antioxidant effects (Nienaber and Eichner, 1995, Severini et al., 1994 and numerous other authors).

Roasting-induced antioxidant capacity

Figure 67 shows the effect of roast coffee powder in soy bean oil on the induction time as determined with the Rancimat® method. The increase of induction time of the oil caused by roast coffee powder indicates an antioxidant activity. Even with green beans an extension of the time of induction was observed. Increasing effects on induction time with darker degrees of roast suggest an enhancement of the antioxidant capacity during roasting. Nicoli et al. (1997) found a similar development of antioxidant properties of coffee brews in relation to the degree of roast. While they found an optimal degree of roast in which the antioxidant capacity reaches a maximum, our data present a continuous increase up to dark degrees of roast. These contrasting developments may be due to different roasting conditions.

The influence of the roasting conditions on the development of the antioxidant capacity is shown in Table 14. HTST roasted beans exhibited a substantially greater effect on induction time than LTLT coffee on the same degree of roast. This result suggests a superior antioxidant potential in high temperature roasted coffee due to more intense formation of protective Maillard-products. It is in accordance with various previously described differences in the formation of chemical compounds during roasting. However, concerning oxidation processes, this superior antioxidant potential in HTST beans may probably not be effective enough to make up for the considerable disadvantages resulting from a more open microstructure with greater access for oxygen. A similar interaction and process-dependency of these two competitive factors have also been reported for hazelnut roasting by Severini et al.

(1994) and by Perren (1995) as well as for model systems during high temperature treatment by Severini and Lerici (1995).

Nevertheless, comparative results between differently roasted products obtained with the Rancimat® method must be interpreted with due care and attention. The Rancimat® method is subject to fundamental limitations, as it measures merely increases of water conductivity (Sandmeier and Ziegleder,1985). Moreover, with differently roasted coffees other factors than antioxidant activity may be involved. Although very finely ground, differences in the particle size distribution and in gas desorption of these particles may influence the diffusion of antioxidant volatiles into the soja oil and cause different grades of realization of the present antioxidant potential.

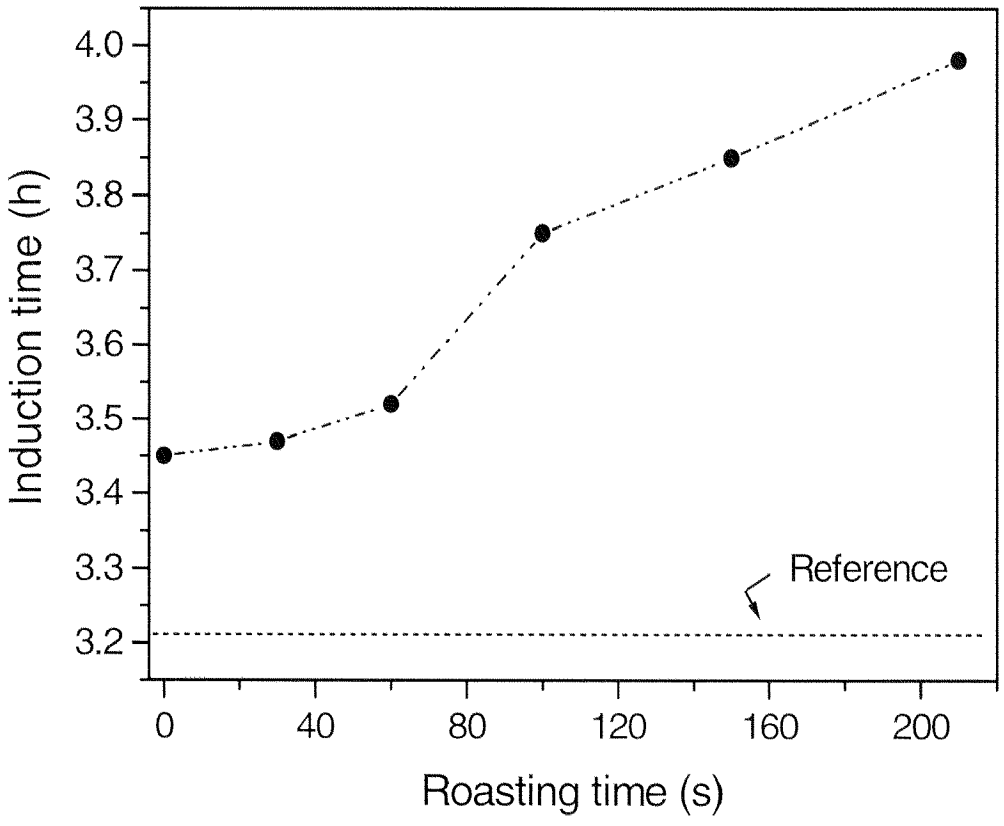

Fig. 67: *Influence of roasting time on the antioxidant properties of ground HTST laboratory roasted coffee, expressed as induction time of soybean oil suspension determined with the Rancimat method. Pure soybean oil as reference (3.22 h). Medium degree of roast at 160 s.*

Tab. 14: *Incremental effect of roast coffee powder from differently roasted beans on the induction time in reference to pure soybean oil. Samples were roasted to the same degree of roast.*

	Increment of induction time (h)	(max. deviation)
Reference: Pure soja oil	0	-
Green coffee	0.28	(0.05)
LTLT roasted coffee	0.32	(0.01)
HTST roasted coffee	0.68	(0.05)

Oxidative reactions

The staling process of roasted coffee beans during storage is accelerated with more intense exposure to oxygen. For this reason, oxidation reactions are most likely to play a key role in the staling process. Recent studies showed an extensive formation of free radicals during the final stages of roasting and a subsequent decrease of these radicals during storage (Santanilla et al., 1981, Baesso et al., 1990, Hofmann et al., 1999a and 1999b). These radicals are known to induce oxidation reactions. However, the lipid fraction of roast coffee turned out to be rather resistant to oxidation. Headspace analysis of stored coffee beans showed only small quantities of typical secondary lipid oxidation products, such as methane, ethane and pentane. These alkanes were already present in minor quantities in freshly roasted beans (see chapter 4.1.4) and slightly increased during storage. A slow formation of pentane was even found during forced oxidation of extracted oil from roasted coffee beans and confirmed the relative stability of the lipid fraction. It may be caused by the protective action of Maillard reaction products. The slow process of oxidation of coffee beans was also reported by Nicoli et al. (1993). The results suggest that oxidation is mainly affecting compounds other than lipids. The considerable oxygen consumption immediately after roasting reported by Hinman (1991) may be used, among others, for the oxidation of sensitive flavor compounds.

The results from headspace analysis from differently roasted beans during storage were difficult to interpret, as it was unclear, whether the measured oxidation products were already present after roasting and desorbed later or if they were the result of oxidation during storage. Nevertheless, it seems that differences in micro-structure and gas desorption of differently roasted beans had an impact on the oxidation processes during storage. Holscher and Steinhart (1992b) proposed a two step staling process with a first step determined by physiochemical processes and a second step by oxidation. It may therefore be assumed, that structural product properties have a major impact at least on these physico-chemical processes, but most likely also on oxidation during the second step. Hinman (1991) found greater rates of oxidation for low-density coffee beans as compared to regular coffees. This points to a substantial influence of the bean pore structure on oxidation. Larger cell wall micropores and increased area of internal surface (4.2.4) may provide easier

access for oxygen and more extensive exposure of sensitive compounds to oxidation in high temperature roasted low-density coffees. Consequently, low temperature roasting processes may lead to a more stable product against oxidation and staling.

For foodstuffs in general and for roast coffee in particular, oxidation is regarded as being exclusively detrimental to the product quality by most authors (Radtke, 1982, Hinman, 1991, and other authors). As a consequence to the extreme, roasting, grinding and packaging processes should employ completely oxygen-free technologies. In general, this may be indeed valid for the most part and may apply to the long-term situation during storage of the product. However, it is worth considering that oxygen may be needed during aroma formation and that a limited extent of oxidation eventually could improve the aroma compounds profile by oxidizing unpleasant compounds such as sensitive sulfur-containing compounds. This hypothesis is supported by a frequently claimed observation that freshly roasted coffee comes to maximum flavor quality only after a few hours of exposure to air. According to this aspect, there may be no requirement for the development of oxygen-free operating conveying, storage bin and grinding equipment.

Nevertheless, the situation within the roaster may again be different, since the elevated temperatures cause greatly accelerated chemical reactions. An oxygen-free final stage of the roasting process could be perfectly effective in preventing the beans from excessive oxidation and might be beneficial for the product aroma. So far, the oxidation processes during roasting are inadequately understood. Further work on the formation of free radicals and oxidation during roasting is required.

Changes of the aroma compounds profile

The different aroma compounds of coffee beans exposed to air and ambient temperature behaved very individually during storage (Table 15). An increase of concentration at first with subsequent decrease later during storage, such as described for furfurylmercaptan by Tressl et al. (1979), was not observed. Acetic acid and 2,3-butanedione exhibited only minor losses during storage. Still, all other compounds listed were subject to a more or less severe loss or decay. A large decrease was found for 2-ethenyl-5-methyl pyrazine, linalool and propyl pyrazine. The average percentage of aroma compound loss for HTST and LTLT roasted beans

was around 57 % and differed only slightly for the two different processes. Absolute aroma compounds quantities after storage were slightly greater in HTST as compared to LTLT products. In contrast, since the average initial aroma compounds concentration was substantially higher in freshly HTST roasted products, the average *loss* of absolute quantities was much higher for the high temperature roasted beans. This finding is clearly visible in Figure 68.

In case of numerous compounds the percentage of loss did not differ greatly between different processes. However, certain compounds showed substantial differences for HTST and LTLT roasted beans. 2-ethenyl-5-methyl pyrazine, 2-furfurylthiol, linalool and 2-methyl butanal experienced substantially higher relative losses in HTST roasted beans. In contrast, ß-damascenone was the only compound to experience considerably greater losses in LTLT roasted beans. Greater relative losses of 2-furfurylthiol seem to be particulary meaningful, since this compound has been described as a key-role player in the staling process (Tressl et al., 1979). From various proposed staling indicators only the butanedione/2-methyl furan ratio (Leino et al., 1992) was applicable to our data. This ratio increased from 2.10 to 2.80, and from 0.93 to 1.22 in HTST and LTLT roasted beans, respectively. A further developed staling process in the HTST coffee may be concluded from these figures, or that the concept of staling ratios is only applicable for different storage conditions but not for the distinction of different roasting conditions.

Unprotected coffee beans are subject to extensive changes in the aroma compounds profile during storage. Aroma compounds are either lost due to diffusion, or they undergo further chemical reactions, such as oxidation. Some authors suggested a close relationship between the gas desorption and the losses of aroma compounds (Nicoli et al., 1993). A more comprehensive view may indicate a play together of the three factors microstructure, gas desorption and oxidation. As a result, roast coffee does not only loose aroma compounds, but also experiences a considerable shift in the proportion of the compounds, since each compound reacts individually to the various influences. The results provide evidence for a more severe staling process in high temperature roasted coffees than in low temperature roasted products.

Tab. 15: *Loss of selected aroma compounds during storage of high and low temperature roasted coffee beans for 81 days at 25 °C and exposed to air.*

Compound	HTST roasted coffee			LTLT roasted coffee		
	fresh $A_X/A_{IStd.}$ (-)	stored $A_X/A_{IStd.}$ (-)	loss (%)	fresh $A_X/A_{IStd.}$ (-)	stored $A_X/A_{IStd.}$ (-)	loss (%)
Acetic acid	0.56	0.42	25	0.26	0.26	0
2,3-Butanedione	0.21	0.14	33	0.14	0.11	21
ß-Damascenone	0.04	0.02	50	0.05	0.01	80
2,3-Dimethyl pyrazine	0.50	0.19	62	0.33	0.13	61
2,5-Dimethyl pyrazine	1.28	0.46	64	0.94	0.35	63
2,6-Dimethyl pyrazine	1.33	0.49	63	0.96	0.36	62
2-Ethenyl-5-methyl pyrazine	0.11	0.03	72	0.07	0.03	57
2-Ethyl-3,5-dimethyl pyrazine	0.15	0.05	66	0.13	0.04	69
3-Ethyl-2,5-dimethyl pyrazine	0.34	0.13	65	0.28	0.09	68
2-Ethyl-3-methyl pyrazine	0.15	0.06	60	0.12	0.05	58
2-Ethyl-5-methyl pyrazine	0.31	0.10	68	0.25	0.09	64
2-Ethyl-6-methyl pyrazine	0.44	0.14	68	0.36	0.12	67
Ethyl pyrazine	0.71	0.23	68	0.47	0.17	64
2-Furfurylthiol	2.50	0.94	62	0.89	0.45	49
Guaiacol	0.63	0.28	56	0.34	0.14	59
2-Hydroxy-3-methyl-2-cyclopenten-1-one	0.04	0.04	0	0.03	0.01	67
Kahweofuran	0.25	0.09	64	0.15	0.05	67
Linalool	0.06	0.01	83	0.05	0.02	60
2-Methyl butanal	0.46	0.23	50	0.46	0.29	25
3-Methyl butyric acid	2.00	1.14	43	1.27	0.73	43
2,3-Pentanedione	0.63	0.25	60	0.38	0.19	50
Propyl pyrazine	0.07	0.02	72	0.04	0.01	75
2,3,5-Trimethyl pyrazine	0.37	0.13	65	0.29	0.10	66
p-Vinyl guaiacol	2.21	1.09	51	0.98	0.46	53

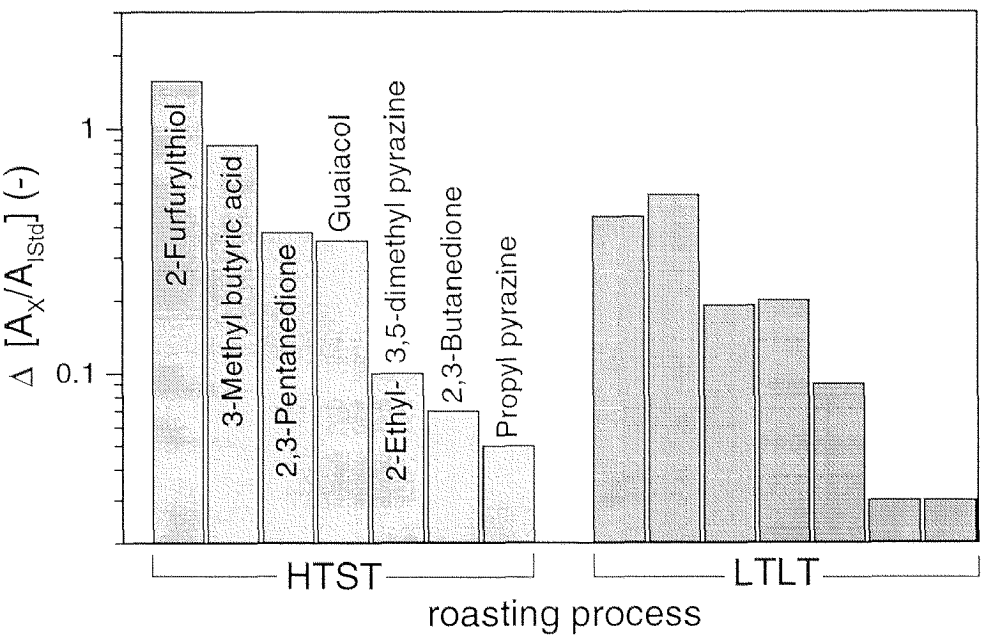

Fig. 68: *Loss of aroma compounds during a storage period of 81 days for HTST and LTLT roasted coffee beans. The beans were exposed to air and ambient temperature during storage.*

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5 Conclusions

5.1 Critical process factors

Hot air roasting of coffee beans is a traditional thermal process which in spite of its great importance in practice is still designed and operated mainly on an empirical basis. The principal objective of the roasting process is to create the desired roast coffee aroma and a flavor-full cup quality. The unprotected aroma fraction of roasted coffee beans is subject to rapid and substantial deterioration after roasting. Instability of compounds in the aroma profiles during storage is a critical factor for any kind of coffee product. Therefore, the most demanding challenge of process development is to achieve favorable chemical and structural conditions in the bean to oppose staling. In order to achieve these process objectives the following roasting factors and transformations during roasting must be taken into account:

Quality of green coffee beans

The botanical variety, the origin and the processing of the green beans have a major impact on the roasting process and the final product quality. The initial water content of the green beans is of particular technological importance, as this factor may be controlled by a more strictly specified procedure of post-harvest dehydration. The water content influences the bean temperature, the development of the bean structure and all chemical reactions.

Process temperature

The development of bean core temperature presents the most important roasting parameter and influences flavor formation and structural product properties to a great extent. Different temperature profiles affect dehydration, which in turn determines the specific conditions for chemical reactions in the bean. This is reflected obviously in the formation of CO_2, browning and flavor development. The realization of a distinct profile of aroma compounds out of the aroma potential of

the green beans is highly dependent on these reaction conditions. Out of the hundreds of volatiles, it is a small number of temperature dependent aroma impact compounds that dominate the aroma of roast coffee. Low temperature conditions result in inadequate formation of aroma compounds. The highest rates of aroma compound formation are observed at a bean water content below 5 g /100 g (wb) and at temperatures exceeding 200 °C. On the other hand, aroma formation is superimposed by an accelerated decay of some aroma compounds at high temperatures during the final roasting stage.

Structural changes of the bean are equally affected by the temperature profile. The driving force for bean expansion as well as the structural resistance opposed to it are factors that are again related to temperature and dehydration. A glass transition phenomena related three states involving development presumably controls structure resistance. As a result, high temperature roasted beans exhibit a greater bean volume, a higher cumulated pore volume and larger cell wall micropores than low temperature roasted coffees of the same degree of roast.

Hot air humidity

The humidity of the hot air must be considered as another important process parameter. Industrial roasters using air recirculation systems can accumulate water from the beans and from water quench cooling so that a significant humidity in the roasting atmosphere may be generated. Elevated humidities cause an increased specific heat capacity of the hot air and result in a more efficient heat transfer. In addition, it is assumed that some reactions and changes that depend on water content are also affected.

Air-to-bean ratio

The amount of hot air in relation to the batch size turned out to be a very important feature of roaster design and operation. Provided adequate mechanical mixing in large batch, the application of a low air to bean ratio results in a coffee of superior cup-quality. In contrast, excessive air streams such as in a fully fluidized-bed lead to a product of bland, dull and flat sensory properties. A lower ratio is assumed to prevent physical aroma stripping and excessive contact with oxygen and to create a favorable "microclimate" enclosing the beans. Conventional conductive type

roasting systems of industrial size generally operate with reasonably low air to bean ratios, mainly for economical reasons.

Gas formation

The large amount of internal gases formed during roasting not only acts as the driving force for structural changes, but also plays an important role concerning mass transfer and staling during storage. The loss of aroma compounds appears to be closely related to gas desorption.

Transformation of structure

The structural organization of the native coffee seed, even after drying, provides far-reaching protection against adverse external impacts. The sophisticated cell compartialization, the storage of lipids within oleosomes, and the unusually thick cell walls obviously fulfil specific physiological tasks. The native structure is completely changed during roasting. The cell compartialization is destroyed, coffee oil is mobilized, and the cell walls become increasingly porous and permeable. The new structural properties of roasted coffee beans depend on the roasting conditions, as outlined above for different temperature profiles. In addition, the present investigations show a strong interaction between bean microstructure and mass transfer involving chemical and physico-chemical processes during storage. A more porous microstructure seems to disadvantageously favor mass transfer and to accelerate the staling process. Greater pore volume and larger micropores in high temperature roasted beans promote faster gas desorption and oil migration, and may enhance access for oxygen, resulting in accelerated loss and decay of aroma compounds. A considerably more stable bean is achieved at low temperature conditions, although at the expense of aroma "strength".

Oxidation

Sensitive aroma compounds and lipids are the target of oxidative processes. Oxidation rates are determined by a complex interaction of a series of promoting and inhibiting factors. Native antioxidants are destroyed, but replaced by a roasting-induced antioxidant capacity of Maillard type products. On the other hand, roasting is known to form a substantial amount of free radicals that induce oxidative reactions. Availability of oxygen can be regarded as the limiting factor for the

progression of oxidation and staling. It is evident that this factor is determined by the structural properties of the roasted beans.

5.2 Process optimizations

Different coffee manufacturers put individual priorities on the desirable product properties, mainly depending on whether they produce roasted beans and ground coffees or soluble coffee. The present investigations clearly show that not all desirable product properties can be maximized at the same time, because not all reactions and changes are reacting in the same direction to changes in process conditions. Therefore, process optimization requires specification of a compromise in target quality.

Roasting technology cannot make up for poor quality of the raw material. However, for a given type of green coffee blend, roasting is the main flavor determinant. High aroma quality is achieved with moderate, non-extreme processes of medium temperatures. Provided a low air to bean ratio, an optimal roasting time should be longer than 6 min, depending on the target flavor profile. A roasting phase at medium temperature is essential in generating sufficient aroma strength. On the other hand, high temperature conditions generally cause an unfavorable aroma profile and should be avoided. A final phase at reduced temperature has an impact on the aroma profile. The target degree of roast should not be set too dark, and the process must be terminated in time because decay of aroma compounds during the final roasting stage. Only green coffee of high quality may withstand more severe roasting conditions.

The highest porosity in bean structure is achieved by high temperature conditions and leads to maximum extraction yield. Nevertheless, such a low density product is believed to provide an unfavorable structure to oppose oxidation and staling. Oxygen contact should be limited precisely to the required level by two measures. First, a low air to bean ratio reduces the amount of air that is in contact with the beans during roasting and creates of a favorable "microclimate" enclosing the beans. Therefore, a roaster design operating with a fairly high proportion of conductive heat transfer may be advantageous. Secondly, the implementation of moderate

temperature profiles assures the generation of favorable structural pre-settings in the bean for storage.

For the most part, there is no requirement for completely oxygen-free roasting, conveying and grinding technology. Some oxygen may actually be needed for aroma formation. On the other hand, the accelerated chemical reactions at elevated temperatures during the final roasting stages might play a key role in the subsequent staling process. Oxygen-free roasting during the final roasting stages may therefore be worth of consideration for further investigations.

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