ORIGINAL PAPER

Chahan Yeretzian · Alfons Jordan · Raphael Badoud
Werner Lindinger

From the green bean to the cup of coffee:
investigating coffee roasting by on-line monitoring of volatiles

Abstract Volatile organic compounds (VOCs), emitted from green coffee beans, during coffee roasting and from a cup of coffee, were all analysed by proton-transfer-reaction mass spectrometry. Firstly, the headspace (HS) of green beans was investigated. Alcohols dominate the HS, but aldehydes, hydrocarbons and organic acids were also abundant. Secondly, we roasted coffee under two different conditions and monitored on-line the VOCs emitted during the process. In a first roasting series, a batch of beans was roasted. After an initial drying phase, dominated by evaporation of water and methanol, the HS concentrations of VOCs such as acetic acid, acetaldehyde, pyridine and methylbutanal rapidly increased and went through a maximum at medium roast level. In a second series, just six beans were roasted. We observed sporadic bursts of some volatiles (furans, butanal, 2,3-pentanedione), coinciding with popping sounds. Other VOCs showed smooth time-intensity profiles (pyridine, pyrazine). These experiments gave a real-time insight into the complex processes taking place during roasting. Finally, the HS of coffee extracts, prepared from beans roasted to different roast levels, were analysed. Most VOCs showed a maximum concentration at medium roast level (e.g. pentanedione, furfural, 5-methyl furfural), while others showed a gradual increase (e.g. pyrrol) or decrease (e.g. methanol).

Keywords Coffee · Aroma · Roasting · On-line · Proton-transfer-reaction mass spectrometry

C. Yeretzian (✉) · R. Badoud
Nestlé Research Center, PO Box 44, CH-1000 Lausanne 26, Switzerland
e-mail: chahan.yeretzian@rdls.nestle.com
Tel.: + 41 21 785 8615, Fax: + 41 21 785 8554

A. Jordan · W. Lindinger
Institut für Ionenphysik, Leopold-Franzens-Universität, Technikerstrasse 25, 6020 Innsbruck, Austria

Introduction

The flavour of a freshly prepared cup of coffee is the final expression and perceptible result of a long chain of transformations, which link the seed to the cup. These include agricultural factors such as the variety of the plant, the chemistry of the soil, the weather, and the altitude at which the coffee is grown. Combined with the way the cherries are picked, further processed and stored, a green bean is obtained that contains all the ingredients necessary for the later development of a typical coffee aroma. Yet the green beans give no clue as to what they might become once roasted. They convey neither the characteristic smell nor the taste of a cup of coffee. To reveal its flavour, coffee has to be roasted.

In terms of value, coffee is the second most important commodity of world trade, behind crude oil. Its total production in 1998 was estimated to be 6.3 million tons of green beans [1]. Relative to the raw material price, an added value of 100–300% is achieved through roasting. Considering the outstanding importance of roasting from an economic as well as flavour perspective, the development of a rational understanding of the physical and chemical transformations taking place during roasting seems highly warranted.

Recently, we embarked on a study of the on-line analysis of volatile organic compounds (VOCs) released during coffee roasting, using state-of-the-art analytical techniques. We have chosen to look at VOCs, rather than colour or temperature, since these are closely related to the flavour of the coffee. Up to now, two approaches have proven to be highly valuable. Both are based on direct injection of roast gas into a mass spectrometer, following soft ionization. This assures little ionization-induced fragmentation, high sensitivity and sub-second time resolution. One approach uses lasers for ionization. Depending on the photon energy, two types of ionization processes are applicable. One can either use resonant multiphoton ionization with ultraviolet (UV) photons, to selectively ionize VOCs out of a complex mixture, or ap-

ply vacuum UV laser radiation, to ionize with a single laser photon and achieve high sensitivity, but little selectivity. Application of two-photon UV ionization to coffee roast-gas is documented in a series of publications [2, 3, 4]. Another approach that we have explored is based on a particular version of chemical ionization, termed proton-transfer-reaction mass spectrometry (PTR-MS) [5, 6, 7, 8]. In recent papers, we have outlined the advantages and limitations of both soft ionization approaches [9, 10, 11]. Here, we present results on the on-line analysis of coffee roasting by PTR-MS.

The aim of this research is to develop strategies and tools for on-line analysis and optimization of dynamic food-processing units. The focus is on flavour formation and release. In this particular work, we investigated the roasting of coffee beans, a process of outstanding importance to the coffee industry. First, we aimed to better understand the links between process parameters and the formation of the typical coffee aroma. Based on this learning we expect, in a subsequent step, to optimize the quality and consistency of a cup of coffee through better control of the roasting process. Recently, we have published part of this on-going research [12]. Here, a more complete report is given.

Roasting is a process during which coffee beans are brought for a given time to a temperature in the range 170–230 °C [13]. A typical roasting process lasts 10–15 min and can be roughly divided into three phases: a drying phase, during which moisture is eliminated, a roasting phase, where a number of complex pyrolytic reactions take place, transforming precursors into the components of roasted coffee, and finally a cooling phase, where the freshly roasted coffee is quickly cooled in order to halt roasting. During the drying step, the beans are brought to around 100 °C, and most of the free water is driven out. The 10–12% moisture content of green beans is reduced to just a few percent. Concomitantly, the smell of the beans changes from green and peasy, to bread-like, and the colour turns yellowish. Once the beans reach about 6% moisture content, the bean temperature rises again and approaches 170 °C. Here the actual roasting starts, and the overall process becomes exothermic [14]. Pyrolytic reactions take place, generating large quantities of gas (5–12 l/kg of mainly CO_2) [15, 16, 17] that lead to high pressures inside closed voids within the porous bean microstructure [18, 19]. Consequently, beans swell by 50–100%. At this stage it is possible to hear the coffee beans pop, when cells explode under the high internal pressure ("first pop"). Coffee starts developing a full body with a nice acidity and rich aroma. Going beyond this stage, the coffee becomes dark roasted. We hear a second more rapid popping ("second pop") and oil appears as small droplets on the surface. While the coffee gradually looses its positive acidity and aroma richness, it gains in body. Further roasting finally leads to charring and the development of a pronounced burnt taste. Finally, rapid cooling (quenching) of the beans puts an end to the roasting cycle.

Concomitant with the physical changes, profound changes in the chemical composition take place [20]. Sucrose, the main oligosaccharide of green coffee, splits into the reducing sugars glucose and fructose. These in turn react with free amino acids and free amino groups of proteins in the Maillard reaction to form aminoketones and/or aminoaldoses after Amadori or Heyns rearrangement of the intermediate glycosylamine adducts [21]. Amadori and Heyns products react further in a complex cascade of reactions, which lead to numerous odorant volatiles and coloured compounds. While the roasting process continues, other reaction mechanisms take place involving the degradation by interaction and pyrolytic cleavage of carbohydrates, nitrogen-containing substances, chlorogenic acids and other organic acids and, to a lesser extent, lipids. This leads further to the formation of water, carbon dioxide and other volatile components. A simplified scheme showing the main classes of volatile compounds formed during roasting from non-volatile precursors in the green beans is presented in Fig. 1.

All these reaction pathways lead to the formation of a wide range of VOCs, some of which are quite abundant in the HS of coffee, and whose formation and release into the HS during roasting is observed on-line by PTR-MS.

An interesting concept, introduced in the United States of America in the early 1970s and later abandoned due to unsatisfactory sensory characteristics, was the so-called high yield coffee [22, 23]. It was observed that a high temperature-short time roasting profile yielded roasted coffee beans of larger volume, lower density and higher extraction yield. Therefore, some manufacturers recommended using only 80–85% of the usual amount of coffee for the same quality of brew. Yet, it turned out that such a brew was lacking in body and was organoleptically less satisfactory. Using a normal dosage of coffee, the cup prepared from a high yield coffee was bitter/burnt and astringent. Although this approach was abandoned in the 1980s, it illustrates an important characteristic of roasting: flavour development during roasting depends on the time-temperature history to which the beans are subjected. Consequently, a rational management of roast quality requires defining and controlling critical parameters of the roast history. Physical characterizations at the start- and endpoint of the process (e.g. temperature, colour, and weight-loss), as is the widespread practice today, only allow an assessment of the flavour profile within narrow process conditions. In more rigorous terms: "flavour quality" that develops during coffee roasting is not a state function, described solely by physical parameters at the start and end point of roasting. It is rather a path-dependent function.

As we enter the twenty-first century, it seems unlikely that the basic technology of applying heat to the beans will fundamentally change. Yet, one innovation that will affect future generations of roasters is intelligent on-line control tools. This will assist in continuously improving
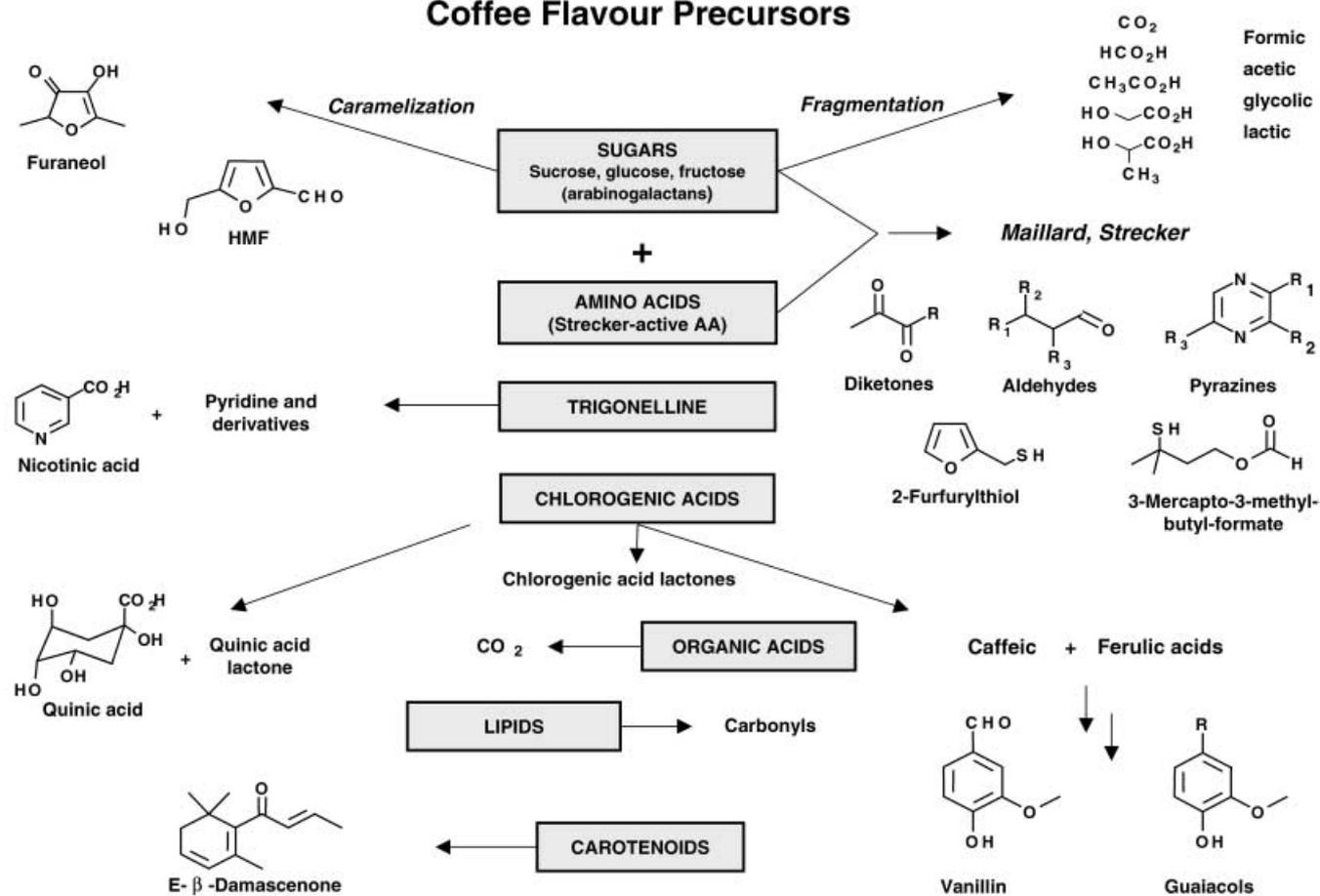
94

Coffee Flavour Precursors

Fig. 1 A simplified scheme showing the main classes of volatile compounds formed from non-volatile precursors in the green beans during roasting
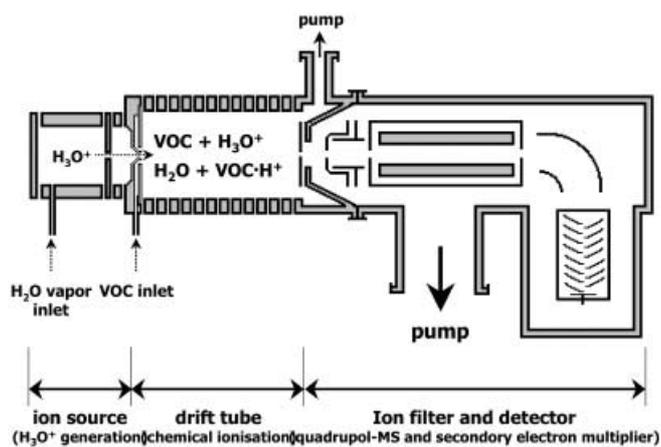

Fig. 2 Schematic representation of the proton-transfer-reaction mass spectrometry (PTR-MS) apparatus. It consists of three chambers. In the first chamber, nearly pure H_3O^+ is generated by electrical discharge in H_2O vapor. A small field drives H_3O^+ ions through an orifice into the drift tube (chemical ionization chamber), while neutral volatile organic compounds (*VOCs*) are introduced coaxially to the orifice, into the drift tube. VOCs with proton affinities exceeding 166.5 kcal/mol ionize by proton transfer from H_3O^+ and are accelerated out of the drift tube into the quadrupole mass filter

consistency and quality of the roast, as well as detecting and correcting instabilities of the roasting operations. Ultimately, this can lead to fully automated roasters, delivering consistently high quality roasted beans. In fact, it is interesting to state that while several highly complex industrial processes are now fully automated, coffee roasting still requires a dedicated and experienced operator.

Throughout these studies, PTR-MS was used to analyse the HS volatile composition, either under equilibrium conditions, or as time-concentration profiles. PTR-MS combines a soft, sensitive and efficient mode of chemical ionization, adapted to the analysis of trace VOCs, with a mass filter (Fig. 2) [5, 6, 7, 8]. Typically, HS gas is continuously introduced into the chemical ionization (CI) cell (drift tube), which contains, besides buffer-gas, a controlled ion density of H_3O^+. VOCs that have proton affinities larger than water (proton affinity of H_2O: 166.5 kcal/mol) are ionized by proton transfer from H_3O^+, and the protonated VOCs are mass analysed. The CI-source was specifically designed to achieve versatility, high sensitivity, little fragmentation, and allow for absolute quantification of VOCs. To achieve these targeted specifications, the generation of the primary H_3O^+ ions on the one hand, and the chemical ionization process on the other hand, are spatially and temporally separated and individually controlled. This allows (1) the maximizing of signal intensity by increasing the genera-

Fig. 3 PTR-MS headspace (HS) profiles of Arabica and Robusta green coffee beans
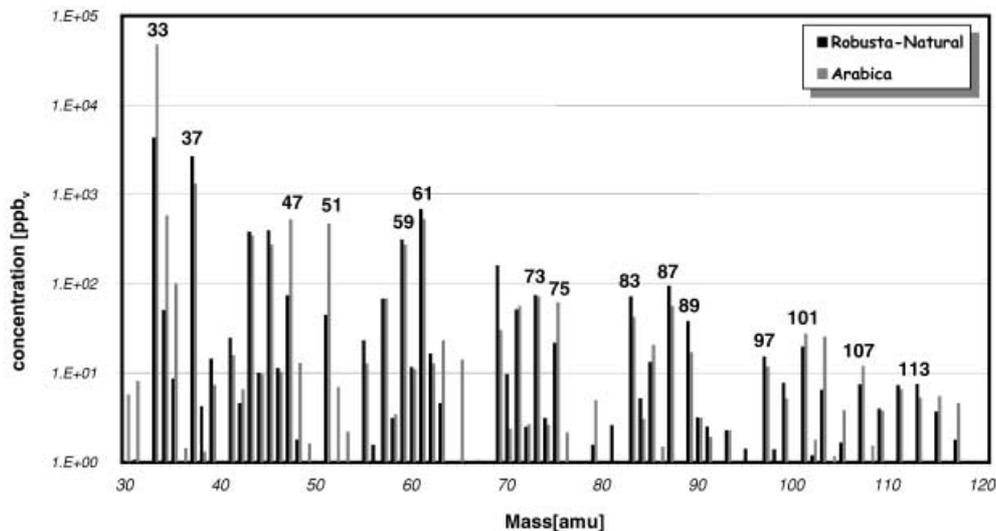
tion of primary reactant ions, H_3O^+, in the ion source, (2) the reduction of fragmentation and clustering by optimization of the conditions for proton transfer in the drift tube, and (3) the quantification of VOCs from measured count rates.

Consequently, the four key features of PTR-MS can be summarized as follows. First, it is fast. Time-dependent variations of HS profiles can be monitored with a time-resolution of better than 1 s. Second, the VOCs are not subjected to work-up or thermal stress and little fragmentation is induced by the ionization step. Hence, mass spectral profiles closely reflect genuine HS distributions. Third, mass spectral intensities can be transformed into absolute HS concentrations, without calibration or use of standards. Finally, it is not invasive. All these features make PTR-MS particularly suited to investigate fast dynamic processes, such as coffee roasting.

Materials and methods

Emissions from green coffee beans

As a starting point of the study, emission of VOCs from green coffee beans was measured. We included two different varieties, a *Coffea arabica* Linn. (known as Arabica) from Bordes-Sto-Domingo and a *Coffee canephora* Pierre ex Froehner (known as Robusta) from Indonesia. Green beans (30 g) were placed in a 500-ml glass vial, which had an inlet and an outlet on the top. Through the outlet, HS gas was sampled at a rate of 17 cm^3min^{-1} and replaced by air entering from the inlet. The HS gas was directly introduced into the drift tube of the PTR-MS, and the mass spectrum averaged over 30 min (Fig. 3). In a separate experiment the HS gas of the empty vial was measured (background) and subtracted from the green bean spectrum. The background intensity was found to be negligible at most masses.

Emission of volatiles during roasting

Two isothermal roasting experiments were performed. In one set-up, a 40 g batch was convectively roasted by a strong flow of hot

air, whereas in another setup, just six beans were roasted. In both experiments, the HS was continuously probed by PTR-MS.

Batch roasting. In the setup shown in Fig. 4a, the roaster was first preheated to the roasting temperature, with hot air flowing through the setup for about 30 min. Then 40 g of Arabica (from Columbia) green beans were placed on a mesh inside the roasting vessel, and convectively heated with a strong flow of hot synthetic air (more than 500 l/min). The temperature of the air was maintained at 180 °C, 185 °C or 190 °C, respectively (isothermal roasting), and 40 cm^3/min of the off-gas leaving the roaster was sampled for HS analysis. This gas was first diluted and cooled by addition of 171 cm^3/min air at room temperature (to avoid condensation on cold spots along the tubings and saturation of the mass spectrometer), and 11 cm^3/min from this total of 211 cm^3/min were introduced into the drift tube. The remaining 200 cm^3/min were discarded through a laboratory exhaust line. All the gas-transfer lines were heated to 60 °C to avoid condensation of volatiles. This experimental set-up was designed to probe the HS profile as it occurs when a batch of coffee beans is roasted. Twenty-two masses were simultaneously monitored with a time resolution of about 40 s. This low time resolution was chosen to screen a large mass range with a good signal-to-noise ratio.

Single bean roasting. In the setup shown in Fig. 4b, a glass vial (roasting vessel) with an inlet and an outlet was placed inside an oven. The oven was heated to either 185 °C or 195 °C and the temperature maintained throughout the roasting process. Via the inlet, a flow of 1700 cm^3min^{-1} air, preheated to the oven temperature, swept the HS from inside the roasting vessel. Of this air, 1% was probed by PTR-MS. Once the roasting vessel was equilibrated to the oven temperature, six green beans (~1 g) were placed in a glass vial. Roasting proceeded at constant air temperature. This experiment was designed to probe the elementary processes occurring at the single bean level.

Emission from brew

Samples of Arabica (Columbia) green beans (60 g) were roasted at 185 °C air temperature for 5, 10, 15, 20 and 30 min, respectively, leading to a range of roasted beans from very light (5 min) to very dark (30 min). Beans (32 g) from each roast level were ground, and coffee suspensions prepared in a glass vial from 2 g ground coffee and 100 ml water at 70 °C. The vial was closed and placed for 80 min in an oven at 40 °C for equilibration. The HS was then sampled via an inlet and an outlet with a stream of air of 17 cm^3min^{-1}, and PTR-MS mass-intensities averaged over 5 min.
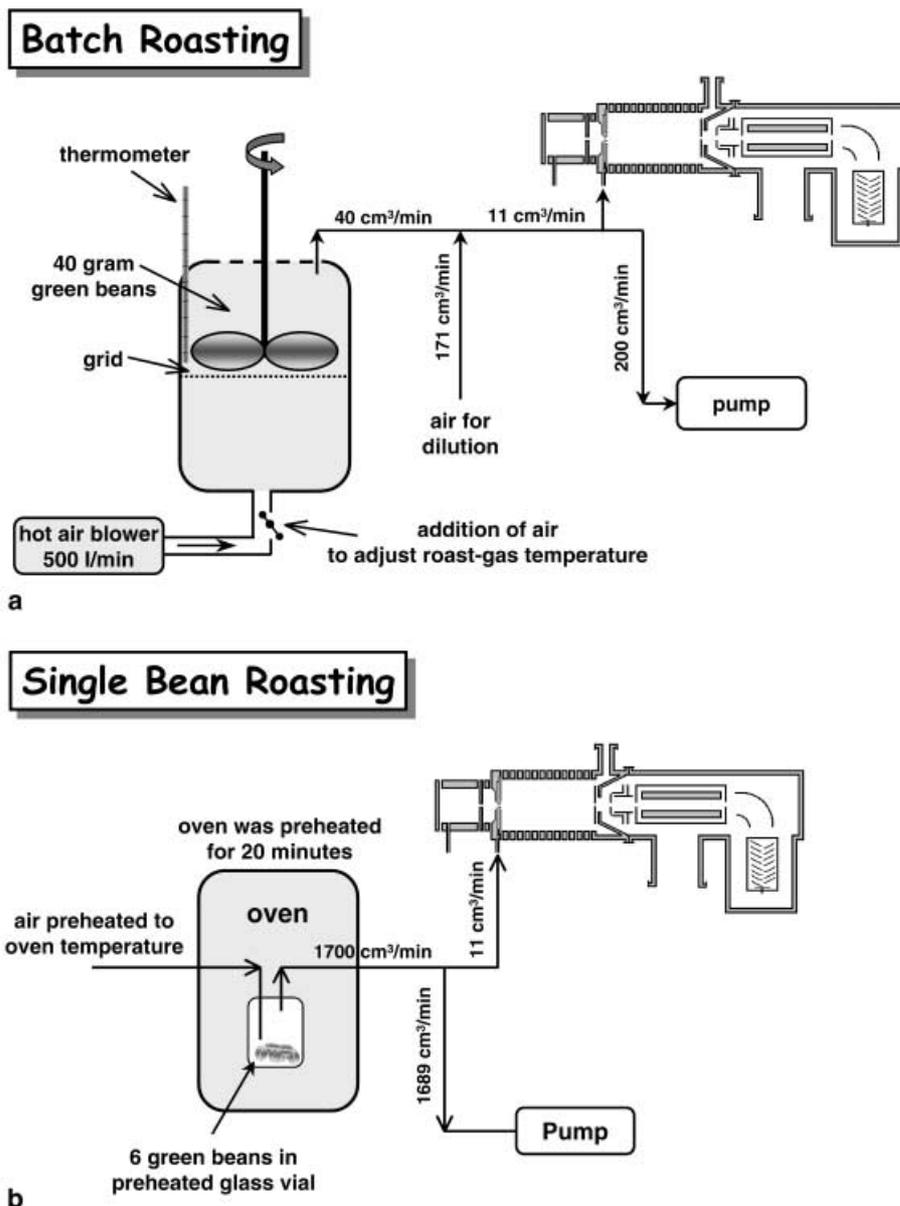
Results and discussion

Emissions from green coffee beans

Until now, the VOCs of green coffee beans have attracted little attention, particularly in comparison to the large amount of research conducted on roasted coffee aroma. This is understandable, since most typical coffee aroma compounds are formed from non-volatile precursors during roasting, and only rarely can they be traced back to volatiles in the unroasted beans. The volatiles of green coffee beans are of limited importance to the aroma of the cup. Yet, in a few cases, flavour and off-flavour compounds have been characterized that appear in green beans and survive the roasting process. Besides directly linking volatiles of green coffee to the roasted coffee aroma, they can also be indirect quality markers of final cup quality. So, one can suspect that the origin (geographic, genetic), post harvest treatment, storage conditions and contamination by microorganisms might all be reflected in the HS profile of green beans.

The first comprehensive analysis of VOCs of green coffee beans dates back to 1968 [24]. Some 50 compounds were reported, but their relative sensory importance was not investigated. In 1976 Vitzthum et al. were the first to explicitly combine instrumental and sensory methods on green coffee [25]. In 1995, Holscher and Steinhart compiled a comprehensive literature review and added new results on the HS of green coffee [26]. More than 200 compounds were listed in this paper. Recently, Czerny and Grosch reported detailed studies on the potent odorants of green beans, using aroma extract dilution analysis [27, 28]. Finally, Cantergiani et al. published an in depth GC-olfactometric study on green Mexican coffee [29, 30].

Table 1 Headspace (HS) composition of green beans. Chemical assignment of proton-transfer-reaction mass spectrometry (*PTR-MS*) HS profiles of Robusta and Arabica green coffee beans, based on references [26, 29, 30, 35, 36]. Considering that the compounds are identified just from their mass and the literature on volatile organic compounds (VOCs) of coffee, these assignments have to be considered as tentative. At a few masses we observe formation of clusters between VOC-H^{+} and H_2O. Besides (H_3O^+)·(H_2O), (methanol-H^{+})·(H_2O) and (ethanol-H^{+})·(H_2O), the other cluster peaks are very low in intensity, showing intensities far below 1% of the intensity of the non-clustered protonated parent peak

Mass+1 (amu)[a]	Compound(s) contributing to PTR-MS mass intensities
33	Methanol
37	(H_3O^+)(H_2O)[b]
45	Acetaldehyde
47	Ethanol
51	Methanol(H_2O)[b]
59	Acetone, Propanal
61	Propanol
65	Ethanol(H_2O)[b]
69	Isoprene
71	(Isopentanol+H^{+}) – H_2O[c]
73	Isobutanal, Butanal, Butanone
75	Propanoic acid, Butanol, Isobutanol
87	3-Methyl-2-buten-1-ol, 2*E*-butenoic acid, 3-methyl butanal, 2,3-butanedione
89	Isopentanol, pentanol, isobutanoic acid, 2-methylbutanol, 3-methylbutanol
97	2*E*,4*E*-Hexadienal
99	2*E*-Hexenal
101	Hexanal, 2,3-pentanedione, 3-methyl butenoic acid
103	3-Methyl butanoic acid, pentanoic acid, 1-hexanol
105	(Phenyl-ethylalcohol+H^{+}) – H_2O[c]
107	Benzaldehyde
113	2*E*-Heptenal
115	Heptanal
117	2 Heptanol, hexanoic acid
121	Phenylacetaldehyde
141	2*E*-Nonenal, 2Z-nonenal
143	Nonanal

[a] The indicated masses correspond to the protonated molecular masses as they are detected by PTR-MS (neutral parent mass+1)

[b] Molecules with strong permanent dipole moments (H_2O and small alcohols) tend to form clusters with water molecules in the drift tube. Due to their relatively strong intermolecular forces, these clusters leave the drift tube intact and are detected concomitantly with the non-clusters, protonated parent molecules. The concentration of (VOC-H^{+})·H_2O clusters is generally below 1% of the concentration of the non-clustered parent

[c] Protonated alcohols (except the very small alcohols such as methanol and ethanol) can fragment via loss of an H_2O-unit. Hence the most intense peak for these compounds are generally at the mass of (alcohol-H^{+}) – 18 amu

An important driver for research on green coffee flavour comes from the sporadic appearance of off-flavours that affect cup quality. A baggy off-flavour was linked to the presence of some hydrocarbons in the green beans [31]. 2,4,6-Trichloroanisol was found to be responsible for a hardish, phenolic, chemical, musty off-flavour [32, 33]. A musty/earthy off-flavour was linked to an increase in the concentration of geosmin and 2-methylisoborneol [29, 30], while a bell pepper, peasy off-note was related to higher concentrations of some alkyl-methoxypyrazines [25, 27, 34].

Figure 3 shows PTR-MS HS profiles of Robusta and Arabica green beans plotted on an identical intensity scale. Based on published work, the major compounds are tentatively assigned in Table 1 [28, 29, 30, 35, 36]. The most abundant compounds in the HS of green coffee are alcohols, in accordance with the most recent and comprehensive study on green (Mexican) coffee [30]. Although less abundant, aldehydes, hydrocarbons and organic acids are also among the more intense HS compounds. In both samples, methanol dominates the HS profile.

Comparing the Robusta with the Arabica, we can state that the Arabica yields methanol and ethanol peaks stronger by an order of magnitude. The most abundant class of compounds in the HS is alcohols, with methanol, ethanol and propanol being particularly abundant in both green coffees. In the Arabica and the Robusta samples, alcohols account for 93% and 53% of the total HS concentrations, respectively. Aldehydes are the second most abundant compound class in the HS and account for 1% (Arabica) and 3% (Robusta). Finally the third most abundant HS compounds are acids with 0.2% (Arabica) and 0.6% (Robusta). Whether the observed variations are related to differences among varieties, ripeness at harvest, post-harvest treatment or storage conditions remains to be answered by more systematic studies.

Batch roasting

Arabica coffee (Columbia) was roasted at three different temperatures in the setup shown in Fig. 4a, and the roast gas was monitored on-line. As outlined in the Introduction, the roasting process of coffee can be divided into an endothermic phase during which the water content of the beans is reduced from an initial 10–12% to just a few percent, and an exothermic phase where complex pyrolysis reactions take place in the nearly dry beans, generating a whole range of volatile compounds. The VOCs

Fig. 5 Time-intensity profiles
for eight masses, monitored
during the roasting of 40 g Ara-
bica (Columbia) coffee beans at
190 °C. The *top frame* shows
the profiles on a linear intensity
scale, while the *bottom frame* is
plotted on a logarithmic scale.
Each type of scaling has its
merits and drawbacks
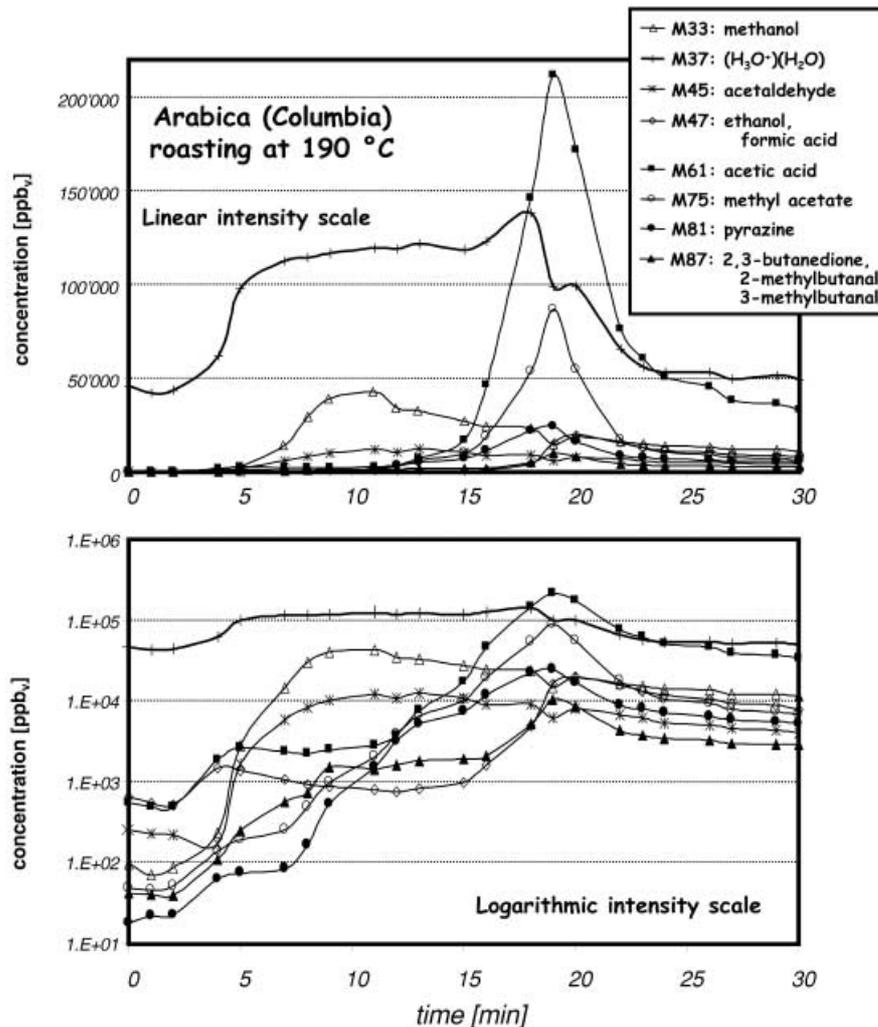
released in these distinct phases are fundamentally dif-
ferent. Most importantly, a large amount of VOCs is
formed during the exothermic phase, almost exclusively
from non-volatile precursors. These compounds give
roasted coffee its characteristic aroma and taste. Out of
the 900 different VOCs identified in coffee [37], less
than 30 are believed to be important flavour compounds
of roasted coffee [38, 39, 40, 41, 42]. Recently, omission
experiments from Grosch and coworkers suggested that
the actual number of key coffee aroma compounds could
be as small as nine [43, 44, 45].

In Fig. 5, 8 out of the 22 recorded time intensity pro-
files of PTR-MS ion traces are shown on a linear as well
as on a logarithmic intensity scale. Roasting was per-
formed under isothermal conditions at 190 °C air tempera-
ture. Referring to the extensive literature on the composi-
tion and quantification of volatiles of coffee, and previous
PTR-MS studies on the HS of coffee [12], the masses
shown in Fig. 5 can be assigned as follows: 33, methanol;
45, acetaldehyde; 47, ethanol and formic acid; 61, acetic
acid; 75, methyl acetate; 81, pyrazine; 87, 2,3-butanedi-
one, 2-methylbutanal and 3-methylbutanal. At some mass-
es, one single compound completely dominates the PTR-

MS ion-intensity. When, as in the case of mass 87, several
compounds significantly contribute to a given mass, they
are cited in order of decreasing importance. Particularly
interesting is mass 37. It corresponds to a protonated wa-
ter cluster, $(H_2O \cdot H)^+ \cdot (H_2O)$ whose time-intensity profile
reflects the drying of the beans during roasting.

Once the roasting process had started, we first ob-
served the water concentration (37 amu) to increase in
the HS, followed by methanol (33 amu). After 15 min,
while drying was still ongoing, the HS concentrations of
a series of compounds such as acetic acid (61 amu), eth-
anol and/or formic acid (47 amu) and pyrazine (81 amu)
– a fragment of furfuryl alcohol $[M+H-H_2O]^+$ also at
81 amu – strongly increased. This was followed by a de-
crease in the water signal. The increase of the VOC HS
concentrations continued until about 19 min roasting
time, where a maximum was reached for most VOCs.
From the literature it is known that acetic acid is most
abundant at medium roast level [13, 46], consistent with
the observation that a medium roast was reached at
around 19 min (visual inspection and tasting). The final
decrease was initially quite fast, but levelled off at longer
times as the beans became dark roasted.

To investigate the effect of the roast-gas temperature on the roast process, we roasted coffee beans at three different temperatures (180, 185, and 190 °C), but under otherwise identical conditions. In Fig. 6, time-intensity traces of eight masses are shown, while roasting Arabica (Columbi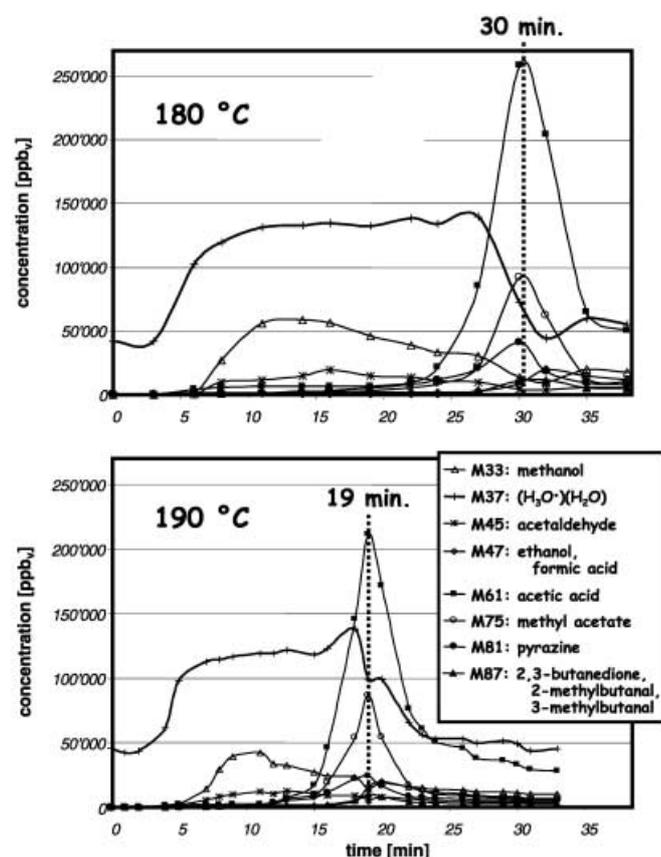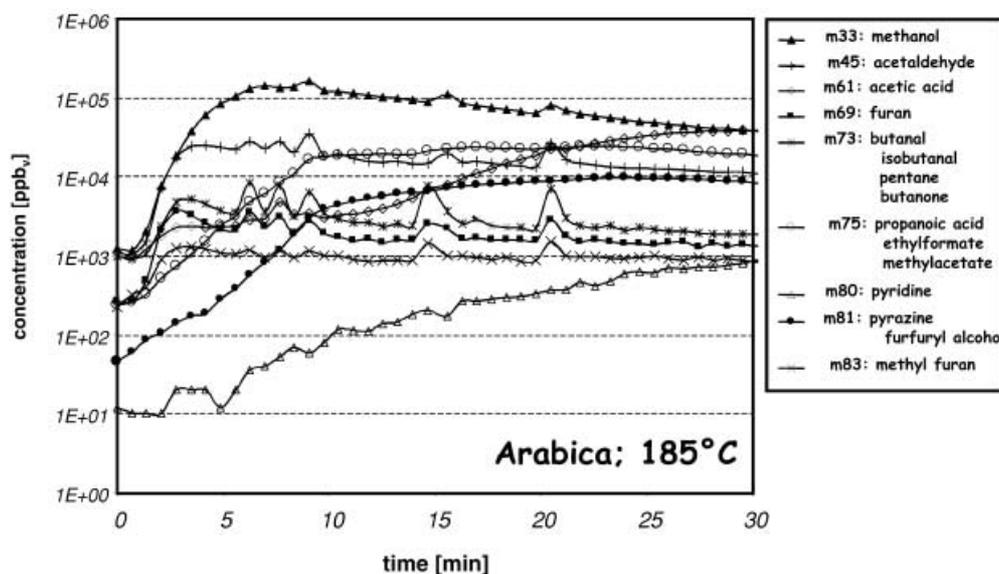a) beans at 180 °C and (top frame) and 190 °C (bottom frame). We see that an increase of only 10 °C shifts the maximum (medium roast level) from 30 min to 19 min. This amounts to a decrease of 37% in roast time, for medium roast. We also observed a sharpening of the ion-intensity profiles around the maximum. Expressing the sharpness by the full-width at half-maximum (FWHM) of the acetic acid trace, we observe a decrease of the FWHM from 5.7 min at 180 °C to 4 min at 190 °C. This amounts to a sharpening of 30%. Considering that roast-times of 5–10 min are common practice, we understand how delicate the job of an operator is.

Fig. 6 Time-intensity profiles for volatile compounds during the roasting of Arabica (Columbia) coffee beans at 180 °C and 190 °C

Single bean roasting

The setup shown in Fig. 4a is designed to monitor an averaged HS over a large number of beans (batch roasting). Yet, considering that the "elementary unit" in coffee roasting is the individual bean, it is crucial to also investigate the progress at the single bean level, rather than observing statistically averaged phenomena. Many of the current attempts to model coffee roasting start from estimated or measured physical and chemical properties of individual beans, and complement these with thermodynamic models for mass and energy transfer through the bean structure [47]. An accurate understanding of the processes at the single bean level is, therefore, crucial to these roasting models.

A setup was designed, in which only six beans are roasted and a smaller stream of gas is used to sweep the HS gas. Robusta and Arabica beans were roasted at 185 °C and 195 °C and ion intensity profiles of 60 masses were simultaneously monitored, with a time resolution of 40 s. Fig. 7 shows nine time-intensity traces for the roasting of six Arabica beans at 185 °C. Shortly after the beans were placed inside the roasting vessel, we observed an increase in HS intensities. Superimposed on some smooth emission curves were peaks, indicating

Fig. 7 Time-intensity profiles for volatile compounds during the roasting of six Arabica beans at 185 °C. The experimental conditions were chosen such that emissions from single beans could be observed

transient increases of headspace concentrations. The most pronounced peaks appeared at mass 73. At precisely the same time that these peaks were observed, one could hear popping sounds from inside the roaster, emanating from "popping" of single beans.

Large amounts of non-odorous gases are formed during roasting, originating from a variety of reactions. About half of this gas is believed to be released during roasting. The remaining gas is entrapped inside the cellular structure of the beans and is gradually released over several months. Most of these gases are water and CO_2 with smaller amounts of CO and N_2. The VOCs repres-

Fig. 8 Three selected time-intensity profiles are shown which exhibit synchronous and strong bursts of volatiles (roasting of six Arabica beans at 185 °C)

ent just a few percent of the emitted gases. The internal pressure built-up within closed cavities can reach 25 bar before the pressure is released by popping [13]. Popping sounds can be heard during the roasting process. At each of the individual poppings, CO_2 is ejected into the HS, together with volatile compounds that have accumulated inside these cavities. We, therefore, interpret the observed sharp peaks superimposed on the smooth time-intensity curves as VOCs that are released during bean popping. Figure 8 shows three masses with different intensities of bursts, the profile at mass 73 being the one with the most pronounced transient increases.

As can be seen from Fig. 7, the intensities of some masses, such as 75, 80 and 81 do not seem to be affected by these poppings. Hence, data indicate that there are two categories of compounds: those that are violently released during popping, and those that are released in a continuous manner over time. Currently we can think of two possible explanations, as to why two different types of release patterns exist. Either VOCs are generated/released in physically distinct areas within the bean microstructure, and not all find their way into closed cavities from which they are released during poppings, or alternatively, physical interactions of the volatiles with non-volatile bean material strongly reduces the vapour pressure inside the cavities, and hence their release during popping.

Isothermal roasting experiments at 195 °C with Arabica beans from the same batch as above (Fig. 9) and of Robusta beans at 185 °C (Fig. 10) show the same separation into two groups of compounds. Some showed distinct bursts of volatiles, coinciding with popping sounds and some showed smooth time-intensity curves not affected by popping. In Table 2, we collected masses that show bursts of volatiles concomitant with popping
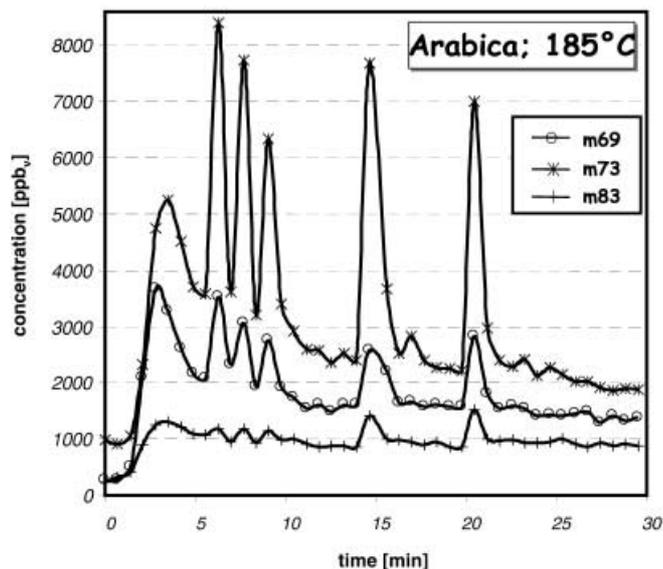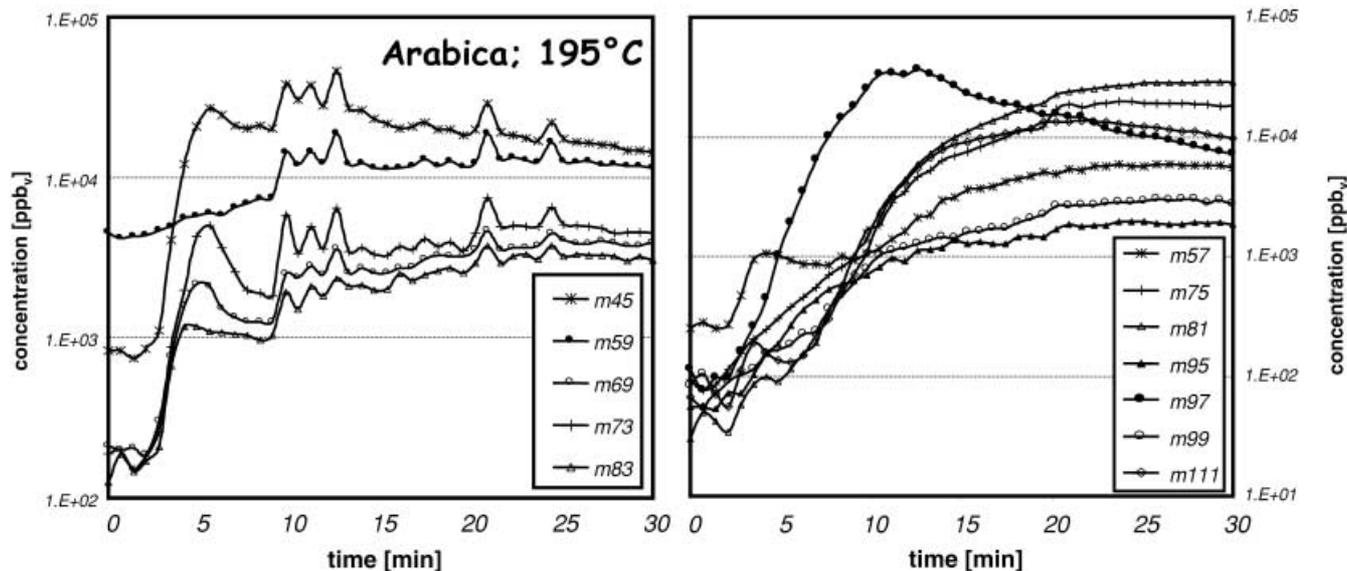

Fig. 9 Time-intensity profiles for volatile compounds during the roasting of six Arabica beans at 195 °C. The *left frame* shows a collection of masses that exhibits synchronious bursts of volaltiles, while the *left frame* shows a selection of masses which have rather smooth time-intensity profiles

Table 2 Emission of VOCs during bean popping. A list of masses and corresponding compounds for which bursts of volatiles are observed, concomitant with popping sounds. Data from three distinct experiments are combined. One experiment corresponds to roasting of Robusta beans at 185 °C air temperature (isothermal roasting), while the two others correspond to Arabica beans being roasted at either 185 °C or 195 °C. The relative intensity of the bursts of volatiles are also included in the table (*rows 2,3* and *4*). *S* strong, *M* medium, *W* weak

Mass: parent+1	Arabica 185 °C	Arabica 195 °C	Robusta 185 °C	Compounds[a]
31	W	W	W	Formaldehyde
33	M	M	W	Methanol
41	W	M	M	Fragment of 3-methylbutanal
45	S	S	S	Acetaldehyde[b]
47		W	W	Ethanol, formic acid
49	M			Methanethiol
51	W		W	Methanol(H_2O)
59	S	S	M	Acetone, propanal
61	W	S		Acetic acid
63	?	M	M	Dimethylsulfide, acetaldehyde(H_2O)
69	S	M	M	Furan
73	S	S	S	2-Butanone, isobutanal, butanal
83	S	S	S	2-Methyl furan, (3-methylfuran)[c]
87	S	M	M	2-Methylbutanal, 3-methylbutanal, 2,3-butanedione
97	W		W	Furfural, (C_2-alkyl furan)[c]
101	S	M	M	2,3-Pentanedione
115	W		W	Hexanedione, furfurylthiol,...[d]

[a] Compounds that strongly dominate at the mass

[b] CO_2 cannot be protonated by PTR-MS

[c] Compounds in parentheses have a minor but possibly not negligible contribution to the mass spectral intensity

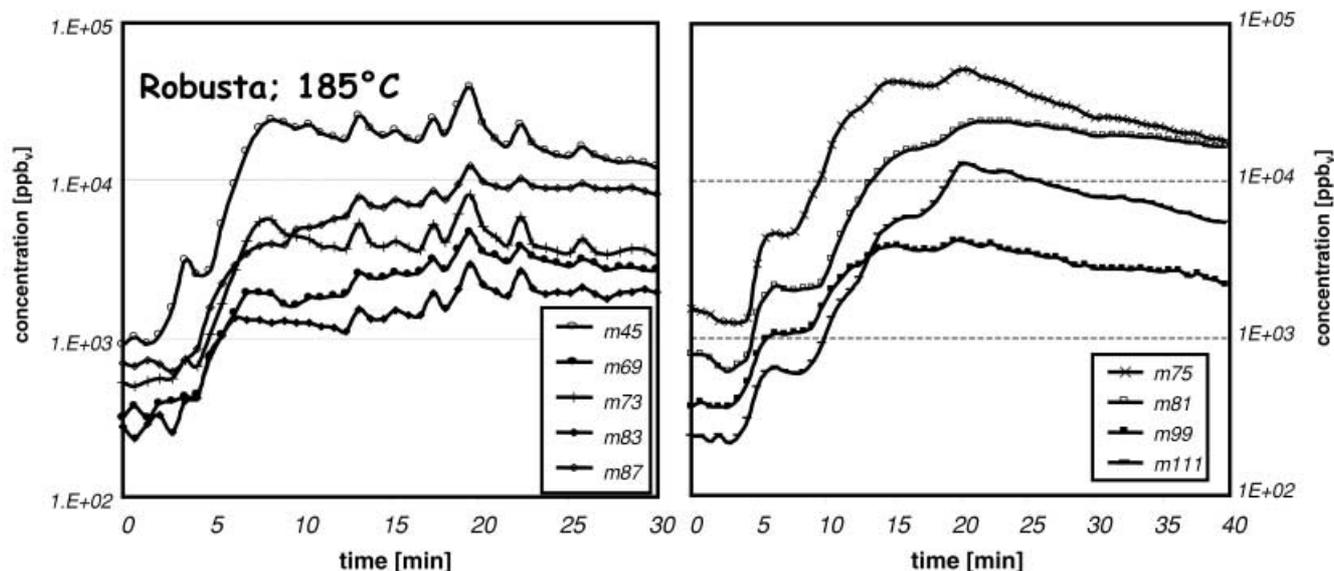[d] Several other compounds could contribute to this mass spectral intensity

Fig. 10 Time-intensity profiles for volatile compounds during the roasting of six Robusta beans at 185 °C. The *left frame* shows a collection of masses that exhibits synchronious bursts of volatiles, while the *right* frame shows a selection of masses which have rather smooth time-intensity profiles

sounds, during experiments with Arabica at 185 °C and 195 °C and Robusta at 185 °C. The relative intensities of the bursts are marked with S(strong), M(medium) and W(weak). Bursts at mass-intensities 45, 73, 83 have consistently been judged as strong, throughout all experiments.

It is important to point out that measured PTR-MS time-concentration curves are aggregated observables, comprising the kinetics of the formation of VOCs as well as the kinetics of their release. The experiments reported here *a priori* cannot determine the relative share of the two processes. Whilst roasting progresses, several of the observed volatiles are known to be generated from precursors in the green beans. Yet roasting is also known to modify the bean structure, porosity and composition and hence alter the release properties of the bean material and bean structure. While presence or formation is a prerequisite for release, alteration of release properties will un-

Fig. 11 HS profiles of a suspension prepared from coffee roasted to medium level. The mass spectrum is plotted on linear (*top frame*) and logarithmic (*bottom frame*) intensity scales
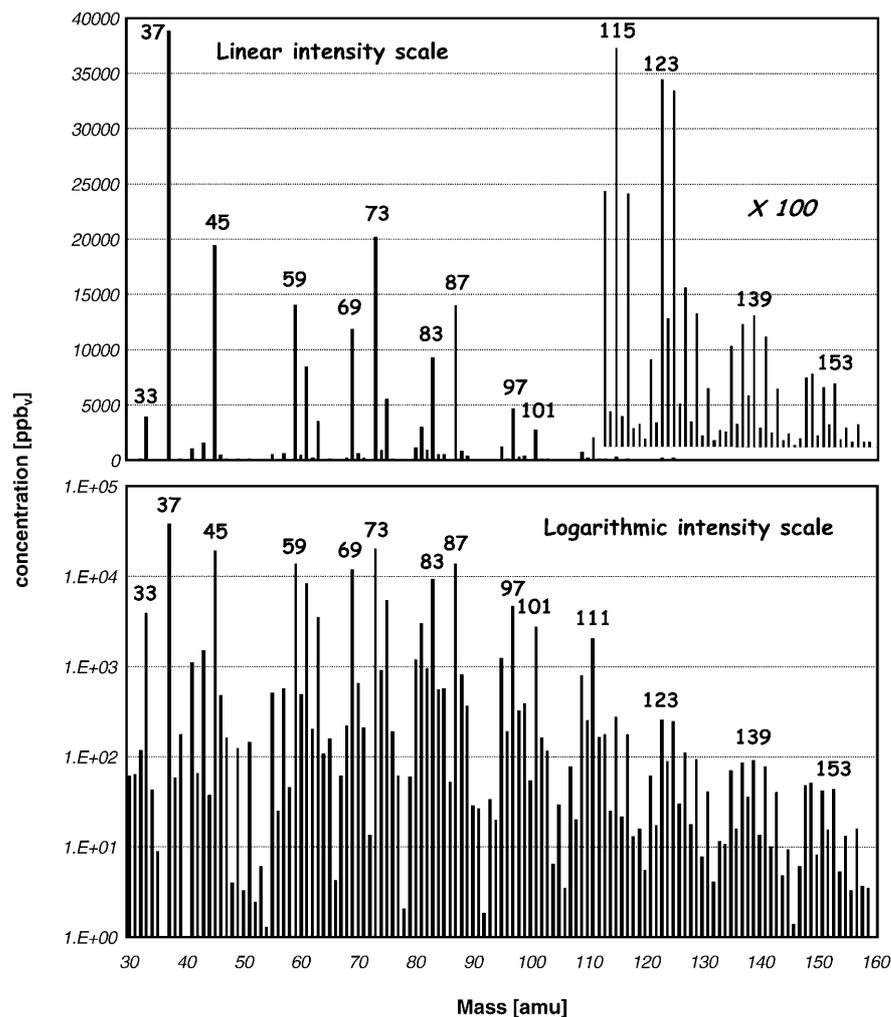
doubtedly modulate the observed HS concentrations. The bursts observed in single bean experiments are obviously a manifestation of abrupt release following structural changes, and are not related to formation kinetics.

Emission from brew

Once the green coffee beans had been roasted, they were ground and extracted. Figure 11 shows a PTR-MS HS profile of a coffee suspension, prepared from beans roasted to medium level. Plotted on a linear intensity scale (top frame), a series of mass peaks dominate the HS profile. The most prominent ones are 37 [$(H_3O^+) \cdot (H_2O)$], 45 (acetaldehyde), 59 (acetone), 69 (furan), 73 (butanal, isobutanal, pentane, butanone), 83 (methylfuran), 87 (2-methylbutanal, 3-methylbutanal, 2,3-butanedione), 97 (furfural), 101 (2,3-pentanedione) and 111 (5-methylfurfural). Plotting the same data on a logarithmic intensity scale (bottom frame) allows intensities over a larger HS concentration range to be visualized. A discussion of coffee-brew HS as analysed by PTR-MS will be the subject of a forthcoming publication. Here, we will focus on the changes of the HS con-

centrations above the cup, as they evolve with roast level. Figure 12 shows the HS intensities of seven masses, prepared from coffees roasted to different roast levels. Six out of the seven selected masses can be assigned to a single VOC and we can assign their absolute HS concentrations from measured PTR-MS count rates. In contrast, 2-methylbutanal, 3-methylbutanal and 2,3-butanedione all significantly contribute to mass 87. Therefore, the indicated concentration in Fig. 12 for mass 87 represents the sum of the HS concentrations of all three compounds.

In analogy to on-line monitoring of the HS gas during roasting, we observe that the maxima in the time-concentration curves appear most often at medium roast level. Acetaldehyde, butanedione, furfural, pentanedione all show distinct maxima for medium roasted coffee. In contrast, methanol HS intensity decreases with roast level, while the pyrrol content in the HS increases continuously.

In conclusion, a quantitative analysis of volatile compounds in the HS of coffee was performed on different stages from green beans to the cup of coffee, using PTR-MS. On the one hand, "static" experiments under equilibrated conditions investigated the HS profiles of

Fig. 12 HS concentrations of various compounds above a brew of Arabica coffee, prepared from coffees that were roasted to various roast degrees. The coffee cups were prepared from 2 g of roast and ground, suspended in 90 ml of distilled water at 70 °C
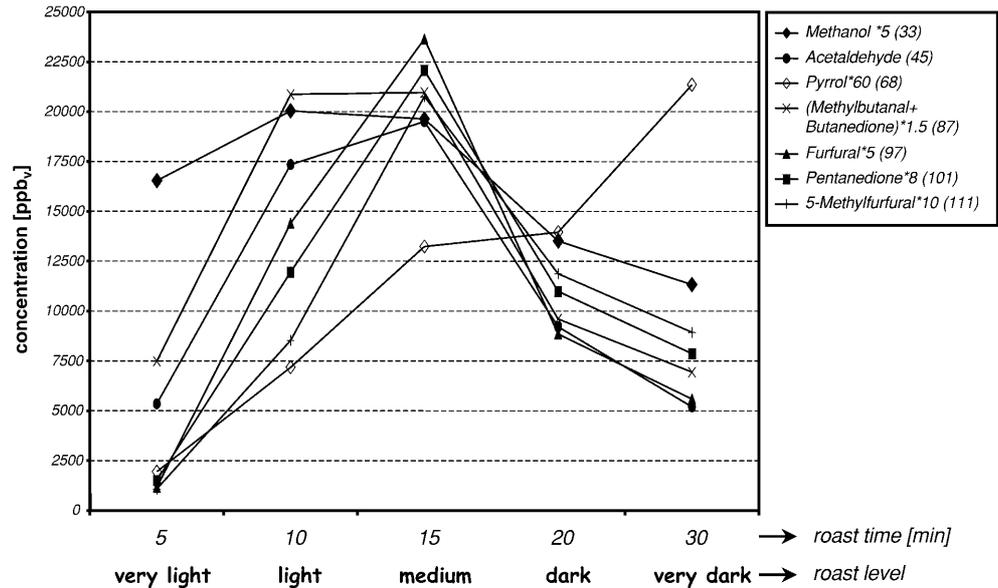
green beans and coffee-brew. While many gas chromatography-based studies have already been published on these products, PTR-MS has the advantage of being fast and of determining relative and absolute HS concentrations over a large mass range. The HS of green coffee beans is strongly dominated by alcohols, which constitute 93% of the total HS concentration in Arabica and 53% in Robusta. Methanol is by far the most abundant VOC in both the HS of Arabica (90%) and Robusta (44%) beans. The next most abundant groups of compounds in decreasing order importance are aldehydes (1–3%), hydrocarbons and organic acids (0.2–0.6%).

On the other hand, the HS evolution during roasting was investigated dynamically. Here we exploited the outstanding property of PTR-MS, to monitor fast changes of HS concentrations at high sensitivity and speed. In a first roasting configuration, batches of beans were roasted at 180 °C, 185 °C and 190 °C, while monitoring the time-intensity profiles at selected masses. These profiles illustrate the different phases of coffee roasting. Initially we observed drying of the beans, characterized by evaporation of water. After this (endothermic) drying phase, the actual roasting started (exothermic). It is characterized by a massive formation and release of volatile compounds. Furthermore a dramatic change in the HS profile over time was observed. Most of the newly formed volatiles go through a maximum at medium roast level. Roasting the beans beyond medium roast leads to an overall decrease in volatile intensities and a change in the profile. These experiments provide a statistically averaged view of the temporal evolution of VOCs, integrated over a large number of beans. Differences between individual beans are smoothed out.

In order to develop an understanding of the roasting process at a more fundamental level, we went on to explore phenomena at the single bean level – de facto, the unit-operation of coffee roasting. For a series of VOCs, we were able to directly observe sporadic and intense bursts, coinciding with popping sounds. Other compounds showed smooth time-intensity curves. This behaviour was distinctively different from that observed with a batch of beans. While release of VOCs from a batch was smooth, the same VOCs showed sporadic and strong bursts when observed at the "unit operation level". The two experiments expose different views on roasting, which are mutually complementary and relevant if one wants to understand, predict and ultimately control the coffee roasting process.

At a more general level, this work demonstrates the potential for on-line monitoring of food processing units via direct analysis of VOCs by PTR-MS. It opens the door to a whole range of novel approaches to study dynamic process in the food industry. It also holds promise for process control via characteristic markers or patterns. Considering that volatiles are released from essentially all types of products and during most processing steps, on-line VOC analysis has the potential to become a truly versatile approach for process and quality control.

References

1. International Coffee Organisation (2001)http://www.ico.org
2. Zimmermann R, Dorfner R, Kettrup A, Yeretzian C (1999) On-line analysis of food processing gases by resonance laser mass spectrometry (REMPI-TOFMS): coffee roasting and related applications.In: 18th International Scientific Colloquium on Coffee. ASIC, Helsinki, pp 136–149
3. Zimmermann R, Heger HJ, Dorfner R, Yeretzian C, Kettrup A, Boesl U (1997) On-line monitoring of food volatiles by laser ionization-mass spectrometry (REMPI-TOFMS): first results for coffee roasting, tea and cocoa.In:Proceedings of the 1st International Convention on Food Ingredients: New Technologies, Cuneo (Italy).UNIDO, Vienna, pp 343–350

4. Zimmermann R, Heger HJ, Yeretzian C, Nagel H, Boesl U (1996) Rapid Comm Mass Spectrom 10:1975–1979
5. Yeretzian C, Jordan A, Brevard H, Lindinger W (2000) Time-resolved headspace analysis by proton-transfer-reaction mass-spectrometry. In: Roberts D, Taylor A (eds) 218th ACS National Meeting: on "Flavour release: linking experiments, theory, and reality". American Chemical Society, New Orleans, pp 58–72
6. Lindinger W, Hansel A, Jordan A (1998) Int J Mass Spectrom Ion Process 173:191–241
7. Lindinger W, Hansel A, Jordan A (1998) Chem Soc Rev 27:347–354
8. Hansel A, Jordan A, Holzinger R, Prazeller P, Vogel W, Lindinger W (1995) Int J Mass Spectrom Ion Process 149/150:609–619
9. Dorfner R, Zimmermann R, Kettrup A, Yeretzian C, Jordan A, Lindinger W (1999) Lebensmittelchemie 53:32–34
10. Fay LB, Yeretzian C, Blank I (2001) Chimia 55:429–434
11. Dorfner R, Ferge T, Uchimura T, Yeretzian C, Zimmermann R, Kettrup A (in press) Laser / chemical ionisation – mass spectrometry as an on-line analysis technique for monitoring the coffee roasting process. In: 19th International Scientific Colloquium on Coffee. ASIC, Trieste, Italy
12. Yeretzian C, Jordan A, Brevard H, Lindinger W (2000) ACS Symp Ser 763:112–123
13. Illy A, Viani R (1995) Espresso coffee, the chemistry of quality. Academic, London
14. Reamy A, Lambelet P (1982) J Food Technol 17:451–460
15. Sivetz M, Desrosier NW (1979) Coffee technology. AVI, Westport, Conn.
16. Radtke R (1975) Das Problem der CO_2-Desorption von Röstkaffee unter dem Gesichtspunkt einer neuen Packstoffentwicklung. In:, 7th International Conference on Coffee Science. ASIC, Hamburg Germany pp 323–333
17. Barbara CE (1967) Gas-volumetric method for the determination of the internal non-odorous atmosphere of coffee beans In: 3rd International Conference on Coffee Science, Trieste (Italy). ASIC, Paris, pp 436–442
18. Schenker S, Handschin S, Frey B, Perren R, Escher F (1999) Structural properties of coffee beans as influenced by roasting conditions. In:, 18th International Scientific Colloquium on Coffee, Helsinki. ASIC, Paris, pp 127–135
19. Schenker S, Handschin S, Frey B, Perren R, Escher F (2000) J Food Sci 65:452–457
20. Clarke RJ, Macrae R (1985) Coffee volume 1: chemistry. Elsevier, New York
21. Ledl F, Schleicher E (1990) Angew Chem 29:565–706
22. Maier HG (1985) On the composition of fast roasted coffees. In: 11th International Scientific Colloquium on Coffee, Lomé (Togo). ASIC, Paris, pp 136–149
23. Kazi T, Clifford MN (1985) ASIC, 11th International Scientific Colloquium on Coffee, Lomé (Togo) pp 297–308
24. Merrit C, Robertson DH, McAdoo DJ (1970) The relationship of volatile compounds in roasted beans to their precursors. In: 4th International Scientific Colloquium on Coffee, Amsterdam. ASIC, Paris, pp 144–148
25. Vitzthum OG, Werkhoff P, Ablanque E (1976) Flüchtige Inhaltstoffe des Rohkaffees. In: 7th International Scientific Colloquium on Coffee, Hamburg. ASIC, Paris, pp 115–123
26. Holscher W, Steinhart H (1995) Dev Food Sci 37A:785–803
27. Grosch W (1999) Key odorants of roasted coffee. In: 18th International Scientific Colloquium on Coffee, Helsinki. ASIC, Paris, pp 17–26
28. Czerny M, Grosch W (2000) J Agric Food Chem 48:868–872
29. Cantergiani E, Brevard H, Amadò R, Krebs Y, Feria-Morales A, Yeretzian C (1999) Characterisation of mouldy/earthy defect in green Mexican coffee. In: 18th International Scientific Colloquium on Coffee, Helsinki (Finland). ASIC, Paris,pp 43–49
30. Cantergiani E, Brevard H, Krebs Y, Feria-Morales A, Amadò R, Yeretzian C (2001) Eur Food Res Technol 212:648–657
31. Grob K, Artho A, Biedermann M, Caramashi A, Mikle H (1992) J AOAC Int 75:283–287
32. Spadone JC, Takeoka G, Liardon R (1990) J Agric Food Chem 38:226–233
33. Holscher W, Bade-Wegner H, Bendig I, Wolkenhauser P, Vitzthum OG (1996) Off-Flavour elucidation in certain batches of Kenyan coffee. In: 16th International Scientific Colloquium on Coffee, Kyoto. ASIC, Paris, pp 174–182
34. Becker R, Döhla B, Nitz S, Vitzthum OG (1988) Identification of the "peasy" off-flavour note in Central African coffees. In: 12th International Scientific Colloquium on Coffee, Montreux. ASIC, Paris, pp 203-215
35. Rhoades JW (1960) J Agric Food Chem 8:136–141
36. Rodriguez DB, Frank HA, Yamamoto HY (1969) J Sci Food Agric 20:15–17
37. Nijssen LM, Visscher CA, Maarse H, Willemsens LC (1996) In "Volatile Compounds in Food", 7th edn. TNO Nutrition and Food Research Institute. Graphische Bedrijven Anraad, the Netherlands
38. Blank I, Sen A, Grosch W (1991) Aroma impact compounds of Arabica and Robusta coffee. qualitative and quantitative investigations. In: 14th International Scientific Colloquium on Coffee, San Francisco. ASIC, Paris, pp 117–129
39. Sen A, Laskawy G, Schieberle P, Grosch W (1991) J Agric Food Chem 39:757–759
40. Blank I, Sen A, Grosch W (1992) Z Lebensm Unters Forsch 195:239–245
41. Semmelroch P, Grosch W (1996) J Agric Food Chem 44:537–543
42. Semmelroch, P.; Grosch, W (1995) LebensmWiss Technol 28:310–313
43. Czerny M, Mayer F, Grosch W (1999) J Agric Food Chem 47:695–699
44. Grosch W, Mayer F (1999) ACS Symp Ser 763:430–438
45. Grosch W, Czerny M, Mayer F, Moors A (2000) ACS Symp Ser 754:202–209
46. Guyot B, Tchana E, Vincent JC (1986) Corrélations entre caractéristiques chimiques du café torréfié et paramètres de torréfactions. In: 11th International Scientific Colloquium on Coffee, Lomé (Togo). ASIC, Paris, pp 319–331
47. Eggers R, Pietsch A. (2001) Chapter 4, Technology 1: Roasting. In: Clarke RJ, Vitzthum OG (eds) Coffee, Recent Developments. Blackwell, pp 90–107