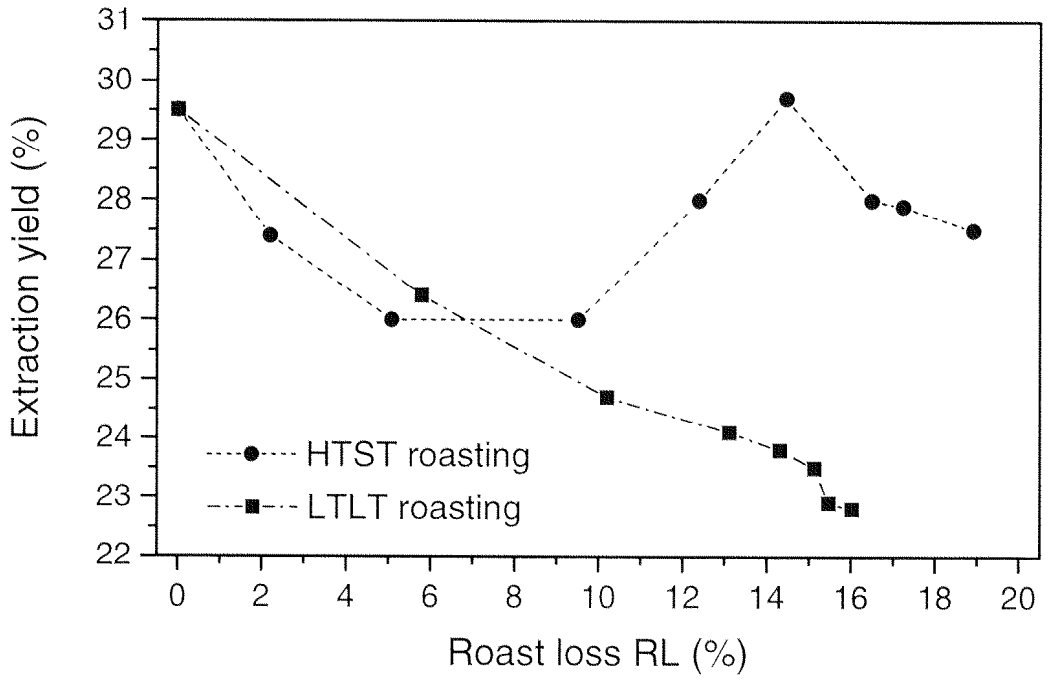

Fig. 22: *Development of extraction yield during high and low temperature laboratory roasting of C. arabica beans from Costa Rica. A medium degree of roast is achieved at a roast loss of 15 %.*

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.

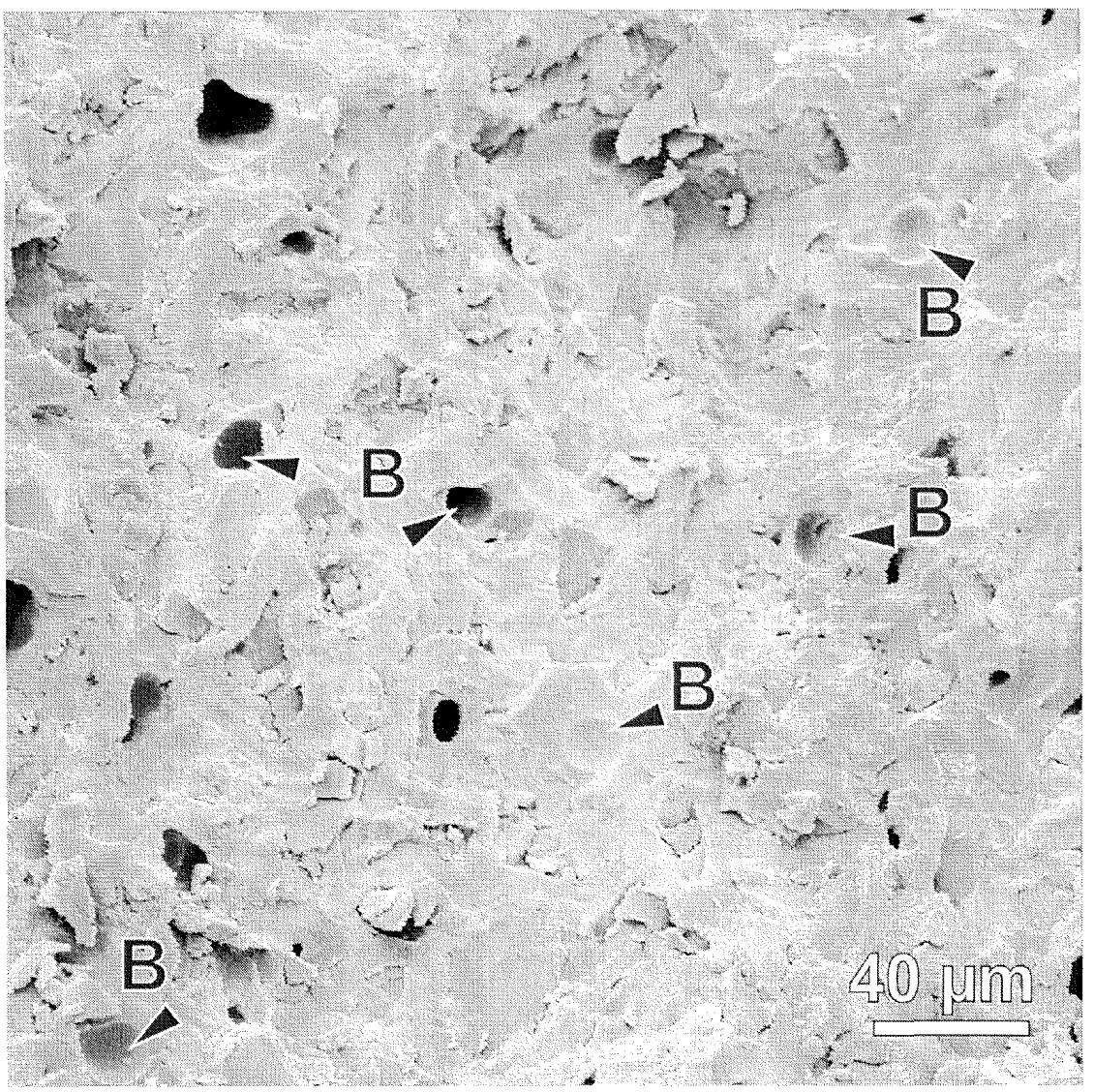

Fig. 23: *Cryo-SEM micrograph of the green coffee bean tissue structure. It clearly illustrates the dense and compact structure in the green bean. Numerous cells show a single large bubble (B) in the cytoplasm. Most probably they stem from the dehydration procedures during the post-harvest processing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

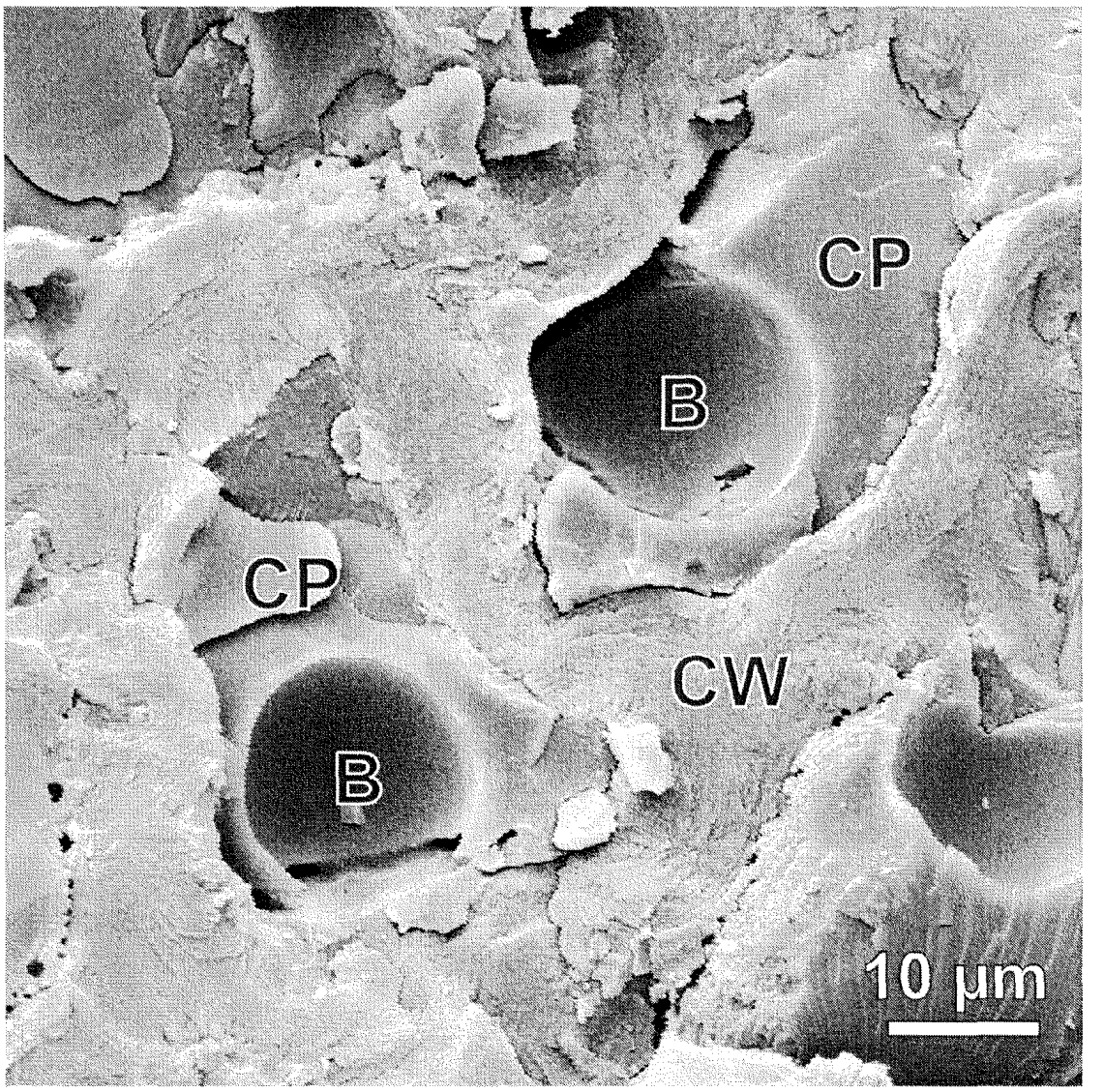

Fig. 24: *Cryo-SEM micrograph of 3 or 4 adjacent cells in the green coffee bean. The cytoplasm of each cell (CP) is surrounded by strong frames of cell wall material (CW). Bubbles (B) in the cytoplasm have no membrane and seem to be gas-filled. They display changes during severe dehydration in post-harvest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

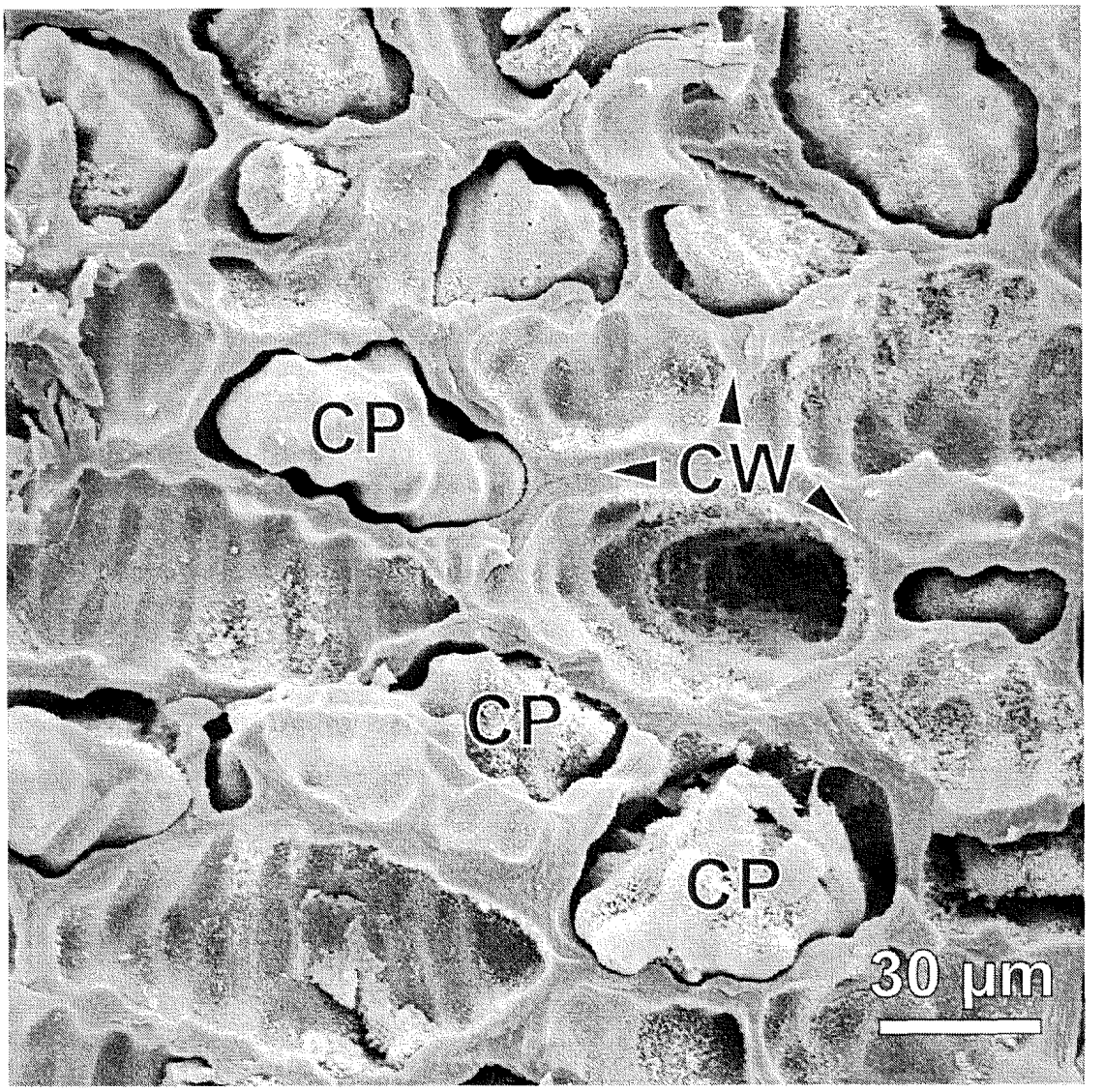

Fig. 25: *SEM micrograph of the green coffee bean tissue structure from a chemically fixed specimen. The cytoplasm (CP) is visible in some cells, whereas it is removed in others due to fractioning during specimen preparation. Surrounding cell walls (CW) are of remarkable thickness and show a striking 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).*

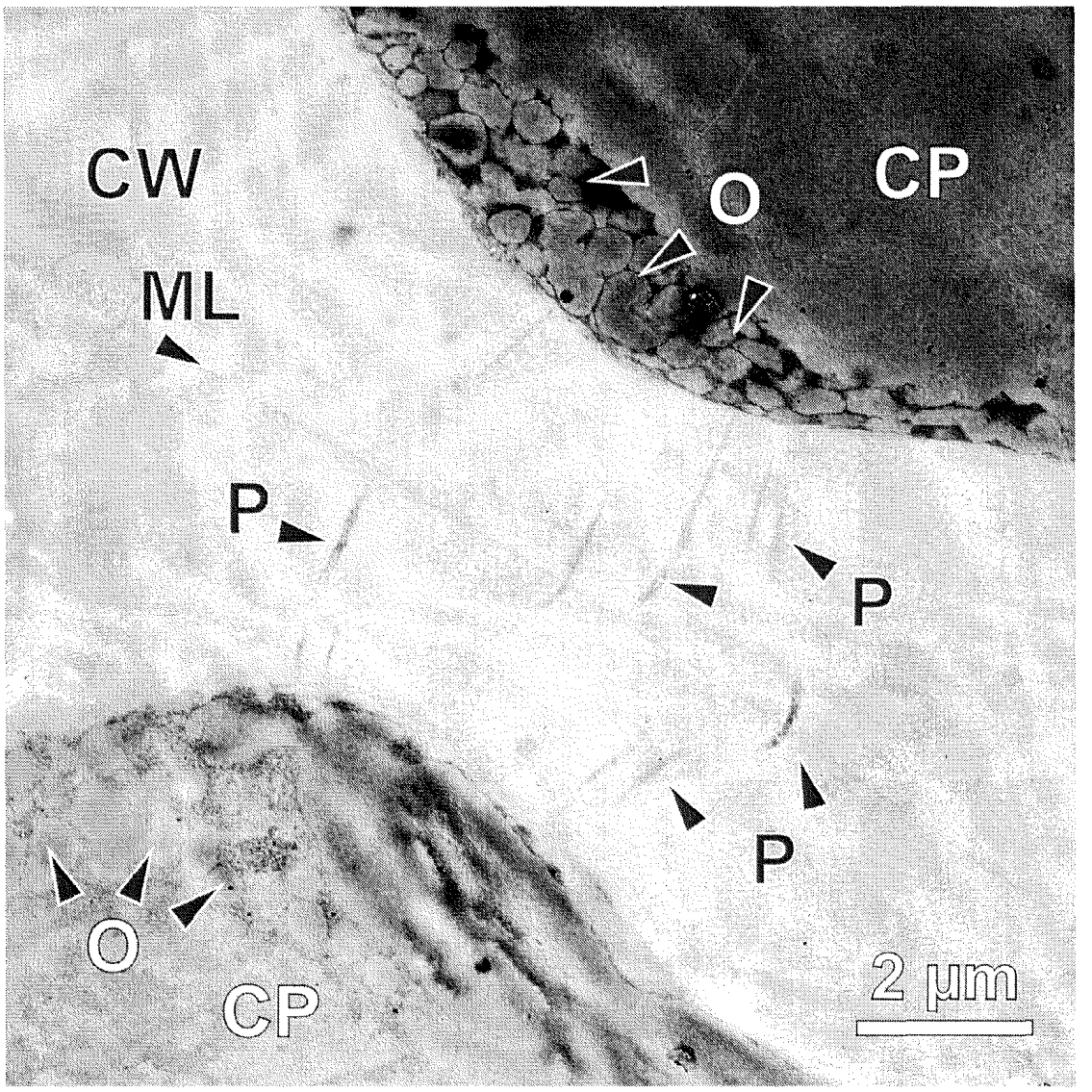

Fig. 26: *TEM micrograph of a cell wall in a green coffee bean. The continuous dark line is formed by the middle lamella (ML), that lies between the thick cell walls (CW) and the cytoplasm (CP) of two adjacent cells. Dark lines perpendicular to the middle lamella are parts of plasmodesmatae channels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

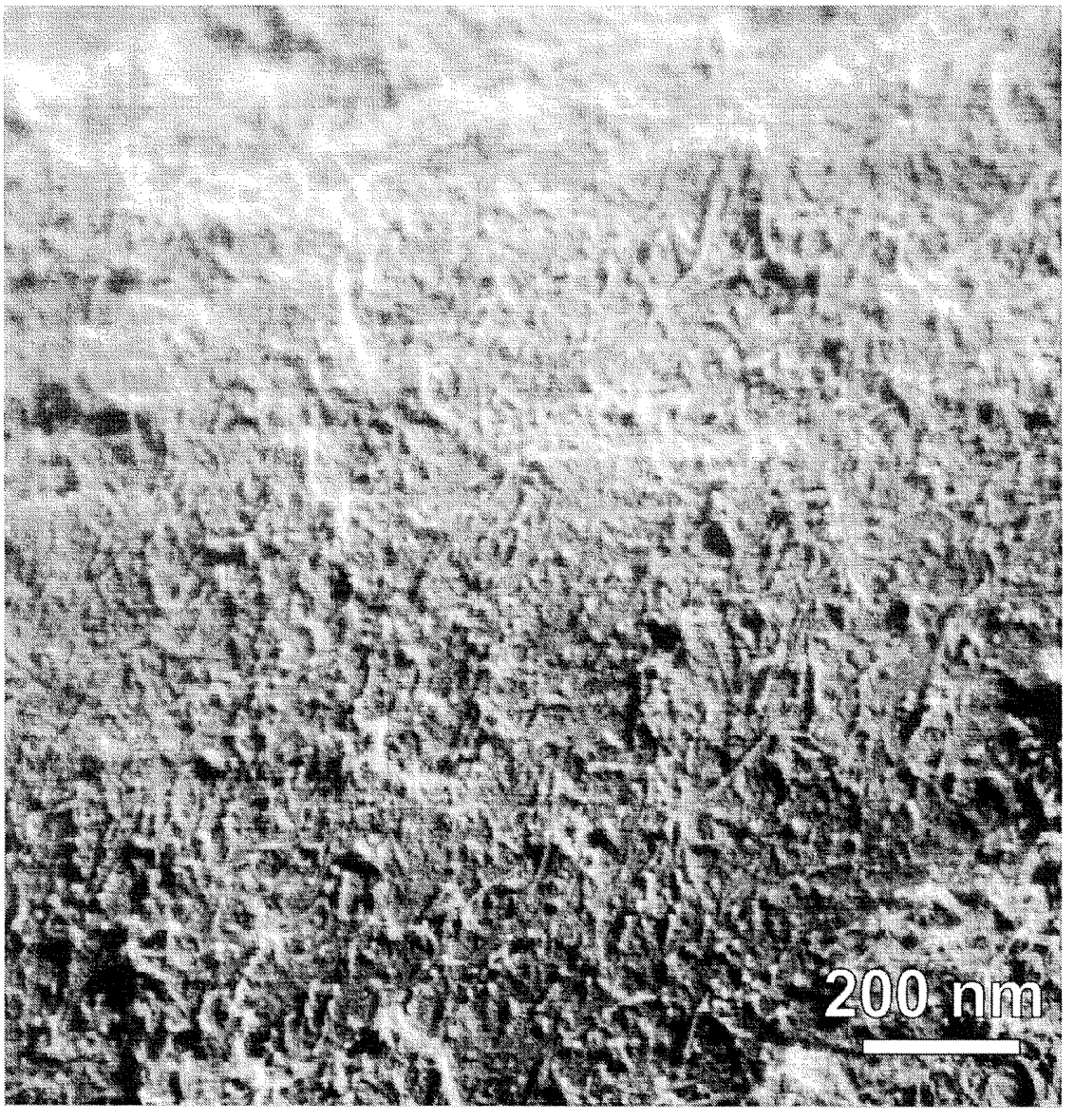

Fig. 27: *SEM micrograph of a cell wall cross section of a chemically fixed, de-oiled and fractured specimen from a green coffee bean. The structure of the fracture surface indicates the presence of a complex three-dimensional network of polysaccharide microfibrils. (Image: S. Handschin).*

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).

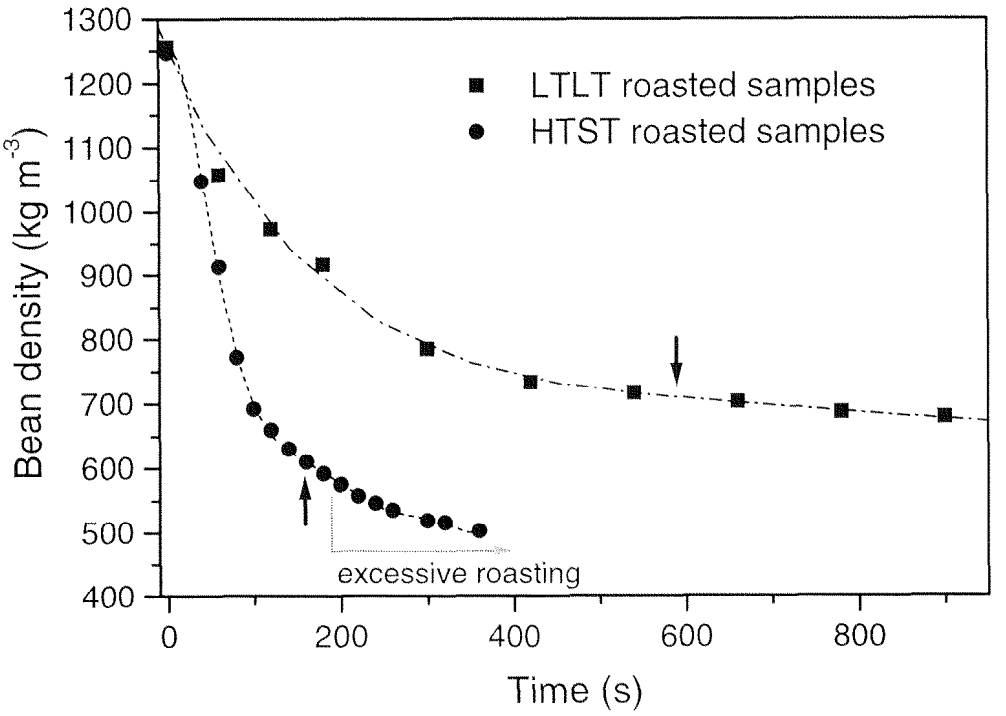

Fig. 28: *Decrease of bean density during high- and low-temperature laboratory roasting. Dotted lines represent trend curves and arrows indicate a medium degree of roast.*

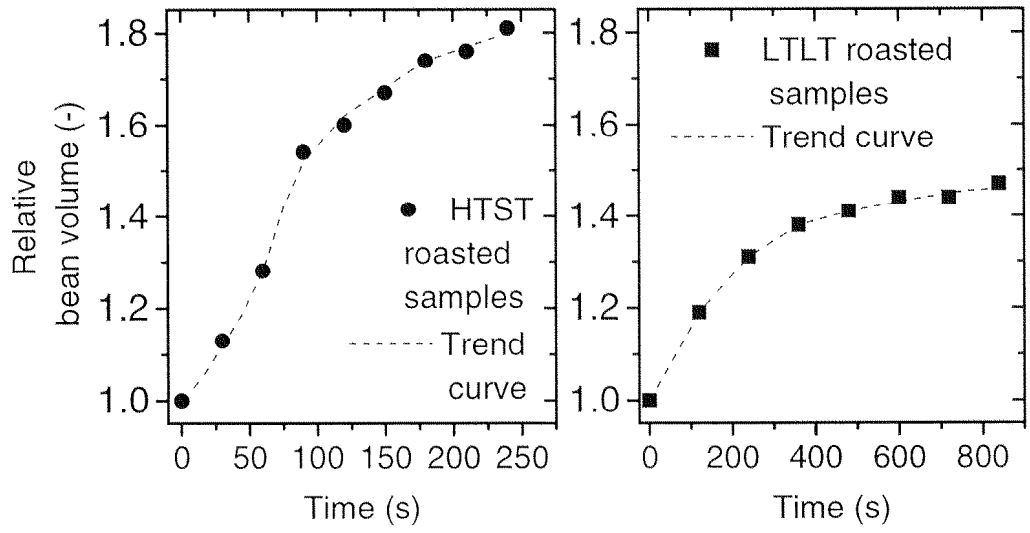

Fig. 29: *Development of bean volume increase during high (left) and low temperature (right) laboratory roasting (C. arabica, Costa Rica).*

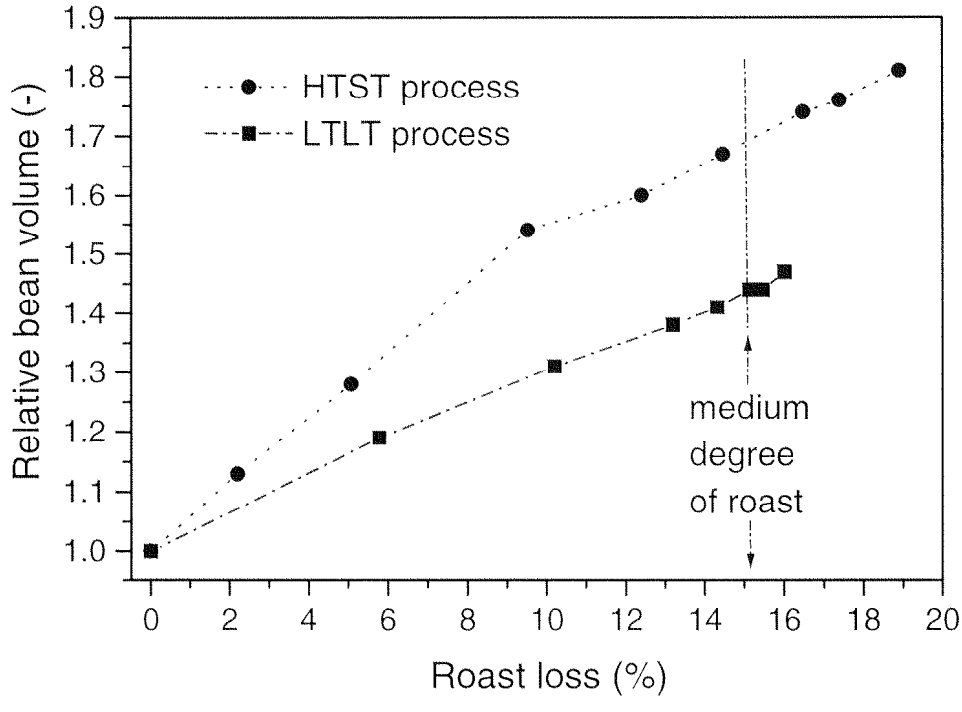

Fig. 30: *Characteristic development of bean volume increase as a function of the degree of roast (roast loss) during high and low temperature laboratory roasting (C. arabica, Costa Rica, identical with raw material in Figure 29).*

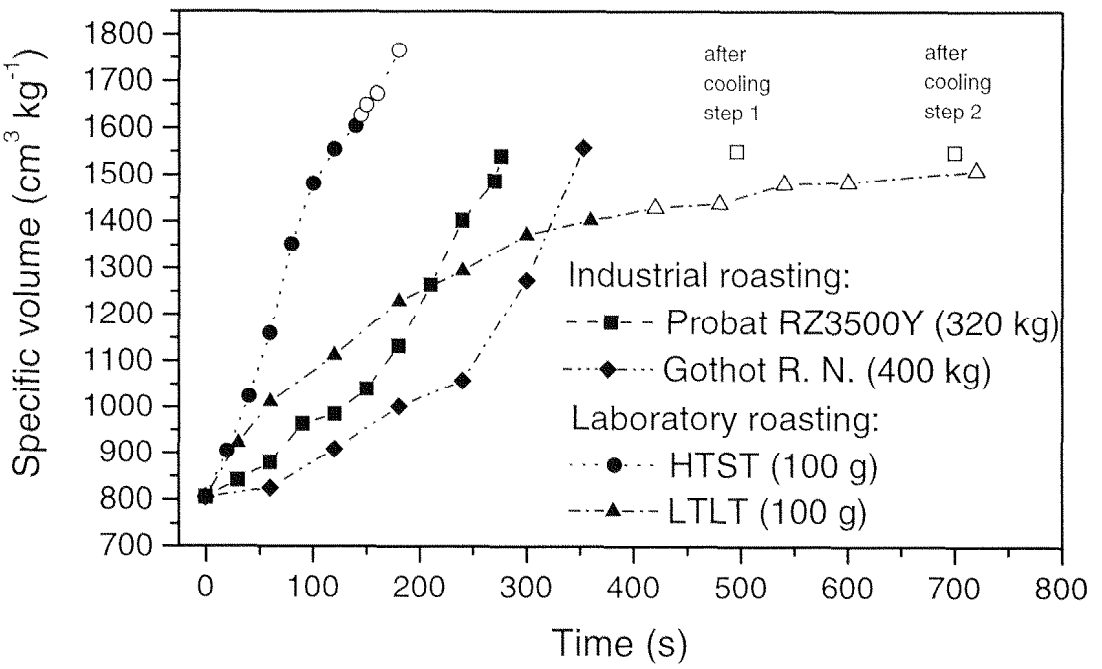

Fig. 31: *Increase of specific bean volume during laboratory and industrial scale roasting. Open symbols indicate samples of a higher degree of roast as compared to the industrial end products. An identical commercial blend of 100 % C. arabica beans was used for each trial.*

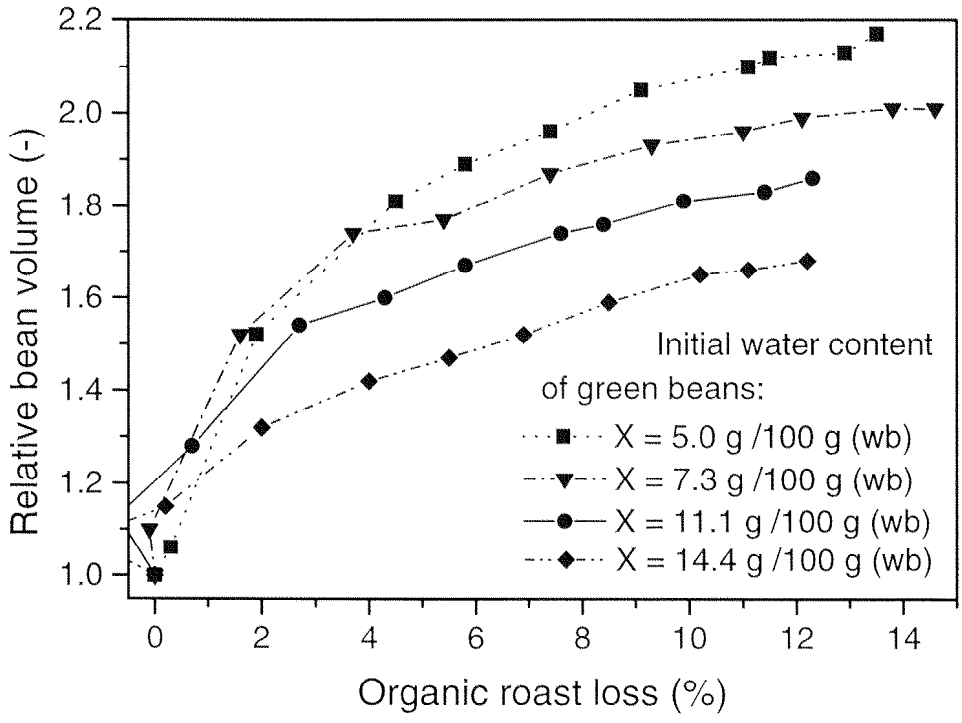

Fig. 32: *Influence of initial water content on bean expansion during HTST laboratory roasting. An organic roast loss of ORL = 7.0 corresponds to a medium degree of roast (C. arabica, Costa Rica).*

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.

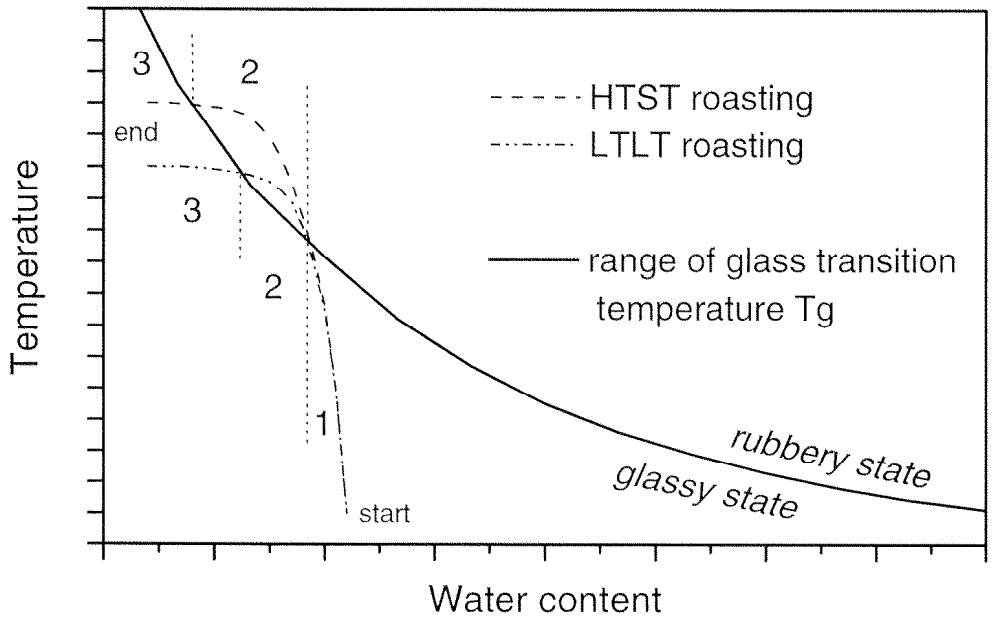

Fig. 33: *Hypothetical state diagram of coffee bean cell wall polysaccharides with T_g range (strictly qualitative assumption) and temperature-moisture development for HTST and LTLT roasting. 1: Heating stage, $T_{bean} < T_g$, glassy state of the bean. 2: $T_{bean} > T_g$, more rubbery state allowing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

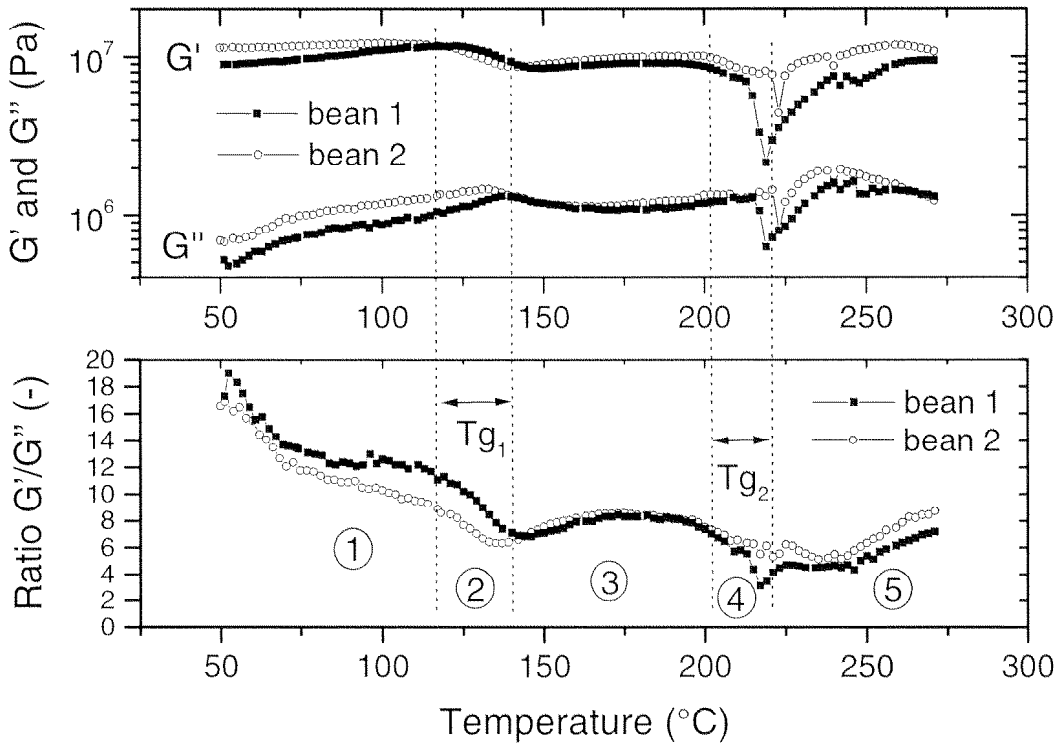

Fig. 34: *Dynamic mechanical thermal analysis (DMTA) of coffee bean slices clamped between a plate-plate measuring geometry. Dynamic testing (oscillation) with a heating rate of 5 °C min^{-1}. G': Storage modulus. G'': Loss modulus. The ratio G'/G'' is a suitable mean to monitor softening phenomena during 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.

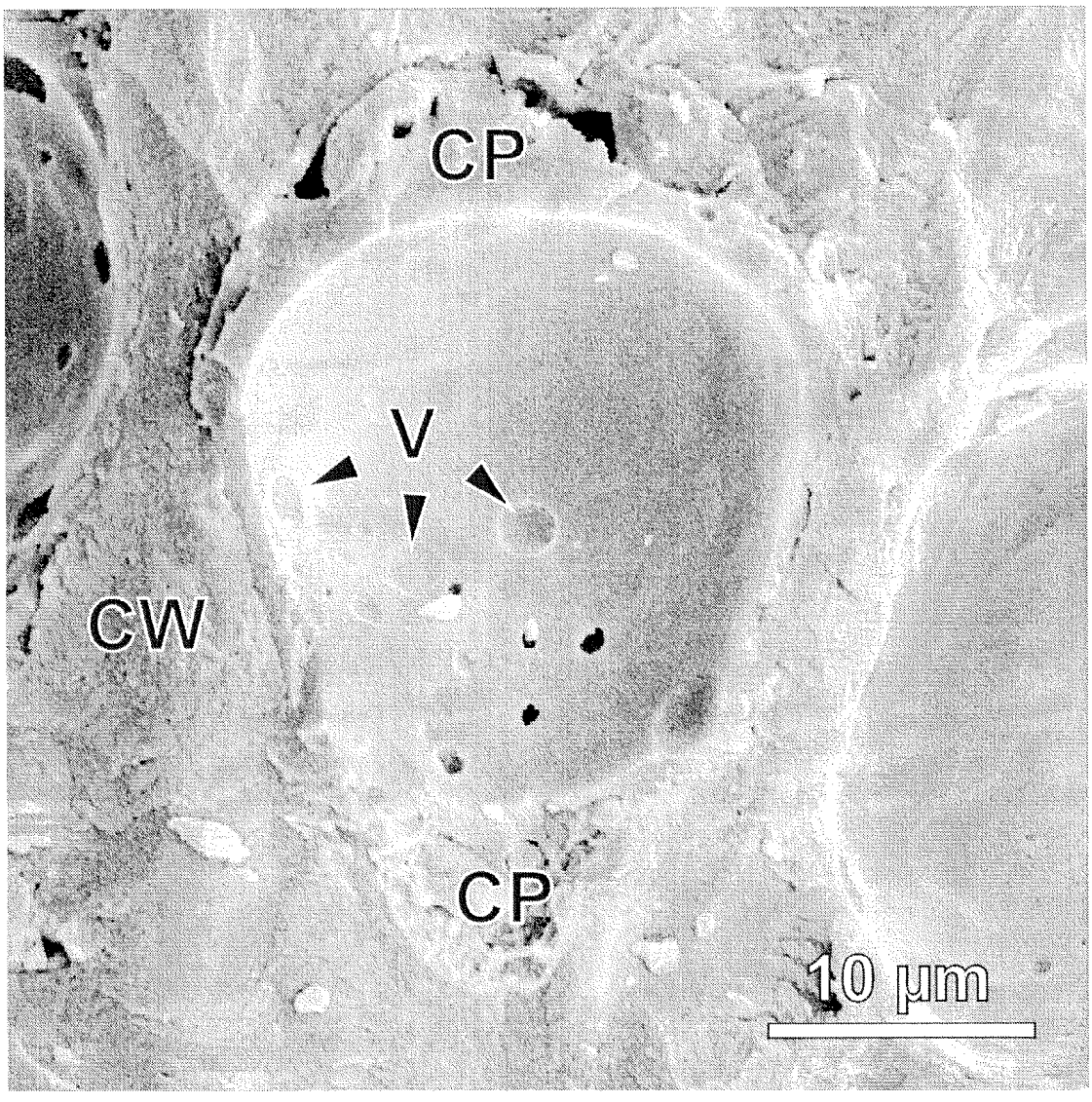

Fig. 35: *Cryo-SEM micrograph of a coffee cell in an early stage of roasting after 60 s of low temperature roasting (LTLT-process). The cytoplasm (CP) is already rearranged and forms a thick layer along the cell walls (CW). A large void occupies the cell centre. Smaller voids (V) of a burst-bubble structure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

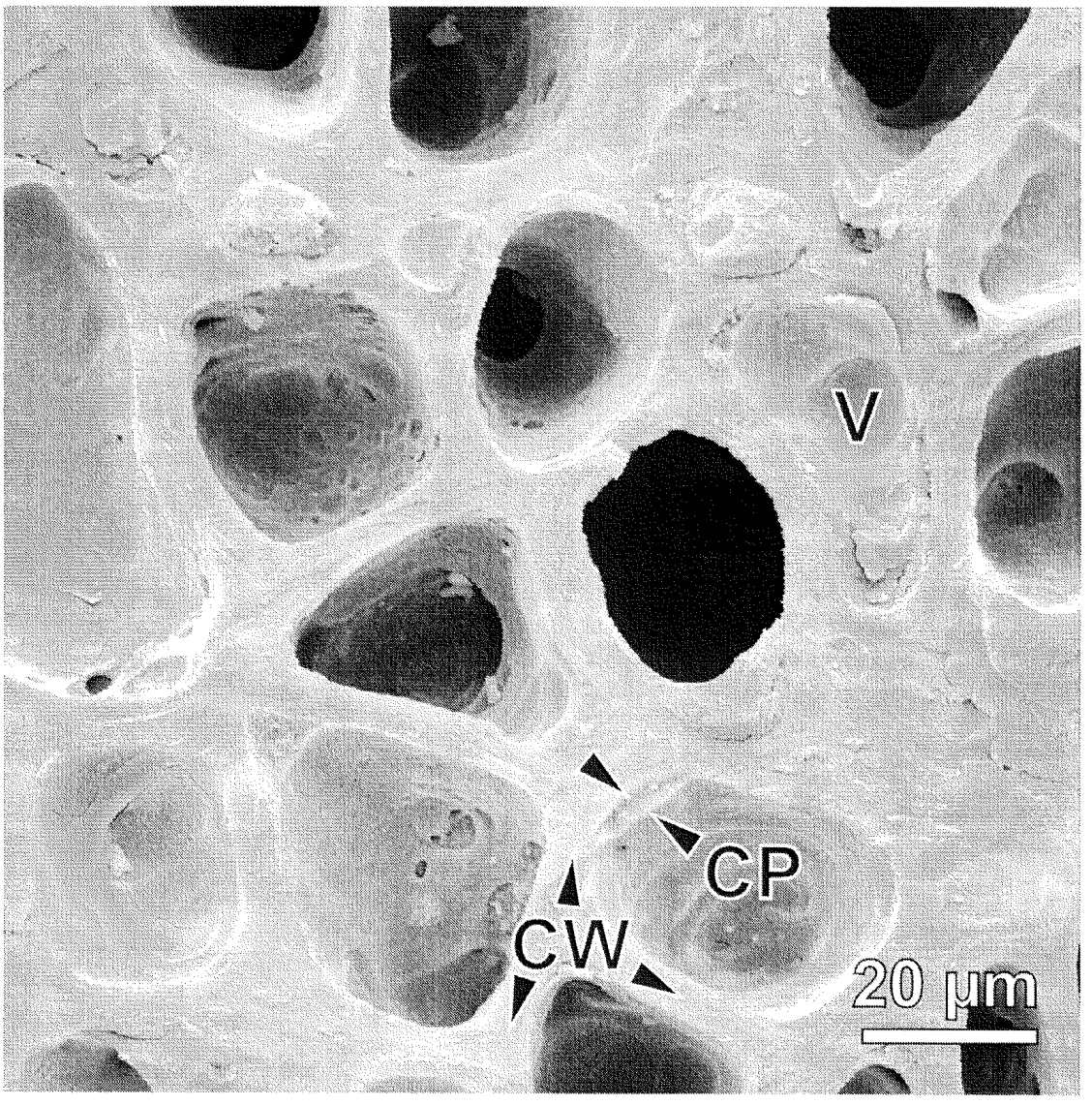

Fig. 36: *Cryo-SEM micrograph of the tissue structure of a coffee bean roasted for 180 s at 220 °C (LTLT). Each cell exhibits changes of the cytoplasm. Irregular layers of modified cytoplasm (CP) stretch along the cell walls (CW). A number of smaller voids (V), but of various sizes, are embedded within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

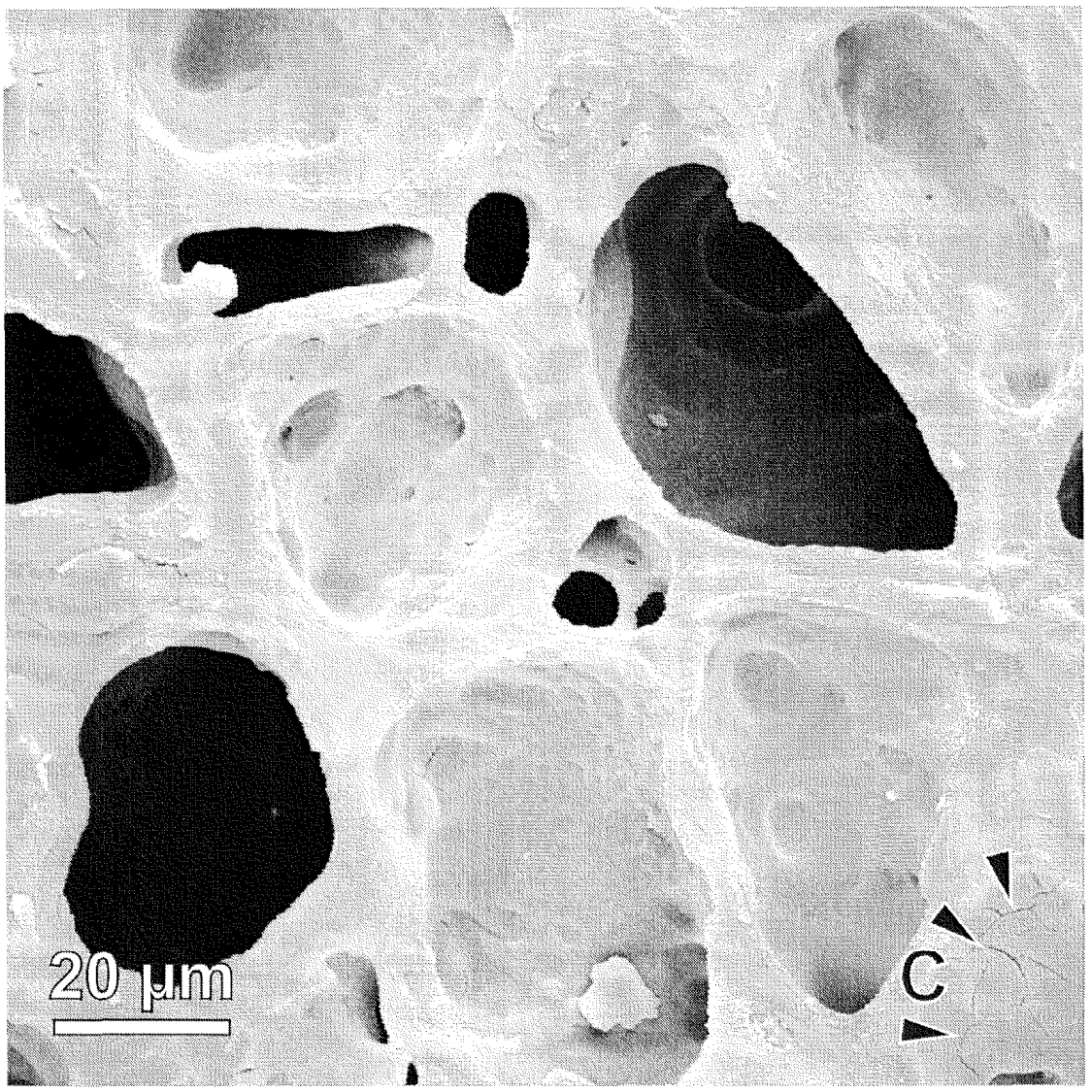

Fig. 37: *Cryo-SEM micrograph of the tissue structure of a LTLT roasted coffee bean after 360 s of roasting. With the proceeding of roasting the microstructural changes developed further. The layer of modified cytoplasm appears somewhat thinner and more irregular. Cracks (C) are preparation artefacts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

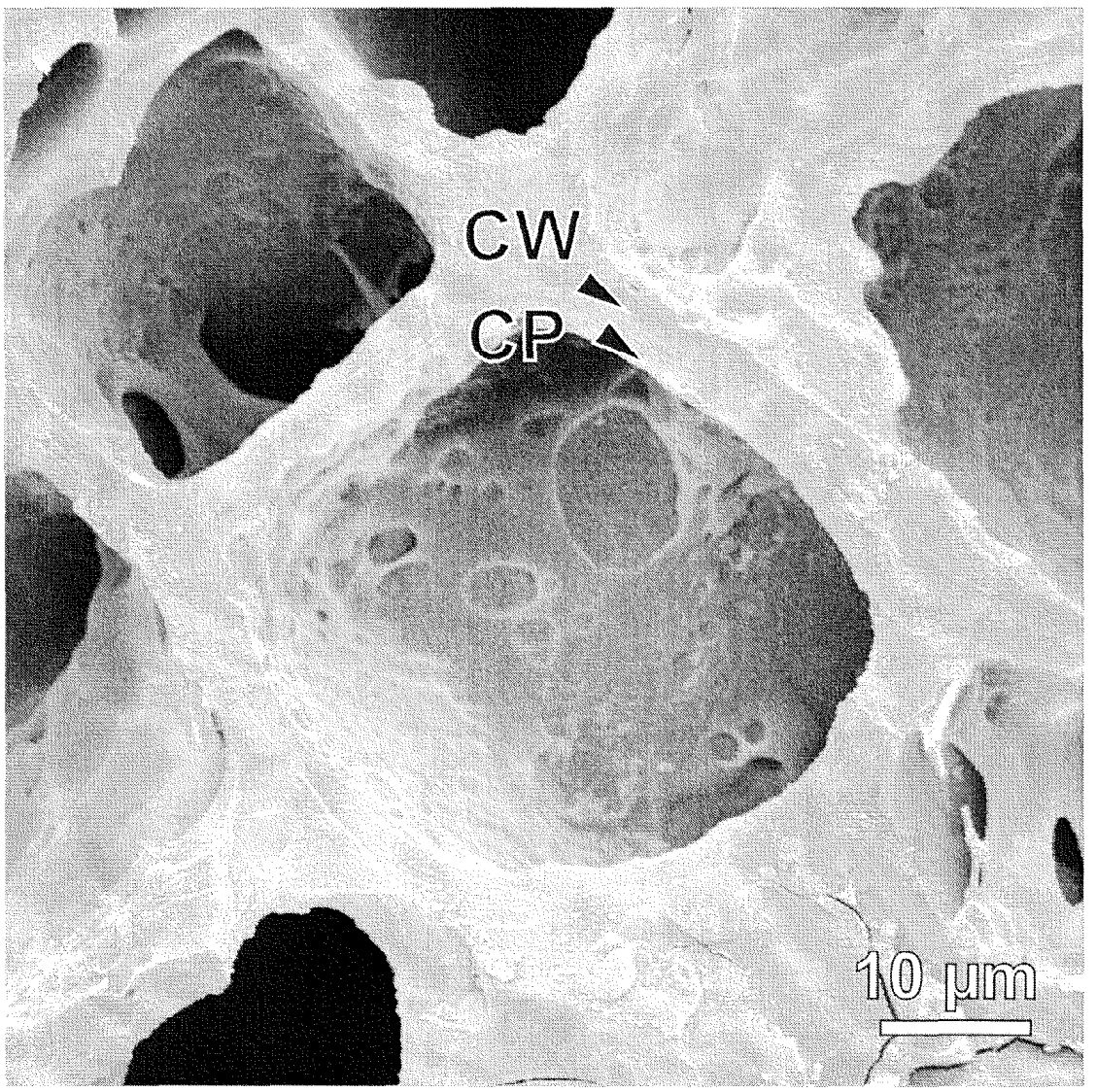

Fig. 38: *Cryo-SEM micrograph of a cell in a fully roasted coffee bean at a medium degree of roast (600 s, LTLT processed). The remaining layer of modified cytoplasm (CP) along the cell wall (CW) is only thin. It exhibits a marked burst-bubble structure with numerous embedded voids. (Image: B. Frey,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

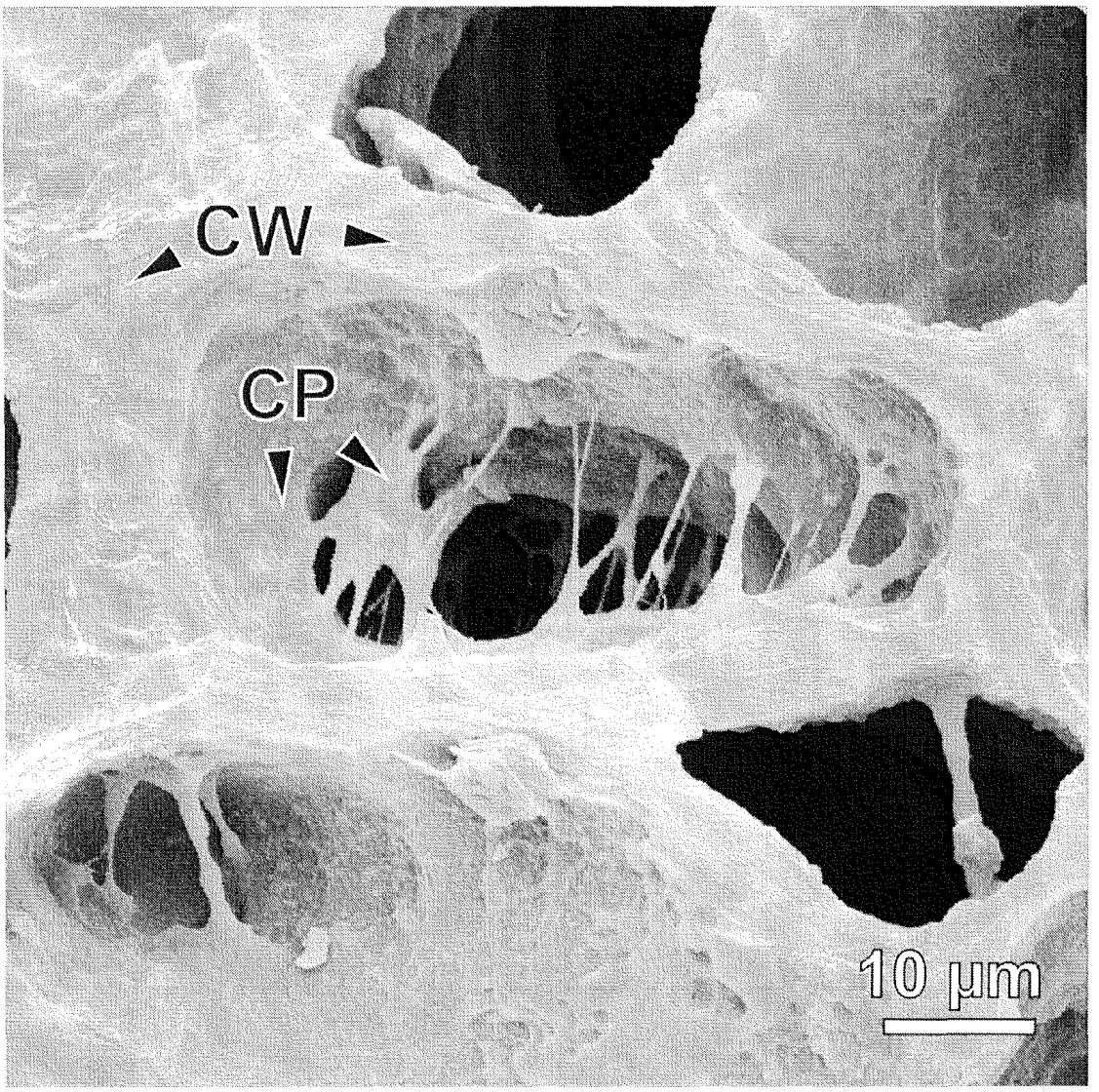

Fig. 39: *Cryo-SEM micrograph of a cell in a fully roasted coffee bean, LTLT roasted for 600 s. It was obtained from the same specimen as micrograph 38 and illustrates the large discrepancies of appearance between different neighboring cells from the same sample. Filament-like cytoplasmic structures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

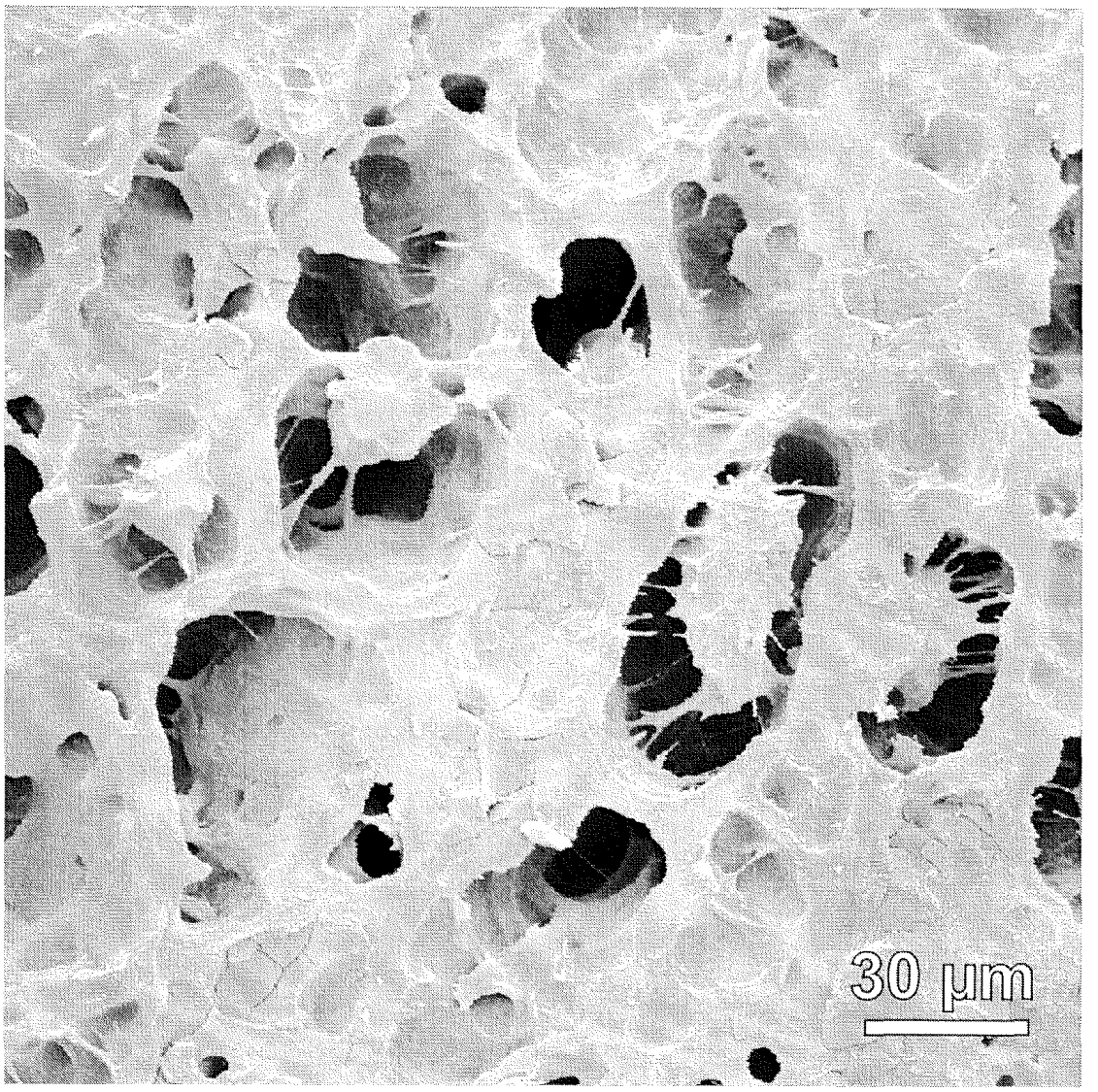

Fig. 40: *Cryo-SEM micrograph of the cell structure in a bean excessively roasted for 780 s (LTLT process). It shows a tissue region with cumulated occurrence of filament-like cytoplasmic structures. The presence of such regions was found to be more frequent and typical with higher degrees of roast.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

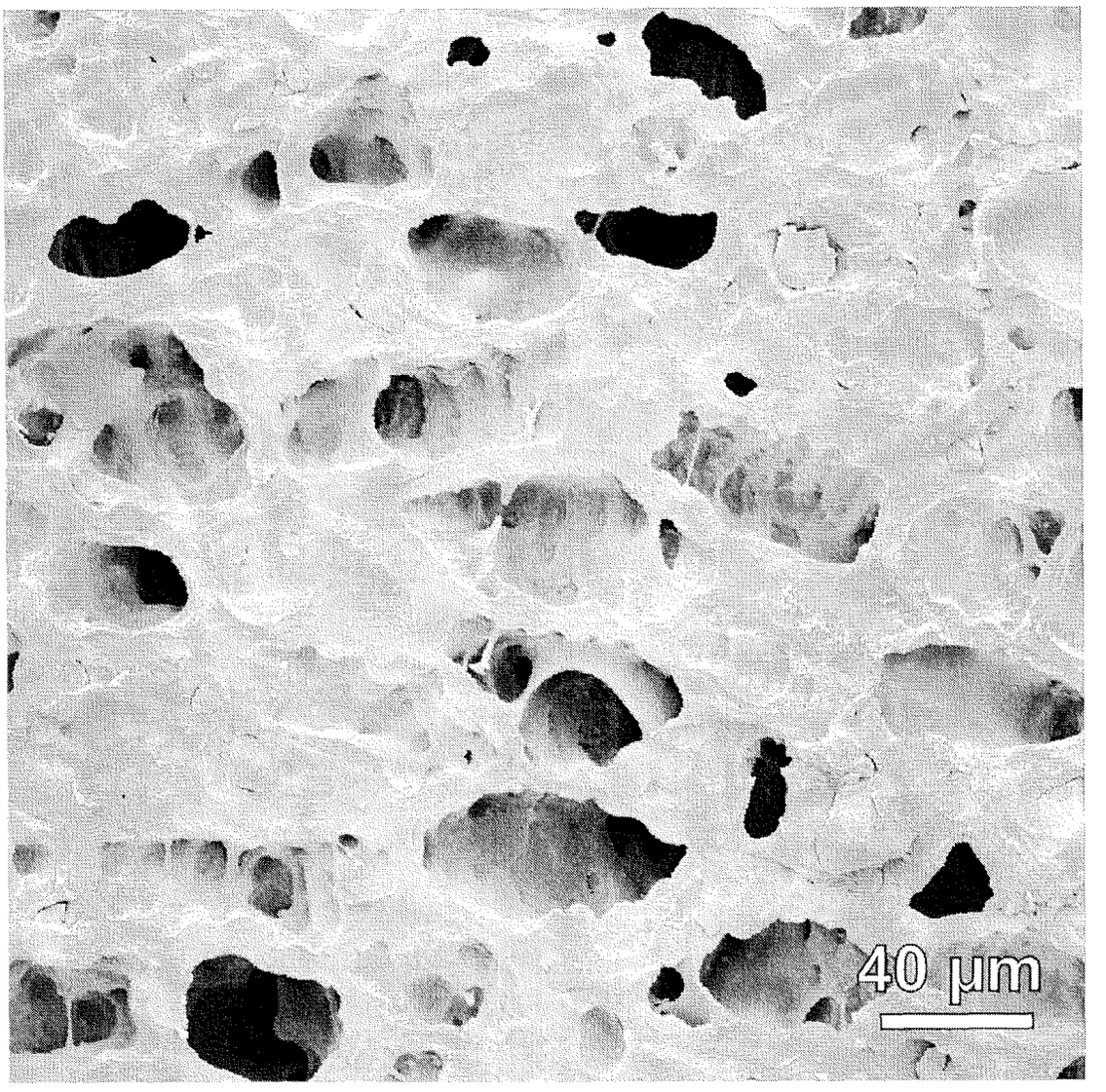

Fig. 41: *Cryo-SEM micrograph of the tissue structure in a high temperature roasted coffee bean (120 s, HTST process). In general, the structure is comparable to the one in LTLT roasted beans. Inhomogenities from cell to cell within the same bean were found to be much more pronounced than possible variations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

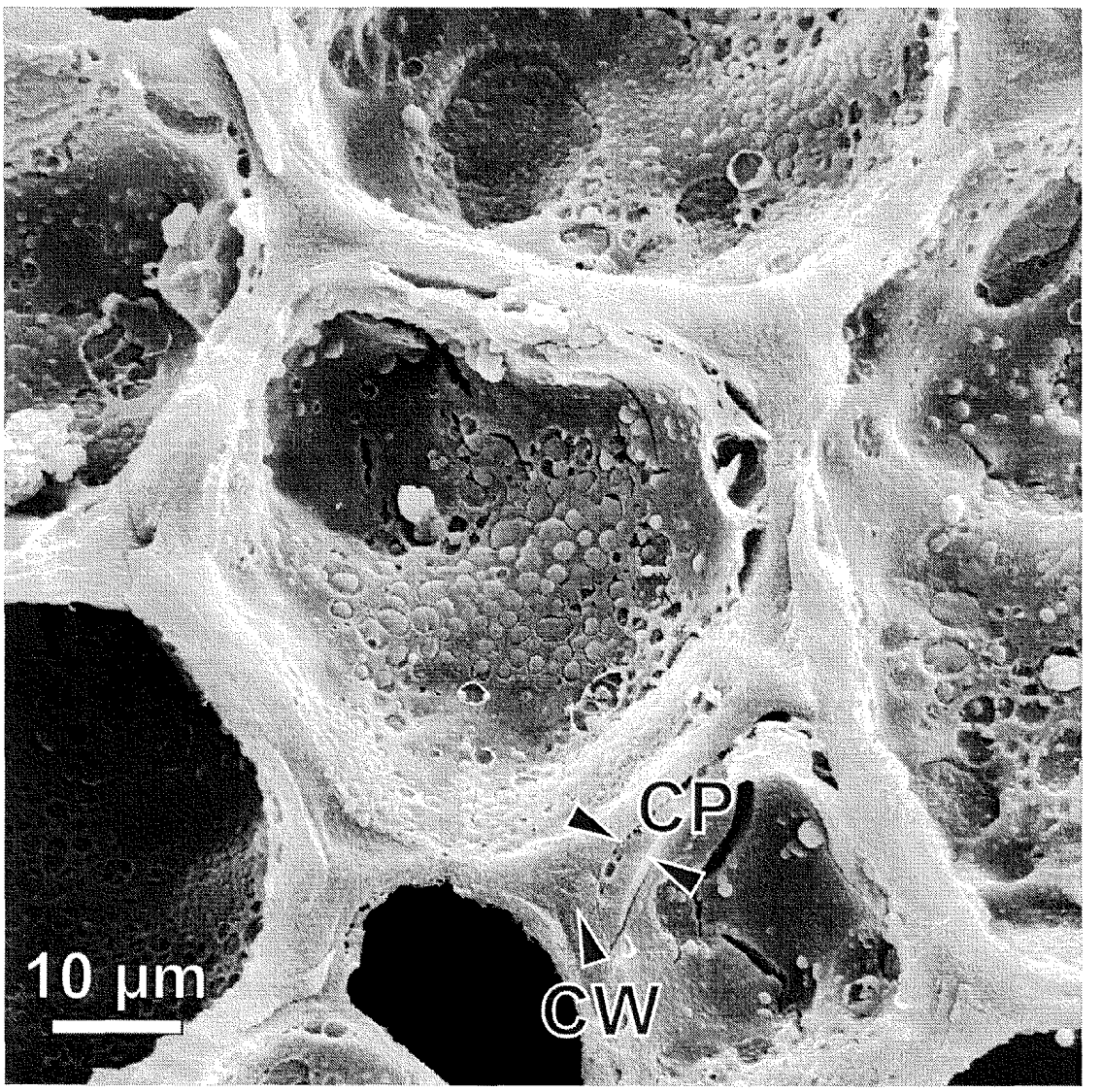

Fig. 42: *SEM micrograph of a chemically fixed specimen from an excessively roasted coffee bean (220 s, HTST process). Layers of modified cytoplasm (CP) spread along the cell wall (CW) framework. The applied preparation technique provides a different image of the layer structure, showing numerous embedded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

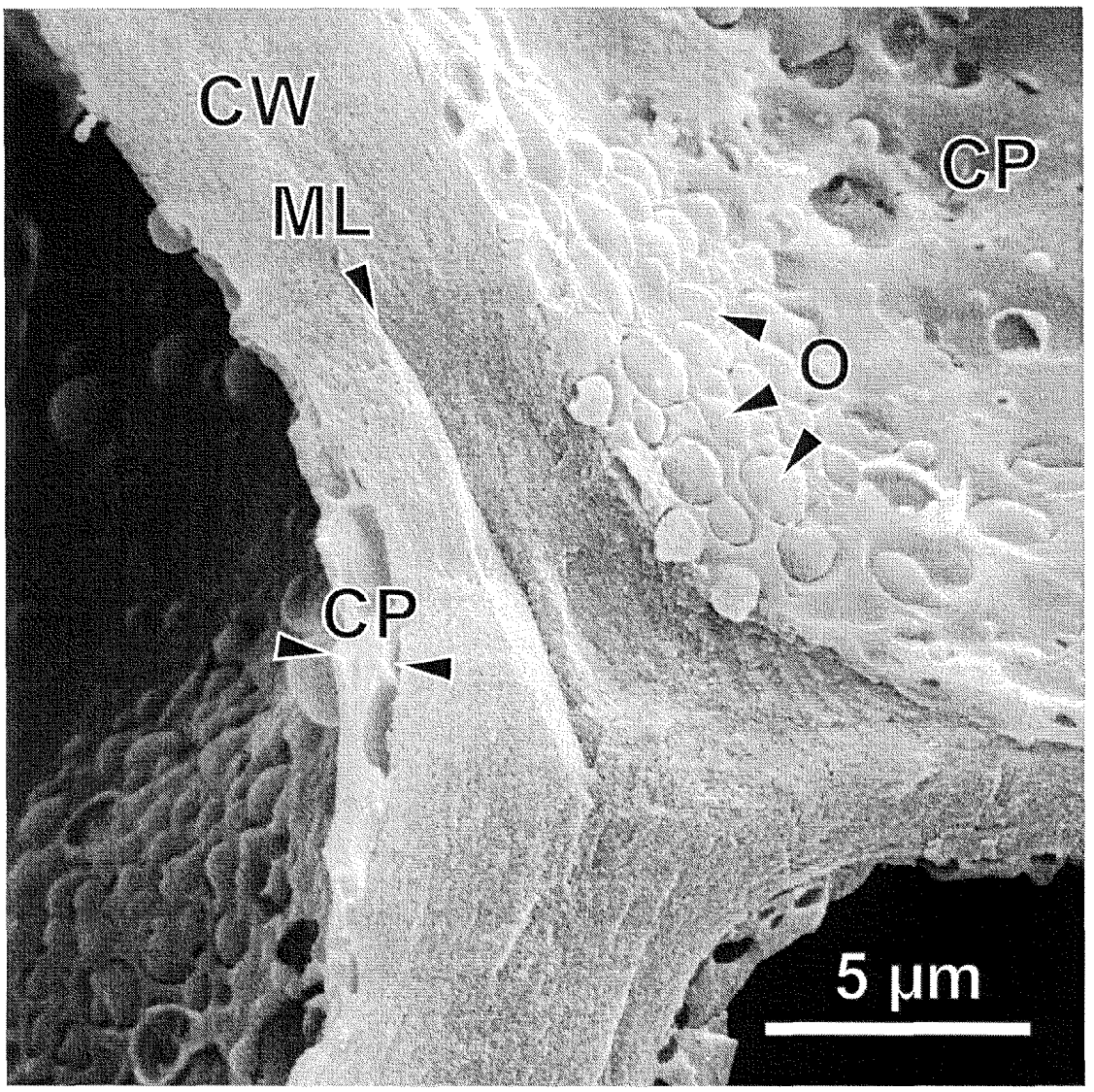

Fig. 43: *SEM micrograph of a chemically fixed specimen from an excessively roasted bean (identical specimen as in micrograph 42). It shows parts from 3 cells, separated by a cell wall (CW) junction. Different fraction behavior of the middle lamella (ML) caused a marked stair within the cell wall. Modified 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).*

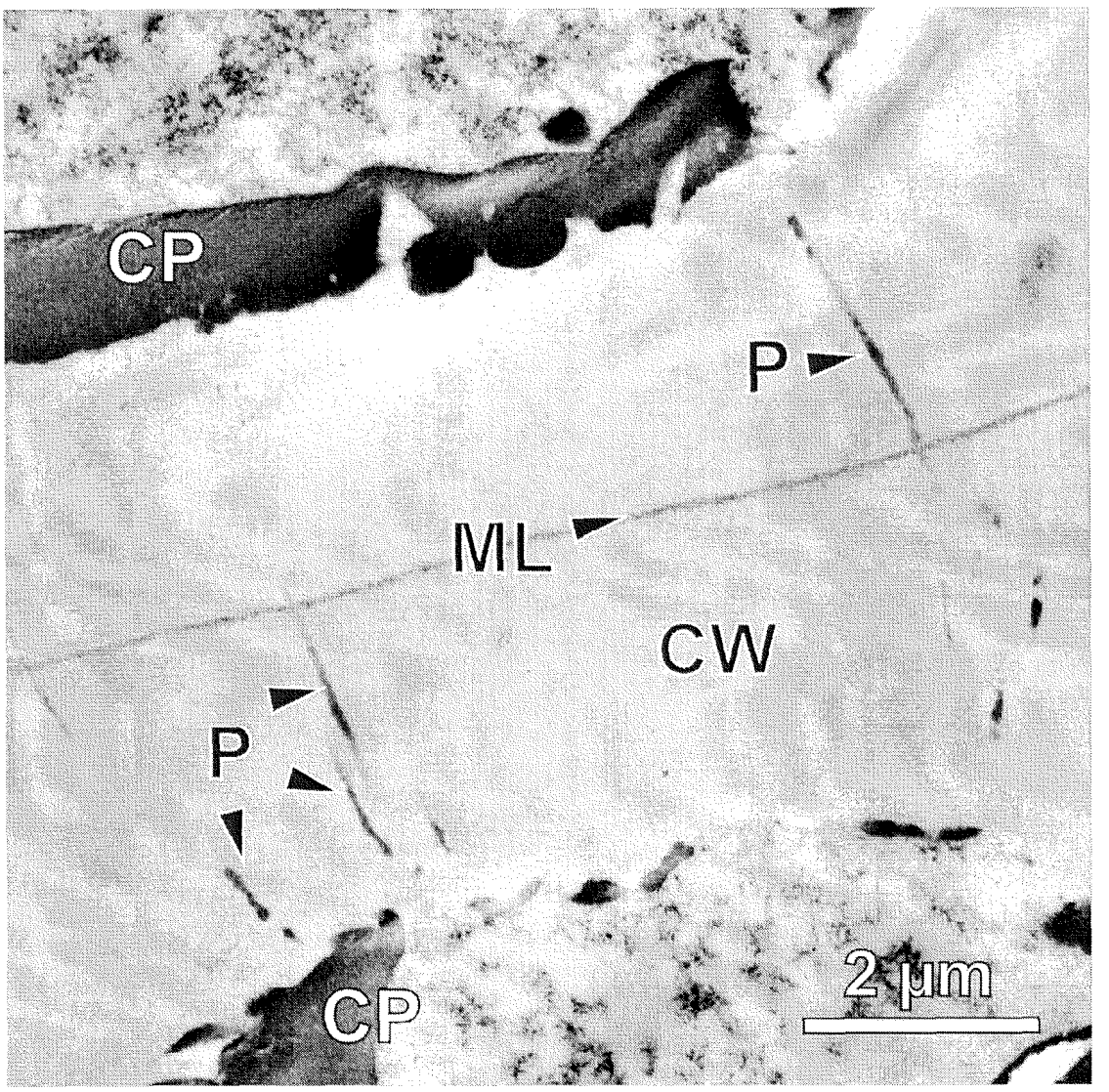

Fig. 44: *TEM micrograph of a cell wall in a partially roasted coffee bean (80 s, HTST process). The middle lamella (ML) forms a continuous black line and separates the cell walls (CW) and the layers of modified cytoplasm (CP) of the two adjacent cells. Parts of modified plasmodesmatae channels (P) are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

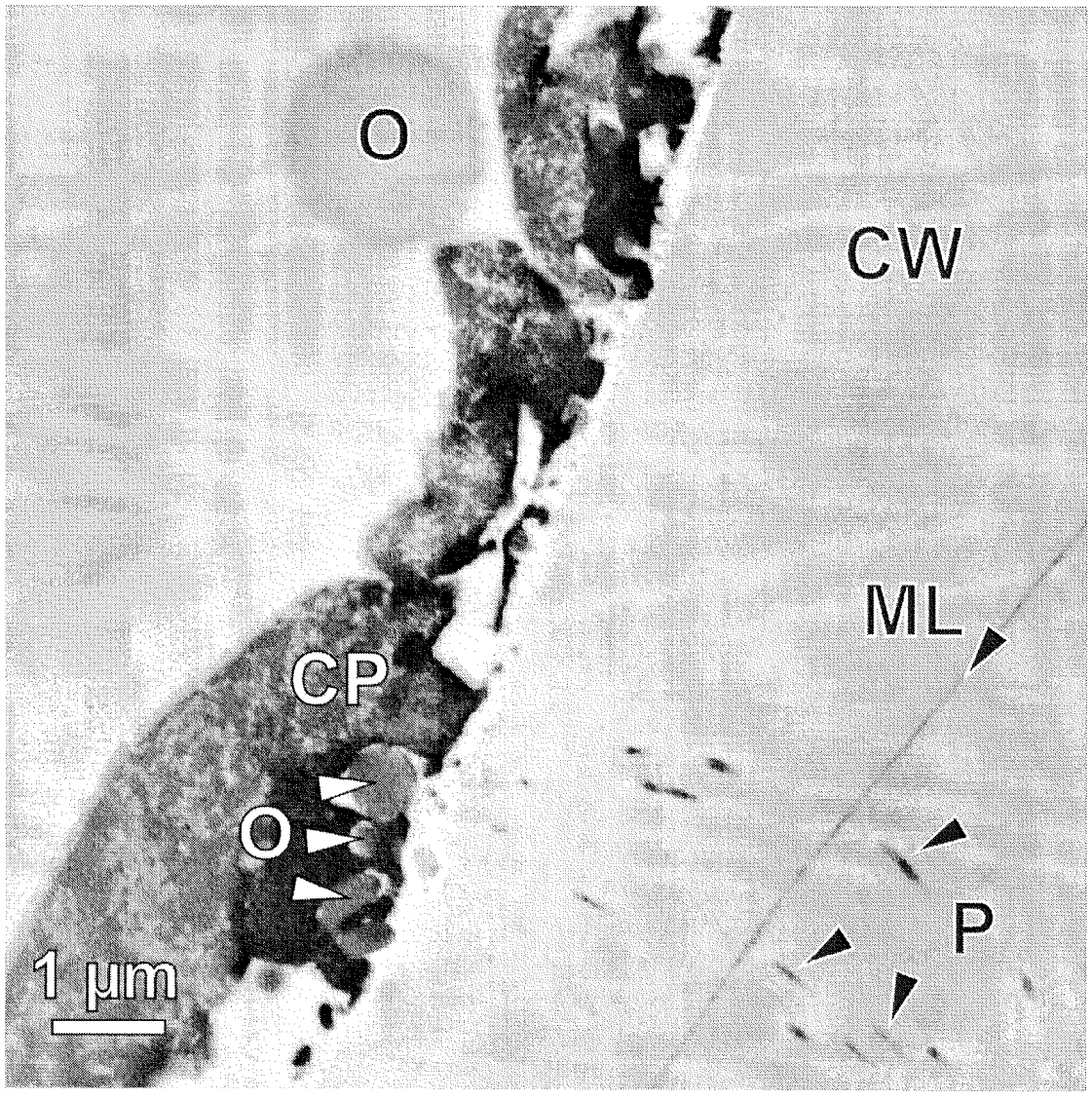

Fig. 45: *TEM micrograph of a cell wall in a partially roasted coffee bean (identical specimen as in micrograph 44). The middle lamella (ML) and parts of presumably modified plasmodesmatae channels (P) are clearly visible. Oil droplets (O) of various sizes lie embedded in the layer of modified cytoplasm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

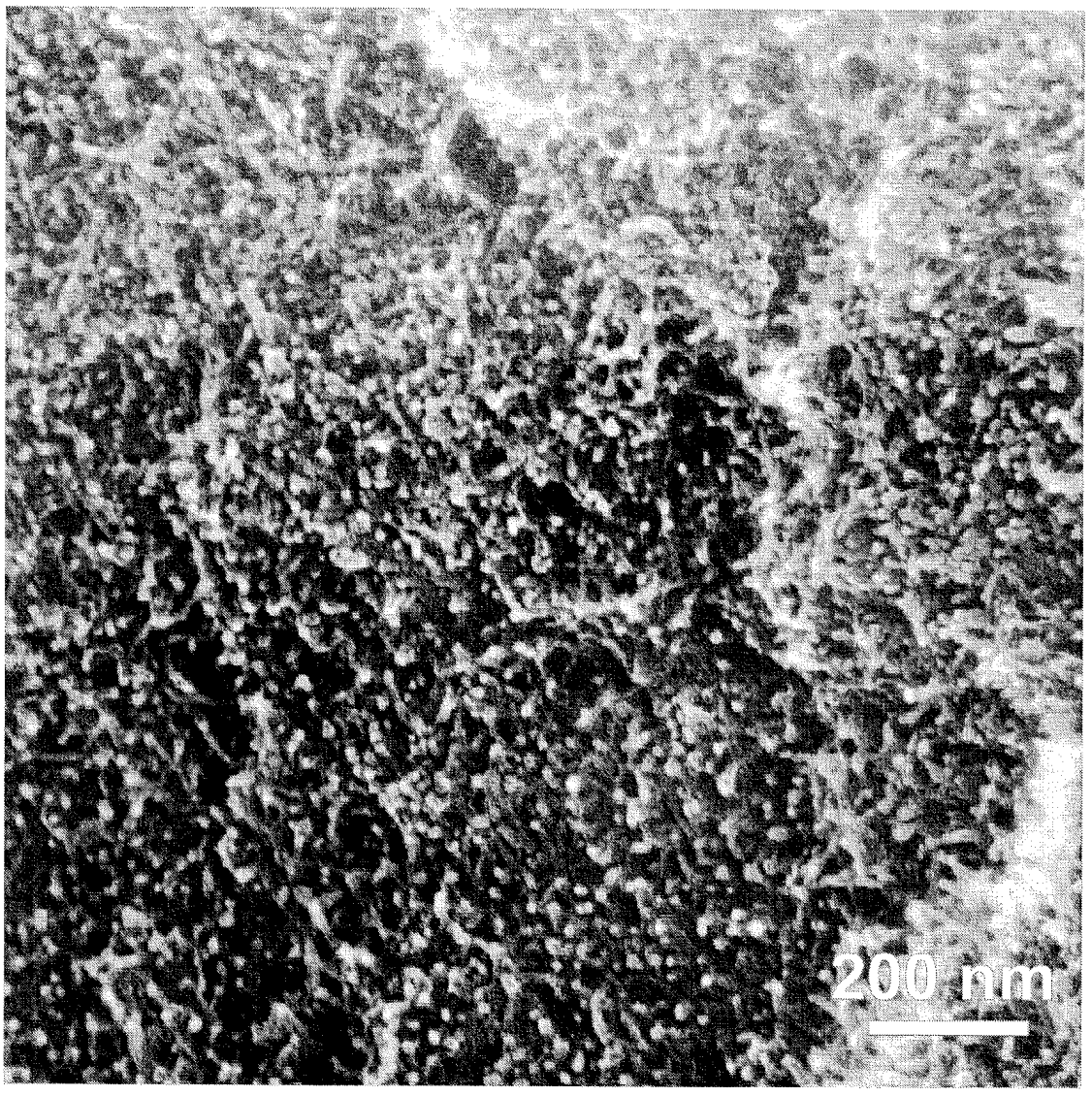

Fig. 46: *SEM micrograph of a cell wall cross section of a chemically fixed, de-oiled and fractured specimen from a fully roasted coffee bean. The structure of the fraction surface suggests fundamental changes in the microfibril network of roasted cell walls as compared to the green bean. (Image: S.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

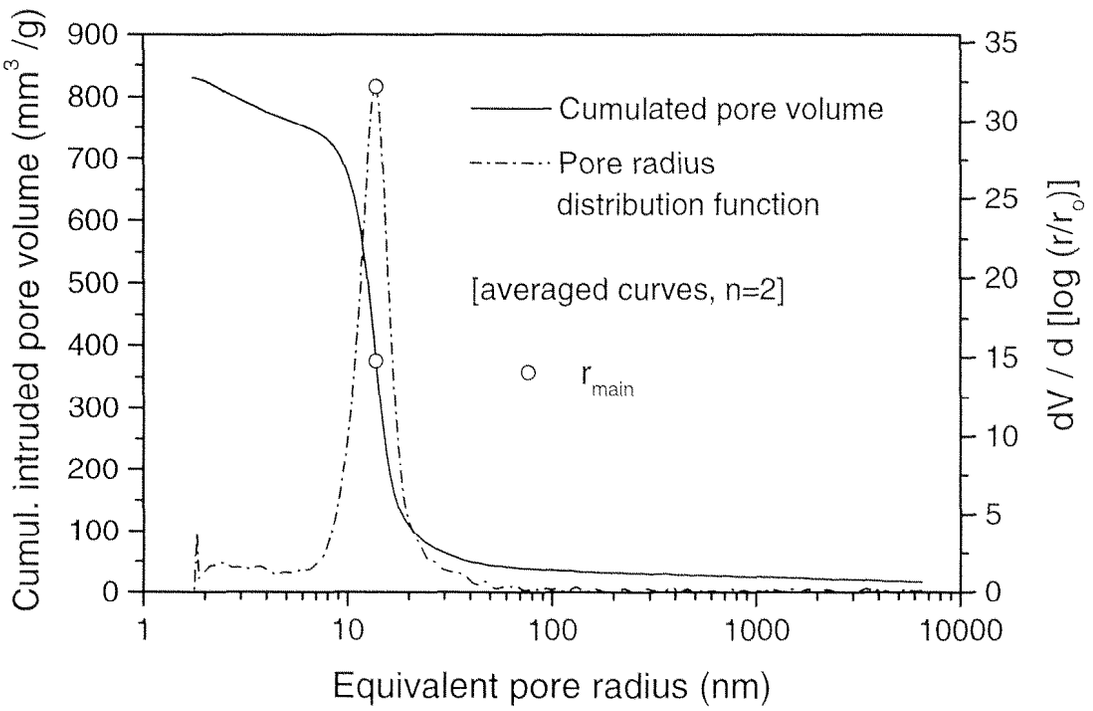

Fig. 47: *Typical porosimetric data obtained from roasted coffee beans (HTST processed sample, 160 s).*

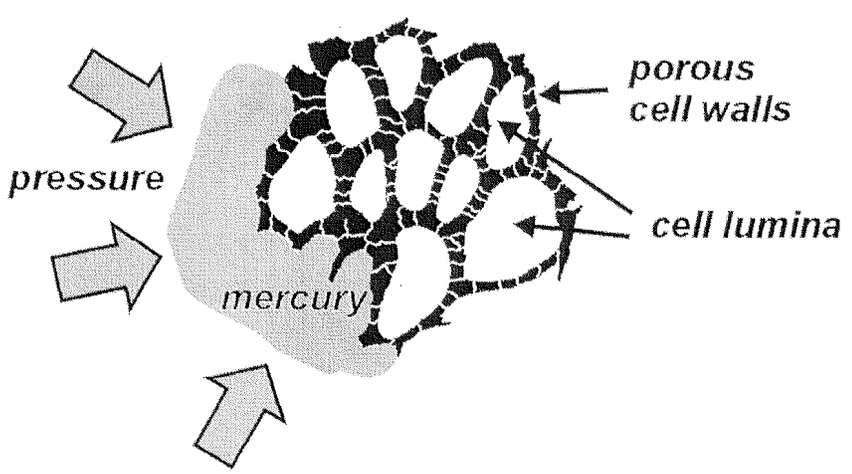

Fig. 48: *Model coffee bean pore system surrounded by pressurized liquid mercury during porosimetric analysis. Access to the cell lumina is provided by small micropores in the cell walls. Only a high pressure corresponding to the small size of these entrance pores will allow for mercury penetration of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

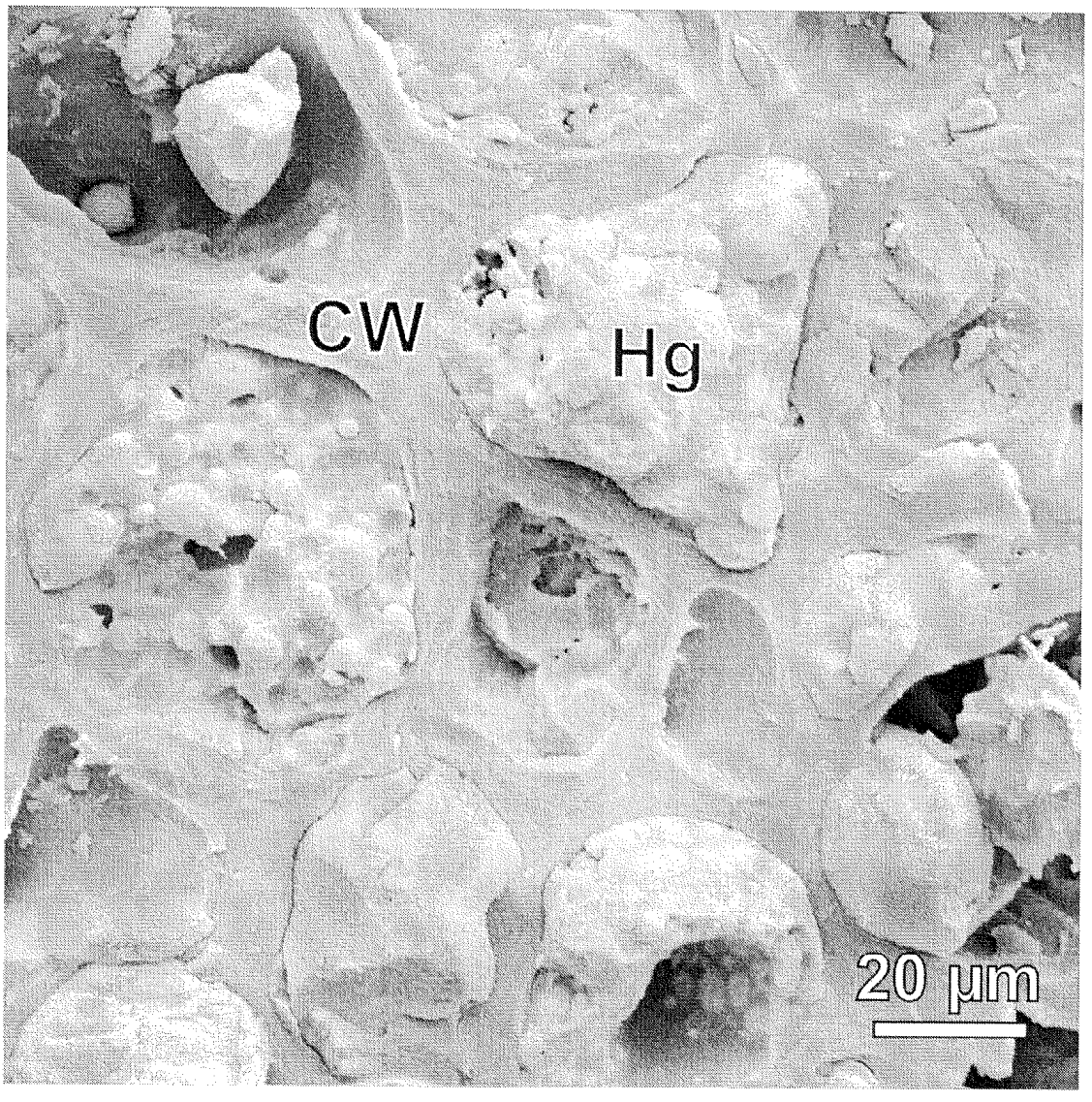

Fig. 49: *Cryo-SEM micrograph of cells in a roasted bean intruded with mercury during porosimetric analysis. The tissue shows an intact cell wall (CW) structure with mercury-filled cell lumina. Mercury (Hg) must have penetrated a cell wall micropore system before intruding the cell lumina. It was then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

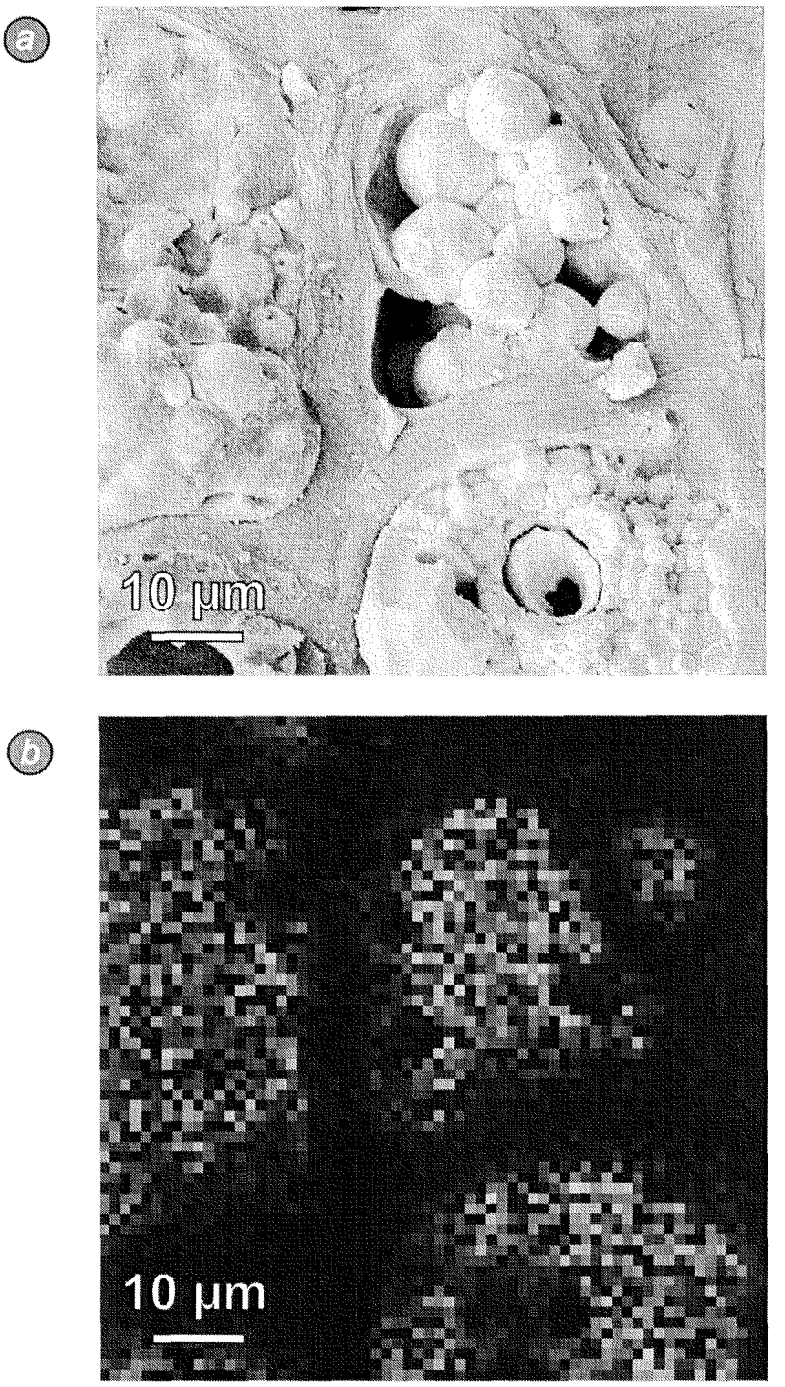

Fig. 50: *Cells of a roasted coffee bean intruded with mercury during porosimetric analysis. 50a: Cryo-SEM micrograph of 3 adjacent cells with integer cell walls. 50b: Mercury mapping obtained by X-ray microanalysis from the same location as in 50a. Bright spots are generated by great mercury net counts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

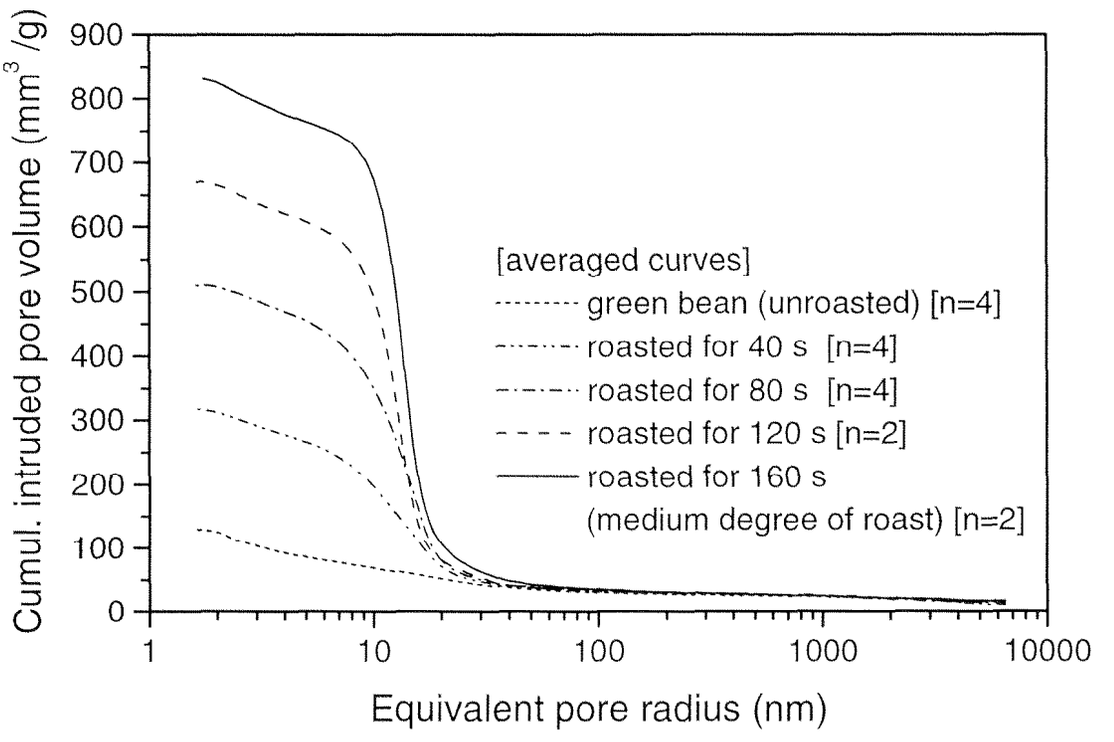

Fig. 51: *Influence of HTST roasting on porosimetric curves of coffee beans with increasing degrees of roast.*

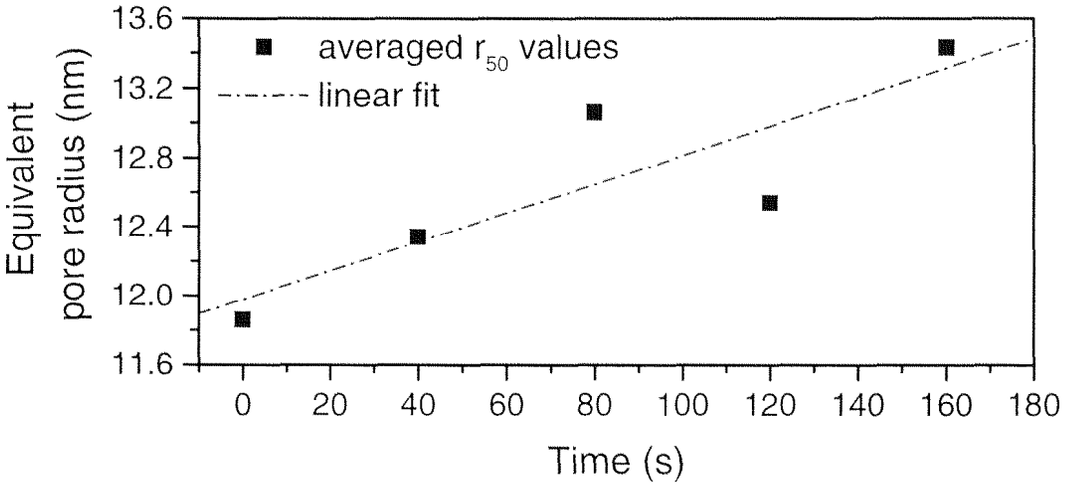

Fig. 52: *Relationship between degree of roast (roasting time) and the averaged pore size at which 50 % of total pore volume is mercury penetrated (r_{50}).*

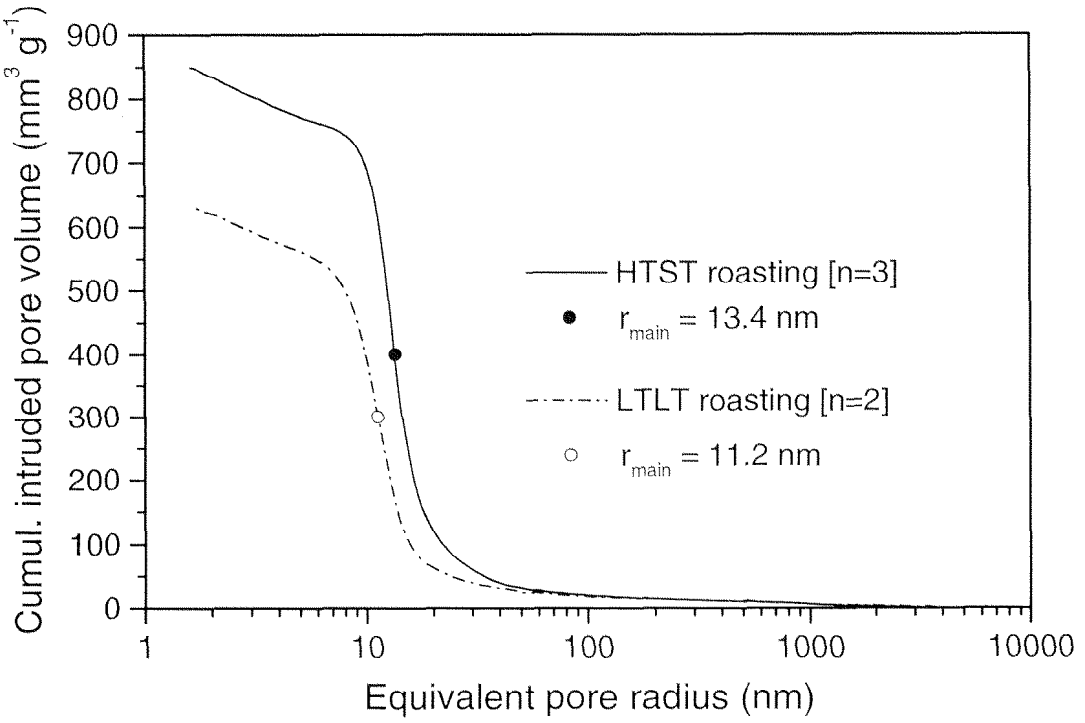

Fig. 53: *Influence of HTST and LTLT roasting on porosimetric curves of beans with identical degree of roast and on r_{main}.*

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.

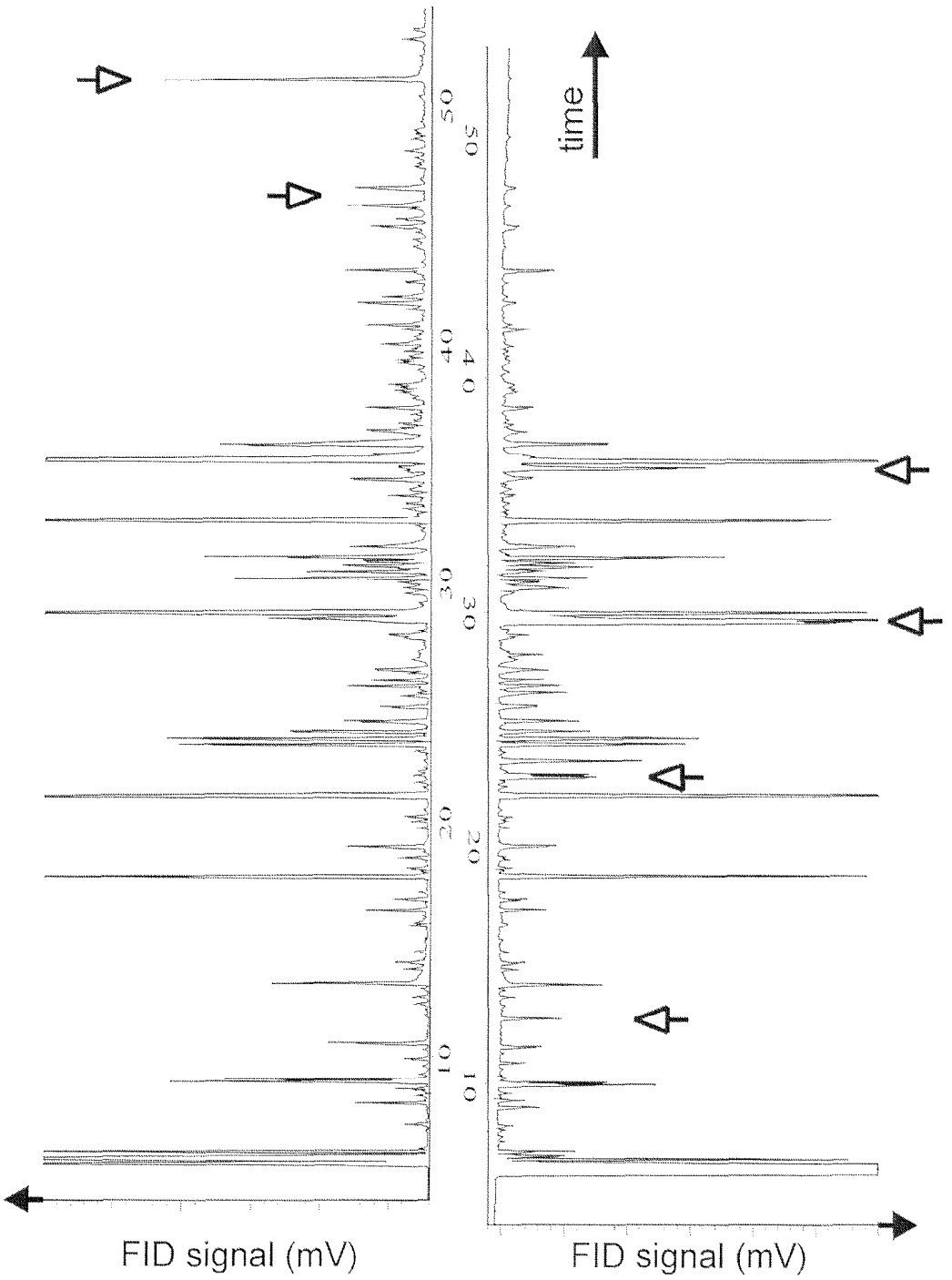

Fig. 54: *GC-FID chromatograms from aroma isolates of LTLT roasted coffee beans. Isolates were obtained by simultaneous distillation/extraction according to Likens and Nickerson, 1964 (left) and by vacuum distillation (right). Open arrows point to examples of inconsistencies between the two chromatograms.*

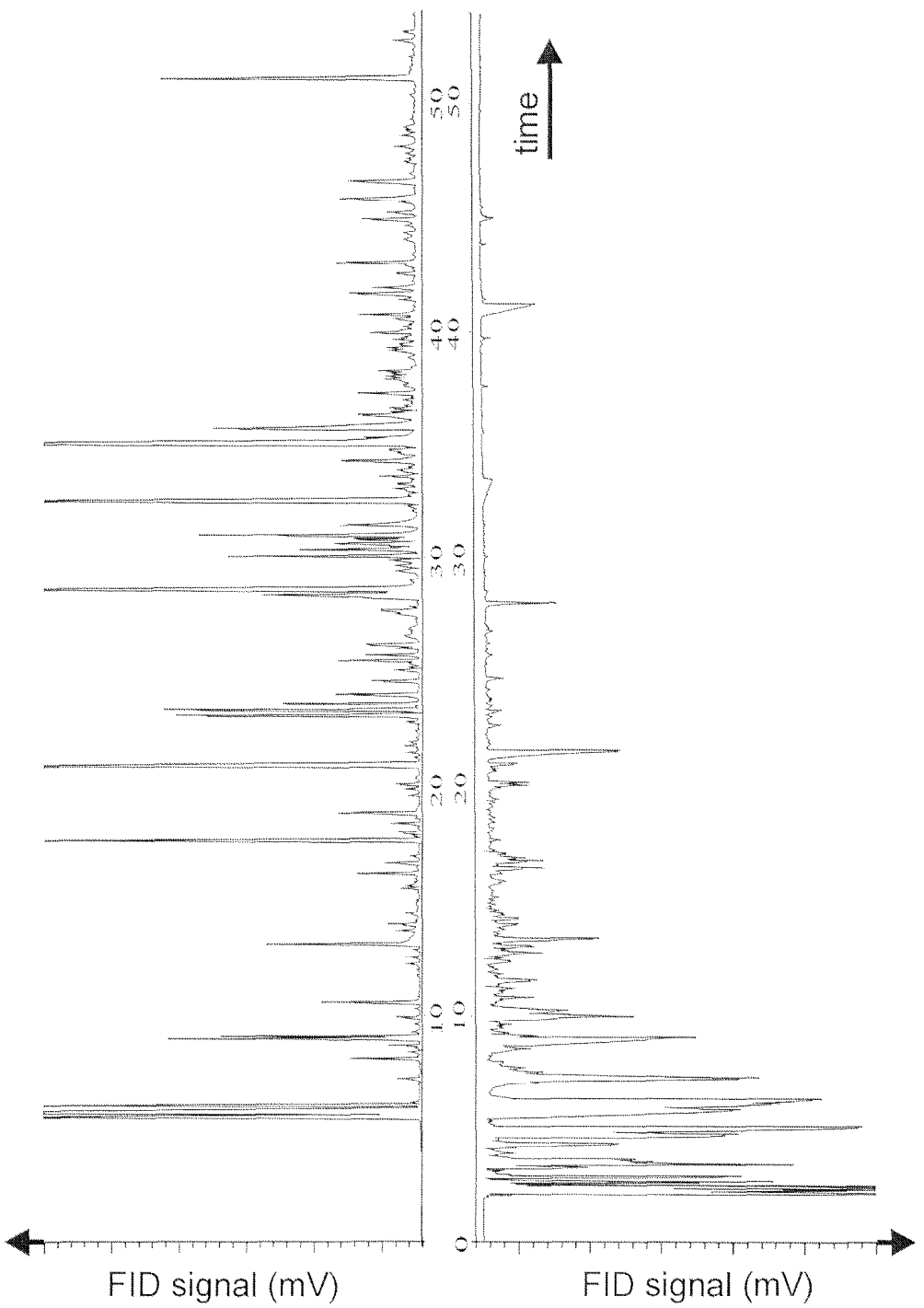

Fig. 55: *GC-FID chromatograms of a SDE aroma isolate from roasted coffee beans. Chromatographic separation of compounds was performed using a 60 m polar capillary column Supelcowax 10 (left) and a 30 m unpolar capillary column DB 5 (right).*

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.

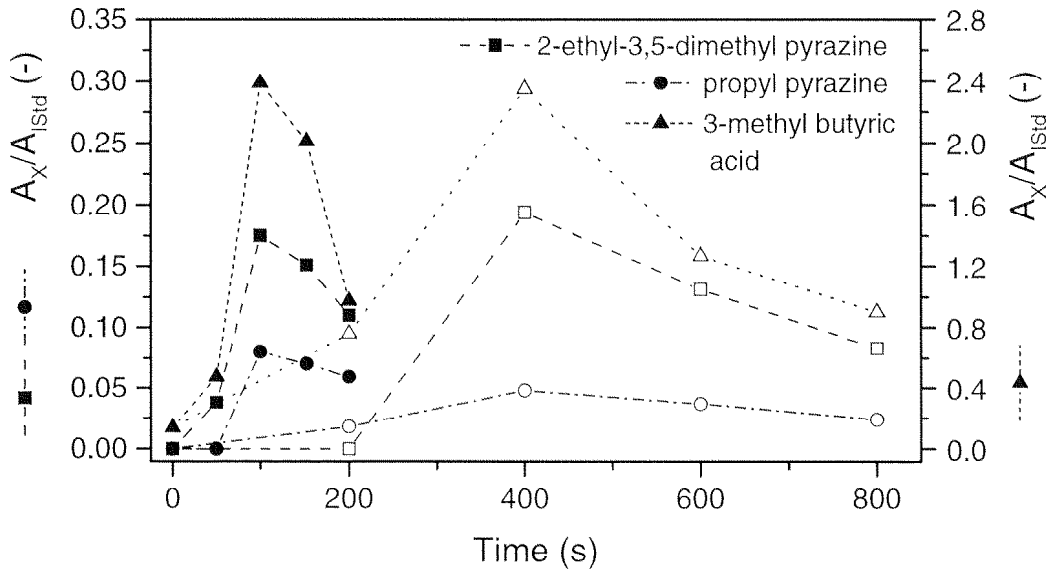

Fig. 56: *Quantitative development of three selected aroma impact compounds during HTST (solid symbols) and LTLT (open symbols) laboratory roasting. Sampling took place at 1/3, 2/3, 3/3 and 4/3 of the normal roasting time to achieve a medium degree of roast.*

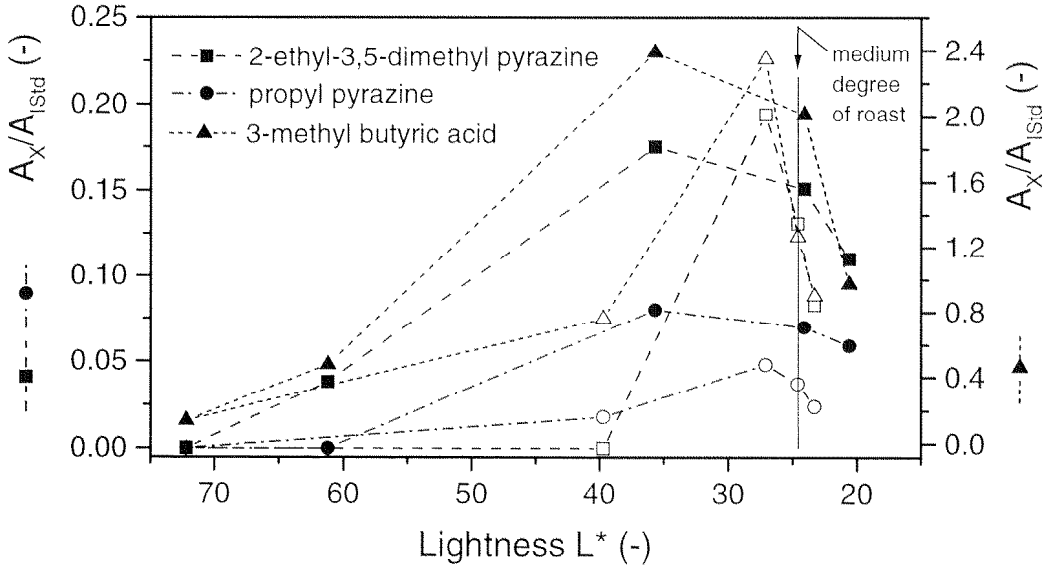

Fig. 57: *Quantitative development of three selected aroma impact compounds in relation to the degree of roast (color). Solid symbols: HTST roasting, open symbols: LTLT roasting. Medium degree of roast is marked by a perpendicular line.*

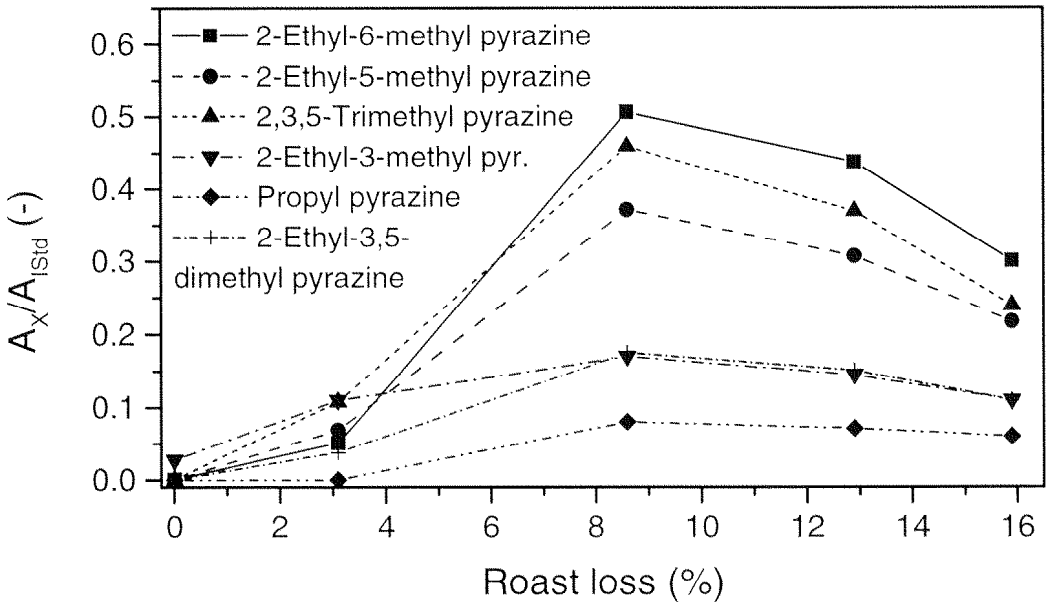

Fig. 58: *Quantitative development of pyrazines during high temperature laboratory roasting related to roast loss. A roast loss of 13 % corresponds to a medium degree of roast.*

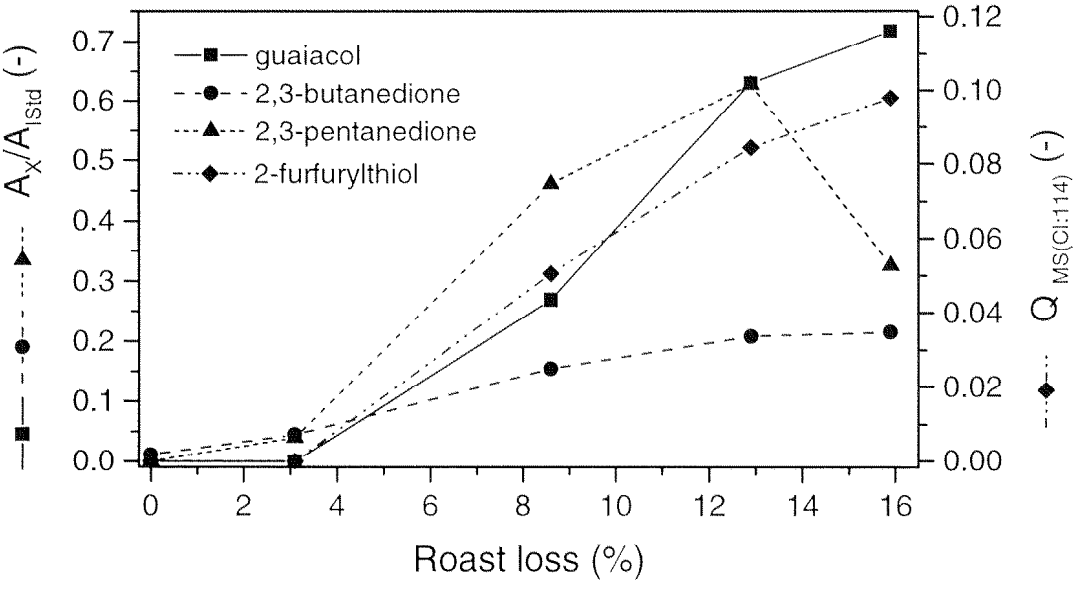

Fig. 59: *Development of relative quantities of various important aroma compounds during HTST laboratory roasting. A roast loss of 13 % corresponds to a medium degree of roast.*

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)

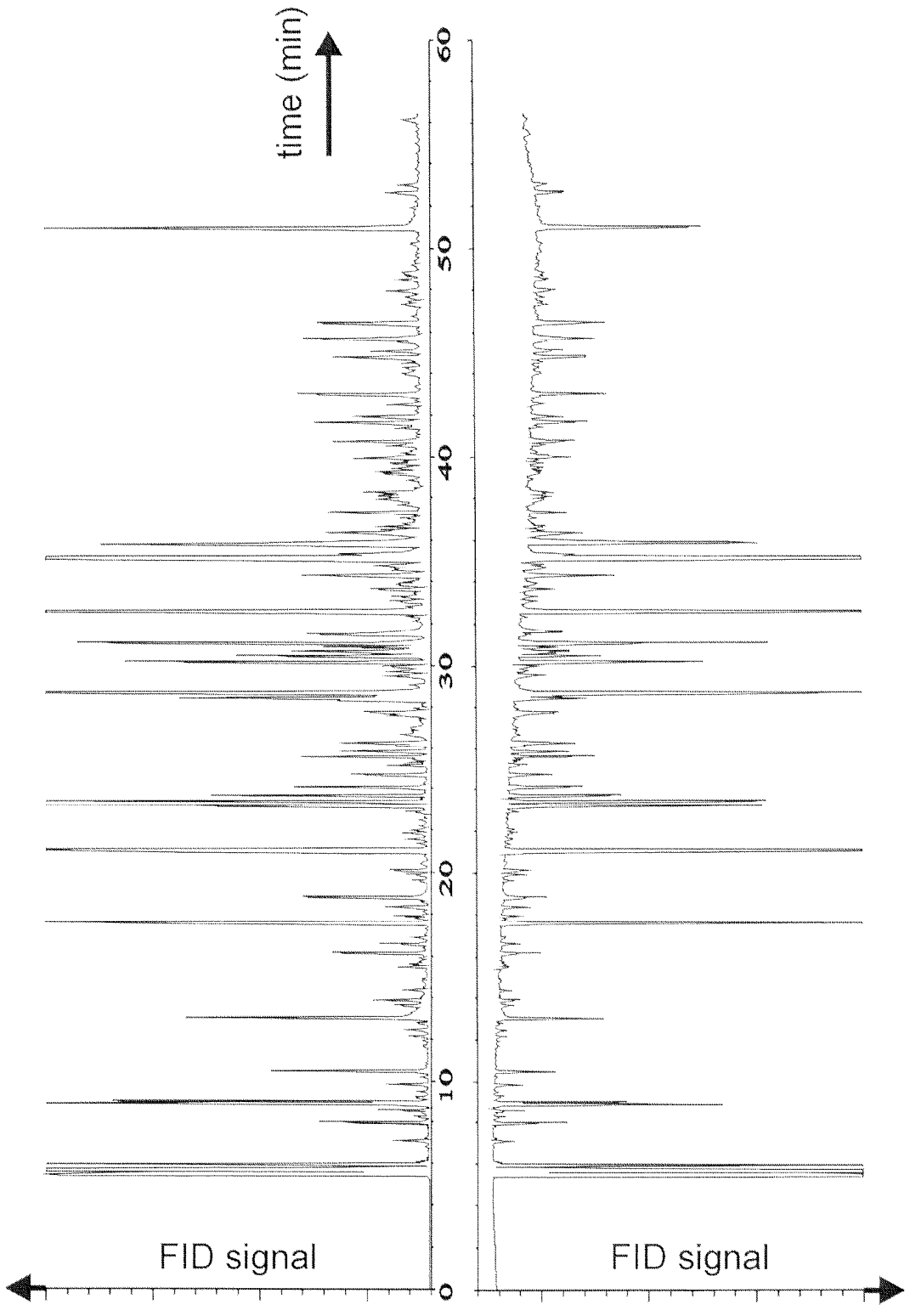

Fig. 60: *GC-FID chromatograms of SDE aroma isolates from HTST roasted (left) and LTLT roasted (right) coffee samples of identical degree of roast.*

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.

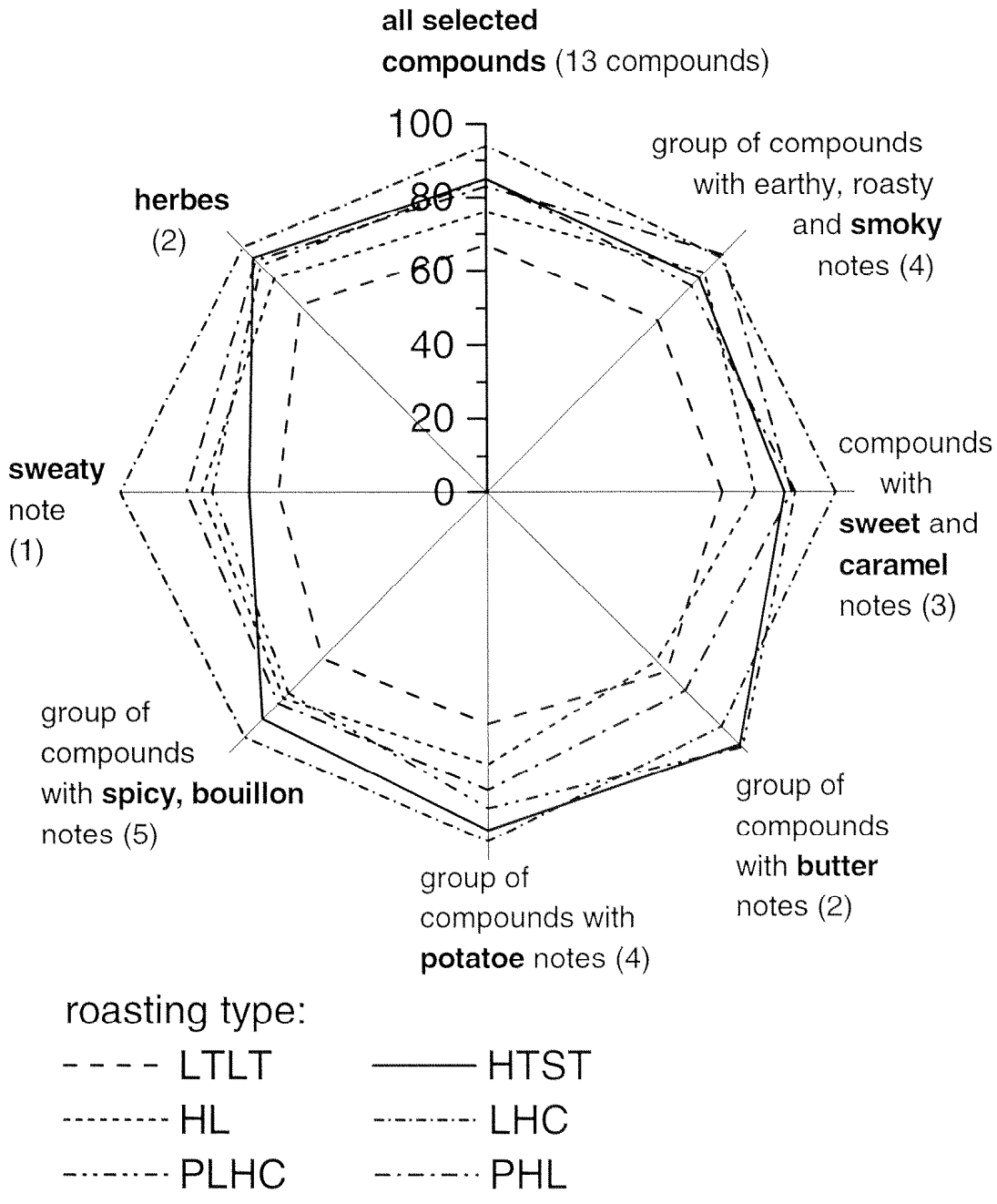

Fig. 61: *Influence of laboratory temperature profiles, leading to identical degree of roast, on aroma compounds grouped according to sensory properties. Normalized presentation with the highest quantity of an aroma compound receiving the value 100, values added up in each group and divided by the number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

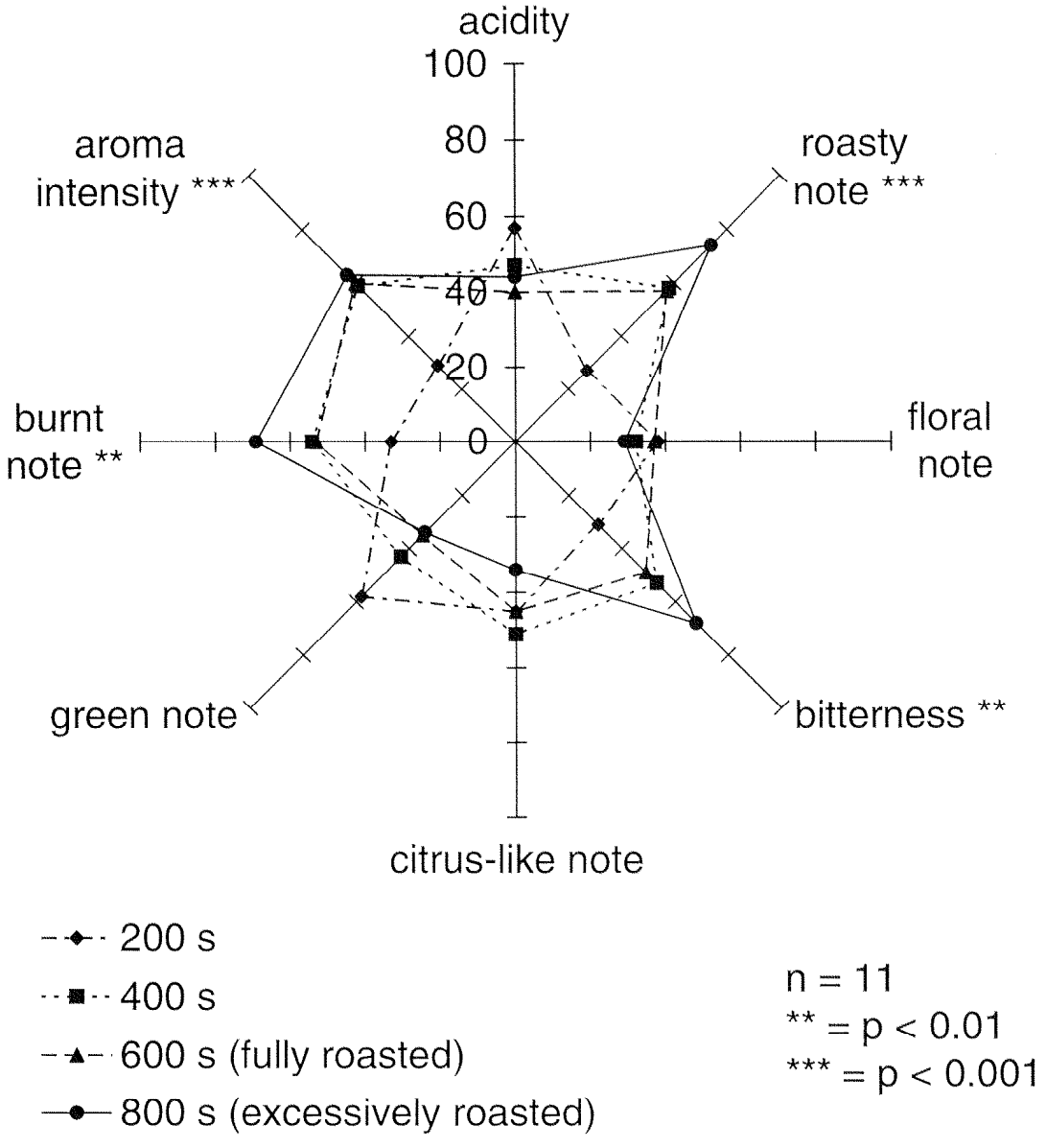

Fig. 62: *Sensory profiles of coffee beverages from LTLT laboratory roasted beans of increasing degree of roast. The product with a roasting time of 600 s corresponded to a medium degree of roast.*

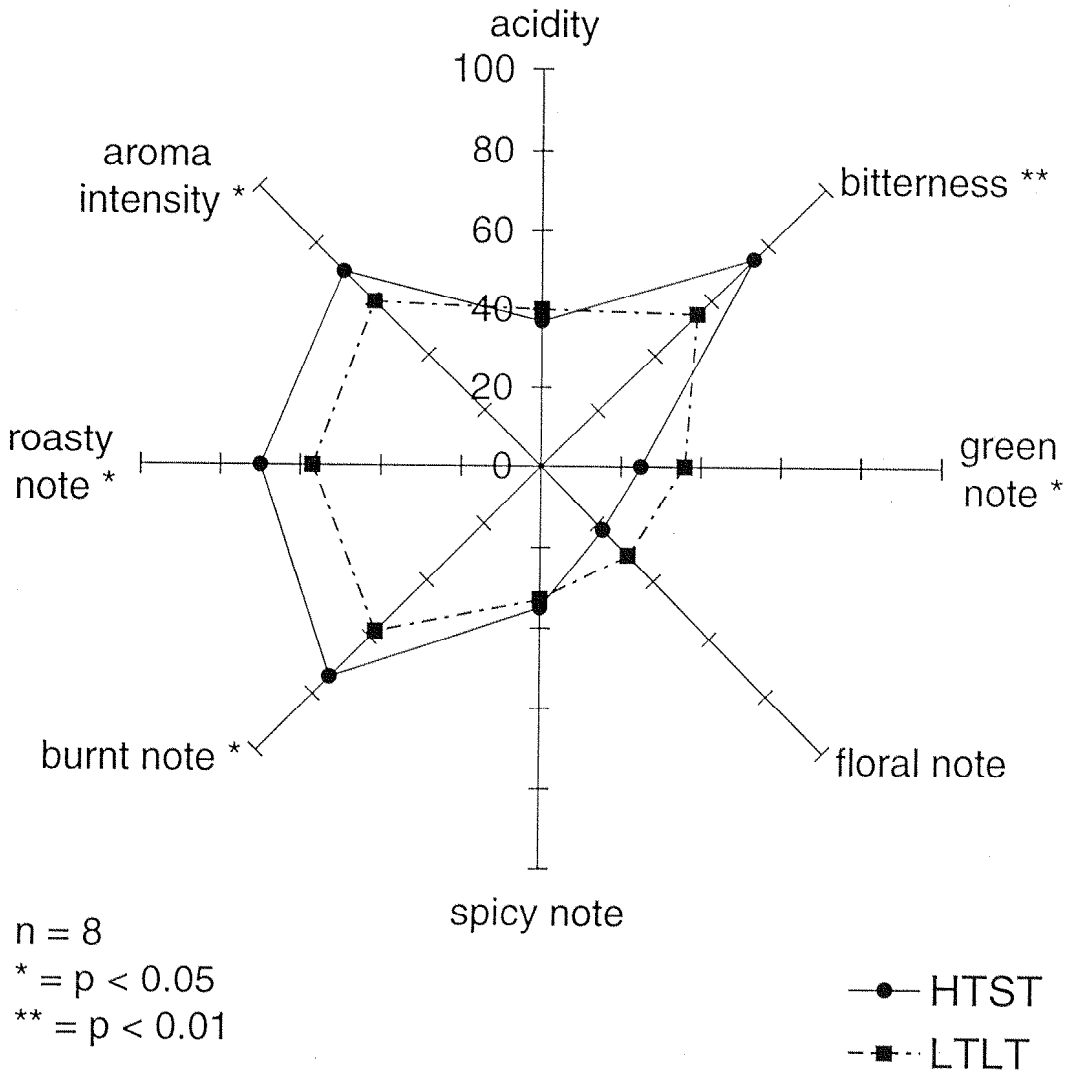

Fig. 63: *Influence of HTST and LTLT laboratory roasting to the same degree of roast on the sensory profiles of the respective coffee beverages.*

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.

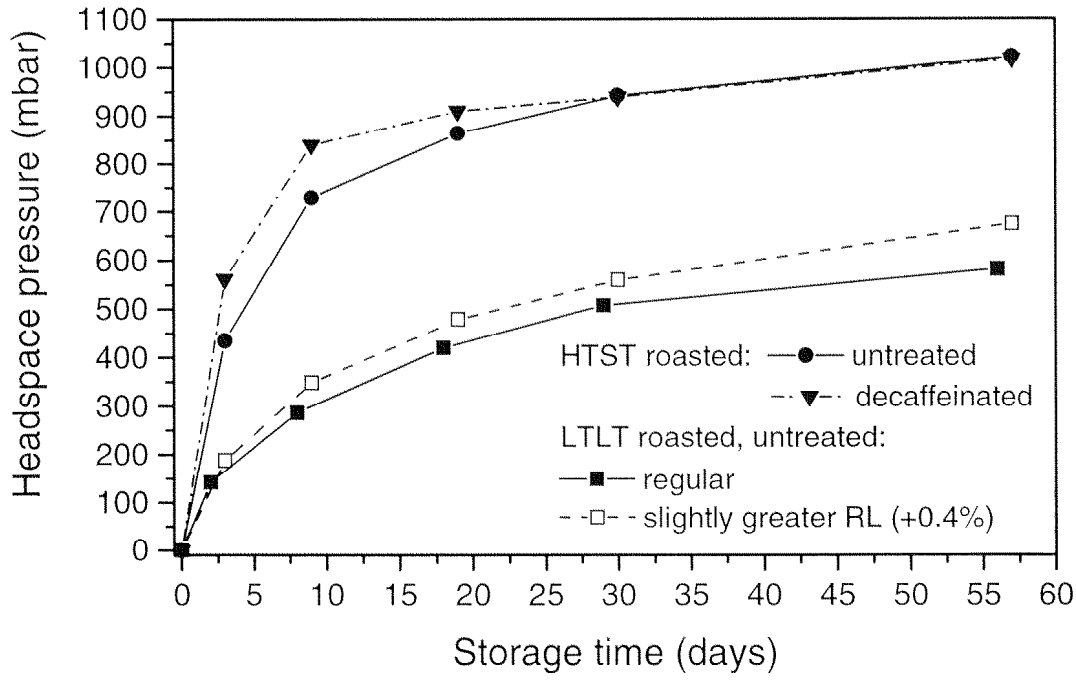

Fig. 64: *Gas desorption during storage of differently roasted coffees with identical degree of roast and of equally roasted coffees with slightly different degree of roast.*

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.

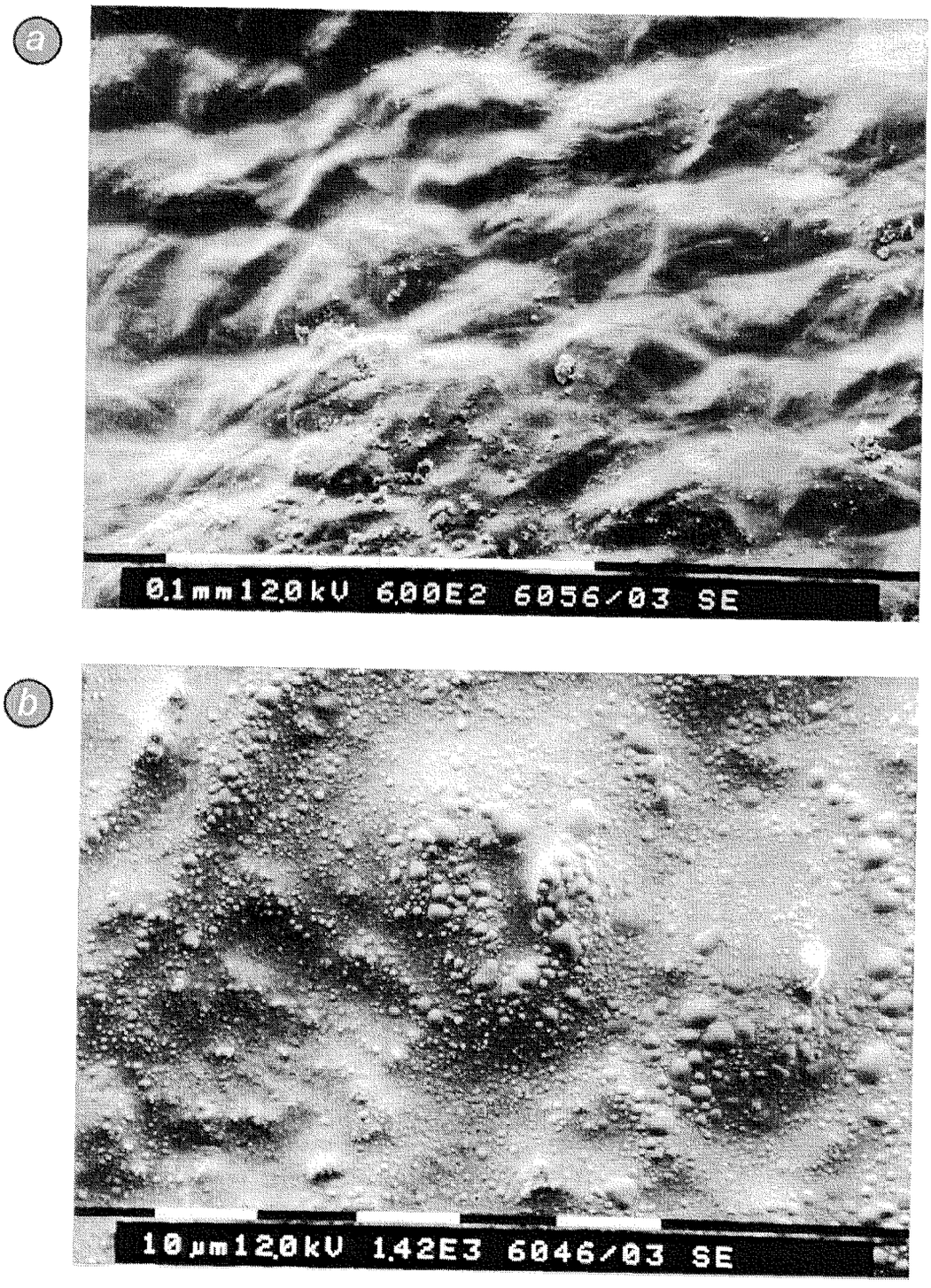

Fig. 65: *Cryo-SEM micrographs of the surface of a high temperature dark roasted coffee bean, illustrating the initial stage of the oil migration process. 65a: Immediately after roasting. Smooth epidermal cell surfaces. 65b: After 1 day of storage. Numerous very small oil droplets cover the surface.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

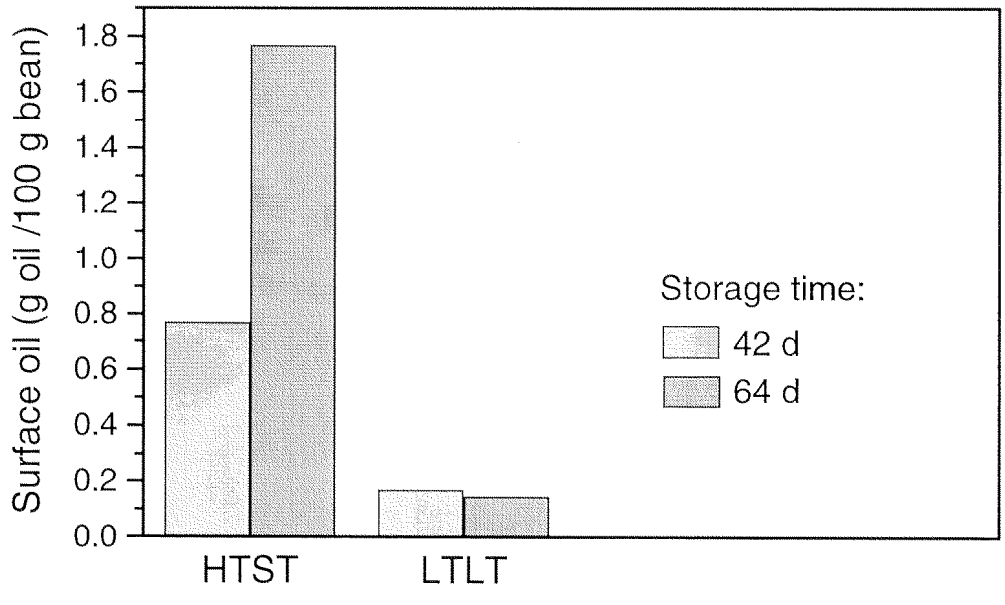

Fig. 66: *Surface oil on HTST and LTLT laboratory roasted coffee beans with identical degree of roast after storage.*

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.

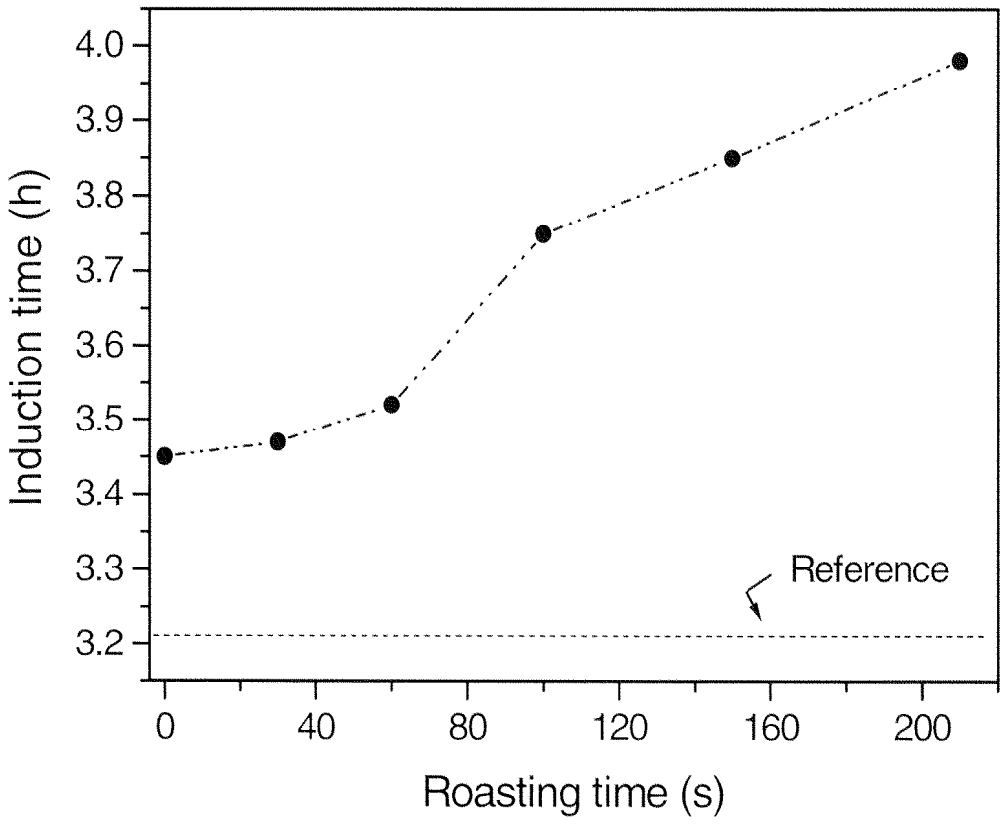

Fig. 67: *Influence of roasting time on the antioxidant properties of ground HTST laboratory roasted coffee, expressed as induction time of soybean oil suspension determined with the Rancimat method. Pure soybean oil as reference (3.22 h). Medium degree of roast at 160 s.*

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

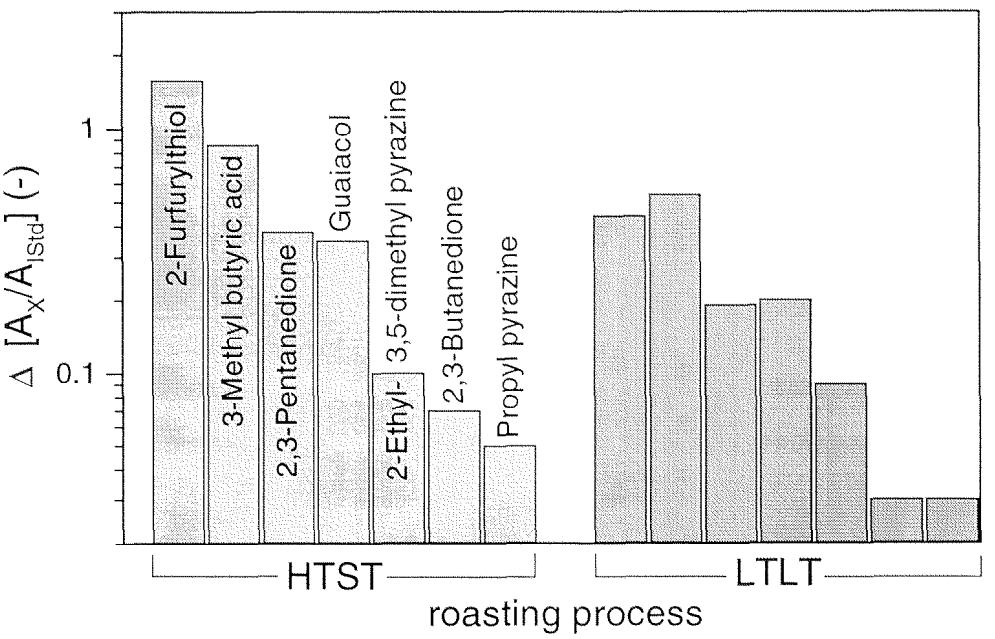

Fig. 68: *Loss of aroma compounds during a storage period of 81 days for HTST and LTLT roasted coffee beans. The beans were exposed to air and ambient temperature during storage.*

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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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