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Laser Mass Spectrometry as On-Line Sensor for Industrial Process Analysis: Process Control of Coffee Roasting

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The objective of the project is to develop on-line, real-time, and noninvasive process control tools of coffee roasting that help deliver a consistent and high-quality coffee aroma. The coffee roasting process was analyzed by direct injection of the roaster gas into a time-of-flight mass spectrometer and ionized either by resonance enhanced multiphoton ionization (REMPI) at 266 and 248 nm or vacuum ultraviolet single-photon ionization (VUV-SPI) at 118 nm. The VUV ionization scheme allows detecting mainly the most volatile and abundant compounds of molecular mass below 100 *m*/*z*, while REMPI ionizes mainly aromatic compounds of molecular mass larger than 100 *m*/*z*. Combining the compounds ionized by resonant and single-photon ionization, ∼30 volatile organic compounds are monitored in real time. Time−intensity profiles of 10 important volatile coffee compounds were discussed in connection with their formation chemistry during roasting. Applying multivariate statistics (principle component analysis) on time−intensity traces of nine volatile coffee compounds, the roasting degree could be traced as a consistent path in the score plot of the two most significant principle components (including 68% of the total variance), for a range of roasting temperatures (200−250 °C).

Coffee is one of the most popular beverages in the world. With a total estimated production of 113.8 million bags (60 kg/bag) and an annual average price of 1.61 $/kg in 1999/2000, it is worldwide among the most traded commodities next to oil and wheat, in terms of value.

Compared to roasted coffee, green coffee is nearly flavorless. Its odor can be described as grassy, earthy, and haylike, and the extract made from ground green beans has no recognizable coffee flavor. However, it possesses adequate texture and contains the ingredients necessary for later development of the coffee flavor. To unlock its potential and develop the desirable coffee flavor, coffee beans have to be roasted.[1]

(A) Coffee Roasting. Roasting induces several visible changes in color, texture, density, and size.[2−6] Besides these, complex physical and chemical reactions take place inside the beans, leading among other things to the formation of coffee flavor compounds.[7−12] In the initial phase of the roasting process, the beans are mainly dried, keeping the bean temperature around 100 °C. Once the beans have lost most of their free water, the temperature rises again. At ∼170 °C, exothermic pyrolytic reactions start. Polysaccharides, proteins, chlorogenic acids, and trigonelline react to form the key flavor compounds of coffee. There are several reviews on the chemistry of coffee roasting and the formation of the coffee flavor compounds available in the literature.[7,13−15]

Considering the complexity of the chemical and physical processes that occur during the exothermic phase, it is not

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surprising that knowledge of the formation of coffee flavor is fragmentary and sometimes speculative. This explains that in order to deliver a consistent quality, one trusts a dedicated and experienced roaster who uses a set of indicators, his senses, and his empirical experience to control the process. This evaluation typically relies on physical measurements at the start and end point of the process (weight loss, color, and temperature). However, an (automated) on-line process control can obviously not be performed by sensory evaluation means as the evaluation samples (here, coffee beans) need to be sampled and evaluated from the process stream. This makes it impossible to determine specific characteristics such as the actual roast degree during the process (Note that the coffee roasting process is rather fast.). Furthermore, many of the attributes that get evaluated are not directly related to the flavor but are indirect indicators of the development of the roasting. Also, they barely take into account that the coffee flavor chemistry depends on the full time−temperature history to which the beans are subjected. Indeed, a rational control of roast quality requires monitoring in real-time flavor relevant properties of coffee, throughout the whole roasting process. Ideally, the roasting progress would be characterized by sensory evaluation sided by instrumental analysis, capable of real-time monitoring of the formation and release of several coffee flavor compounds.

(B) On-Line, Real-Time Analysis of Roaster Off-Gas. The ultimate objective of this work is to develop approaches and tools that provide on-line real-time information about the evolution of the roasting process, based on criteria that are closely related to a central quality criterion—the aroma of coffee. The approach that we propose is real-time monitoring of coffee aroma compounds and related volatile organic compounds (VOCs) in the roaster off-gas.

Roast gas is composed of a complex mixture of gases. These are primarily nonodorous inorganic gases such as CO_2, CO, N_2, and H_2O.[6] Only ∼1% of the gases are VOCs, a fraction of which represents coffee flavor compounds. To monitor in real time detailed, flavor-relevant information during the roasting process, we need methods that are capable of monitoring VOCs at high time resolution, at high sensitivity, and with chemical selectivity.

Several techniques can be envisaged. One approach consists of using gas sensors. These are capable of monitoring small molecules such as CO_2 and H_2O, yet they do not feature chemical selectivity and sensitivity suitable to our objectives. A more recent approach uses sensor arrays, sometimes termed "electronic nose", which exhibit different response patterns to the chemicals in the process gas.[16] The electronic nose concept has been applied with some success to the characterization of food products. However, for on-line analysis of complex and fast process gases, as for example, coffee roasting gas, its usefulness is presently limited.

One other approach is direct inlet MS. In a series of recent papers, the advantages and limitations of various direct inlet MS methods were reviewed.[17−20] A prerequisite for mass analysis is ionization, a process that critically influences the sensitivity and selectivity of the experiment. Electron impact ionization causes considerable fragmentation. Because of overlapping fragment and parent ions, the molecular information is difficult to deconvolute, and little chemical information can be extracted.

Application of direct inlet MS for monitoring complex mixtures of VOCs requires using ionization techniques, which produce little or no fragmentation (soft ionization). Chemical ionization in combination with a quadrupole mass filter, either in atmospheric pressure chemical ionization mass spectrometry)[21−23] or in proton-transfer reaction mass spectrometry (PTR-MS),[24−27] was successfully applied to foods.

An alternative to chemical ionization is selective and soft laser photoionization. Here we use two different laser ionization schemes: resonance enhanced multiphoton ionization (REMPI) and vacuum UV single-photon ionization (VUV-SPI). First applications of REMPI-TOFMS for monitoring coffee brew headspace have been reported.[17,28−30] Further, it has been shown that SPI-TOFMS can be applied to generate on-line overview mass spectra of the major VOCs in coffee powder headspace.[31] The feasibility of direct inlet laser TOFMS for on-line monitoring of VOCs in industrial processes such as waste incineration has been demonstrated previously.[32,33] More recently, we successfully applied laser ionization for on-line monitoring of roast gas.[34]

EXPERIMENTAL SECTION

(A) Direct-Inlet Laser Mass Spectrometric Methods for On-Line Analysis of Complex Mixtures. Direct-inlet MS, using either REMPI or VUV-SPI for ionization, monitors on-line the roaster off-gas. In Figure 1, the photoexcitation energy schemes for REMPI and SPI are illustrated. Technical reviews on REMPI can be found in refs 28, 30, 32, 33, and 35−38, while VUV-SPI is described in refs 31 and 39−41.

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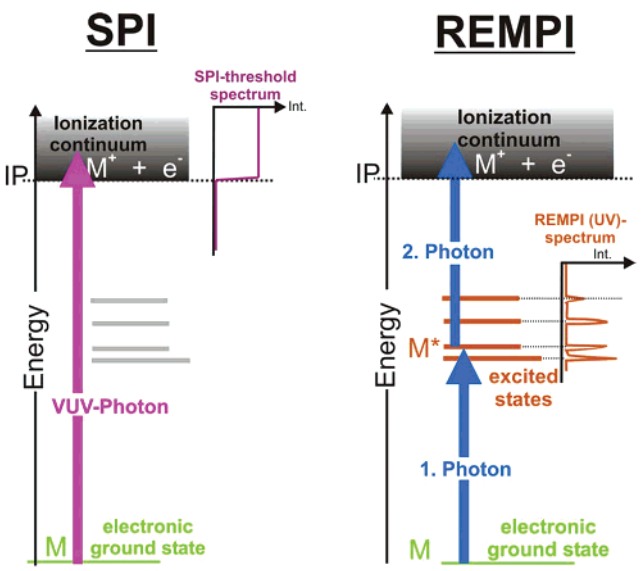

Figure 1. Schematic representation of the REMPI and the SPI ionization process.

REMPI-TOFMS characterizes each detected compound along three dimensions—optical absorption, ionization potential, and mass. This is in most cases sufficient for identification. Due to typically low excess energies upon REMPI ionization, fragmentation can be largely avoided.

REMPI introduces selectivity into the ionization process via the optical absorption properties of VOCs. Molecules absorb a first photon and are excited into a UV-spectroscopic transition state. Absorbing a second photon subsequently ionizes these excited molecules. For a selective and efficient REMPI, the following three conditions have to be fulfilled. (i) UV-spectroscopic condition: The molecule has an UV-active excited state, whose energy corresponds to the energy of the laser photon (resonance condition). (ii) The lifetime condition: The excited state has a lifetime that is long enough for absorbing a second photon for ionization. (iii) Ionization energy condition: The energy of two photons is equal to or higher than the ionization energy of the molecule.

In this study, a home-built mobile device was used (Figure 2), consisting of a reflectron-TOFMS analyzer, an effusive beam inlet system, and a built-in laser operated at two fixed wavelengths—248 and 266 nm (Continuum Nd:YAG laser Surelight, 266 nm; Lambda Physik excimer laser Minex, 248 nm).[33]

VUV-SPI uses vacuum ultraviolet photons to ionize VOCs in a single-photon absorption process. In the present work, 118-nm VUV laser pulses (10,5 eV) were used. Laser VUV photons can be generated by frequency tripling UV laser pulses in a rare gas cell.[42] In contrast to REMPI, SPI only depends on the ionization energy of the compounds, i.e., only those compounds are ionized that have an ionization potential lower than the photon energy. Since many VOCs of coffee have ionization thresholds below 10.5 eV (~118 nm), SPI at118-nm ionization shows little selectivity. The SPI spectrum gives an overview of the most abundant VOCs present in the coffee roast gas. Yet, major constituents of the roast gas, CO_2, N_2, and other inorganic species as well as small aliphatic organic compounds (e.g., methane) are suppressed due to their high ionization potential. In contrary to REMPI carbonyl compounds, furan derivatives and some heterocyclic compounds dominate the mass spectra. Due to the relatively low excess energy upon ionization, the SPI spectrum (similar to the REMPI) shows predominately parent mass ions. The assignment of VOCs in the SPI spectrum is based on the molecular mass, their abundance in coffee as reported in the literature,[43] and their ionization energy.

The SPI-TOFMS measurements were performed on a home-built mobile instrument that consists of a compact linear reflectron-TOFMS analyzer, an effusive gas inlet, and a special laser system.[42] The laser system contains a fixed-wavelength laser (Continuum Nd:YAG laser Minilite II, 1064 nm) and nonlinear optical elements (frequency-doubling crystals, frequency-mixing crystals). Furthermore, the instrument is equipped with a special rare gas cell for frequency tripling to generate VUV laser pulses.[42]

Data acquisition and analysis for both instruments are performed via 250-MHz transient recorder units (Acqiris, DP110 on PC). The acquisition rate for mass spectra is 10 Hz. Data acquisition and analysis are performed with a homemade software package using LabView.

(B) Setup of the Coffee Roasting Experiments. We used two different roasting setups for this study. The first setup was a closed steel cylinder in which coffee beans were placed and roasted on a hot plate. After the cylinder was preheated to 200 °C, it was filled with green coffee beans and sealed with a preheated steel top. The top contained steel pipes for sampling and ventilation. The sampling pipe was directly connected to the sampling unit of the TOFMS, and the roast-gas was analyzed at 10 Hz by REMPI at 248 nm. In a first series of experiments, 20—30 beans were roasted. A second series of trials was performed at high roasting temperatures with just 4—5 beans, and with the sampling capillary directly placed above the beans in the cylinder. First results using this simplified roasting setup were published in ref 28.

The second roasting setup was a laboratory-scale commercial roaster (Probat, BRZ 2, Figure 2b), consisting of two identical rotating drums that can be heated separately. The temperature was adjusted by regulating the heating current and the flow of air through the drum. Beans were roasted at three temperatures (200, 225, and 250 °C, respectively). For each experiment, a charge of 80 g of green arabica beans was filled into the drum and roasted for 950, 600, and 450 s, respectively, according to the applied roasting temperature. Beans were roasted up to a very dark roast and the roaster off-gas was analyzed on-line by REMPI at 266 nm and SPI at 118 nm, respectively.

To assess the roast degree, roasting was interrupted at different times, the beans were rapidly air-cooled, and their weight loss

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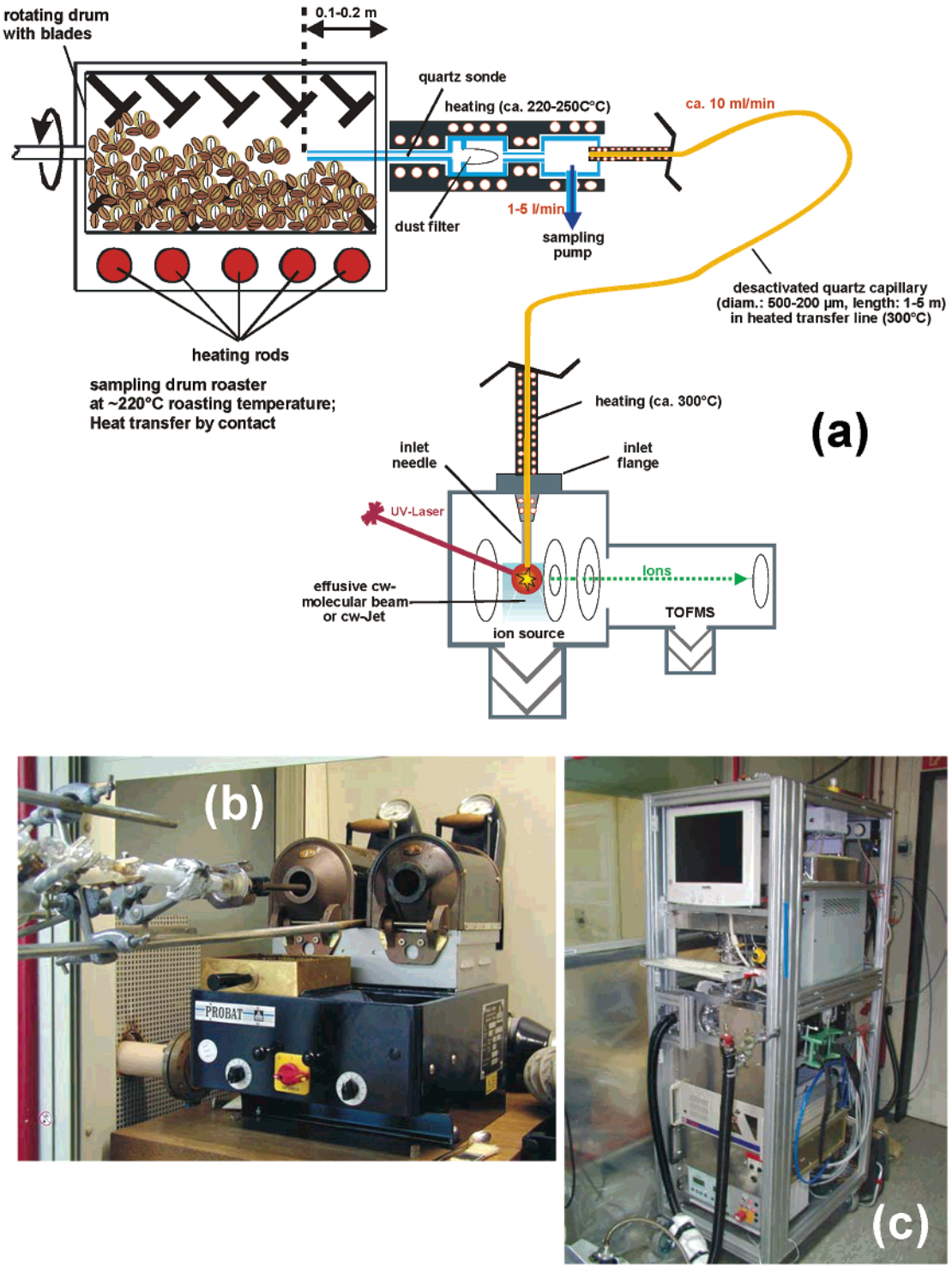

Figure 2. (a) Schematic representation of the laboratory-scale coffee roasting unit with sampling unit and laser mass spectrometer. (b) Photograph of the laboratory-scale coffee roasting and sampling unit. (c) Photograph of the laser mass spectrometer.

was measured. The roast degree was estimated based on total weight loss.[6] In addition, roast degree was estimated by color comparison to whole beans of known roast degree. The two different modes of assessment of roast degree gave consistent results. Finally, the temperature inside the roaster was measured. Roast level was differentiated into light roast, medium roast, dark roast, and overroasted.

(C) On-Line Sampling Technique for Coffee Roasting Off-Gas. A crucial part of the instrument is the sampling system (Figure 2). On-line analysis of VOCs requires minimizing condensations of low-volatile compounds and of coffee oil along the sampling line, to avoid memory effects and obstruction of the capillary inlet. Therefore, it is necessary to heat the sampling line to ~250 °C. Special care was taken to avoid cold spots.

The transfer line from the roaster to the ion source of the TOFMS consists of a deactivated quartz glass capillary. For the roasting experiments in the steel cylinder, a glass tube is

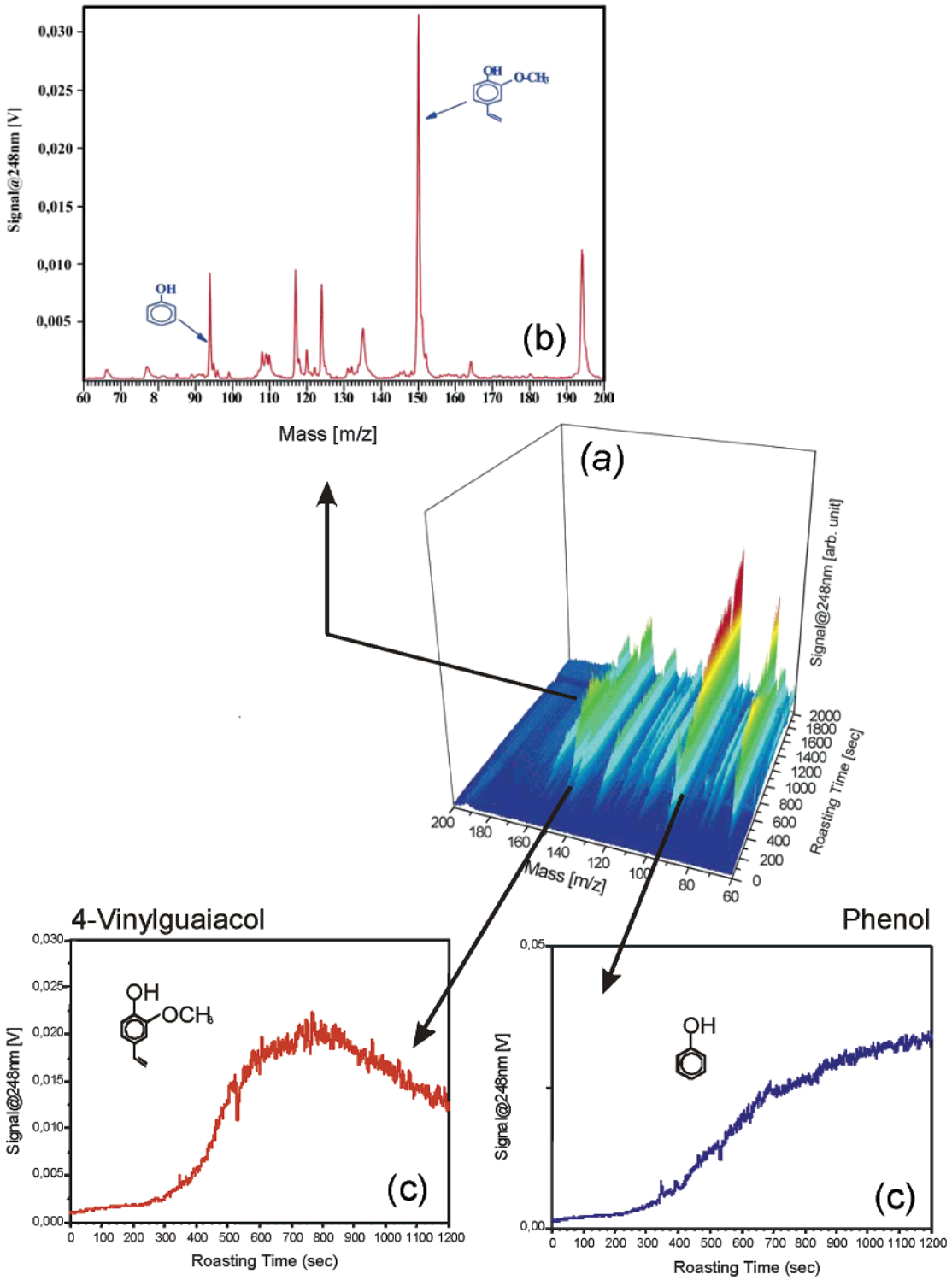

Figure 3. (a) 3D REMPI at 248 nm TOFMS mass spectrum of coffee roasting off-gas while roasting in a steel cylinder at 200 °C. The three dimensions are mass, time, and intensity. (b) Cross section of (a) at a fixed time, corresponding to a mass spectrum at 12 min after begin of roasting. (c) Time−intensity REMPI at 248 nm TOFMS profiles of phenol (*m*/*z* 94) and 4-vinylguaiacol (*m*/*z* 150), corresponding to two cross sections from (a) at fixed masses.

connected to the stainless steel outlet of the cylinder. The off-gas is drawn into the MS by a constant flow rate of 10 mL/min through a quartz capillary (inner diameter 0,32 mm) whose tip is situated in the center of the tube.

In the experiments with the Probat roaster, a quartz tube with an inner diameter of 10 mm reaches ~5 cm into the rotating drum. A constant off-gas sampling stream of 1,5 L/min is pumped through the sampling system. A quartz wool paper filter is integrated into the tube to prevent the capillary inlet system from solid contaminations such as dust or silver skins. Behind the filter, the tip of the quartz capillary is set in the center of the tube, sampling 10 mL/min into the MS.

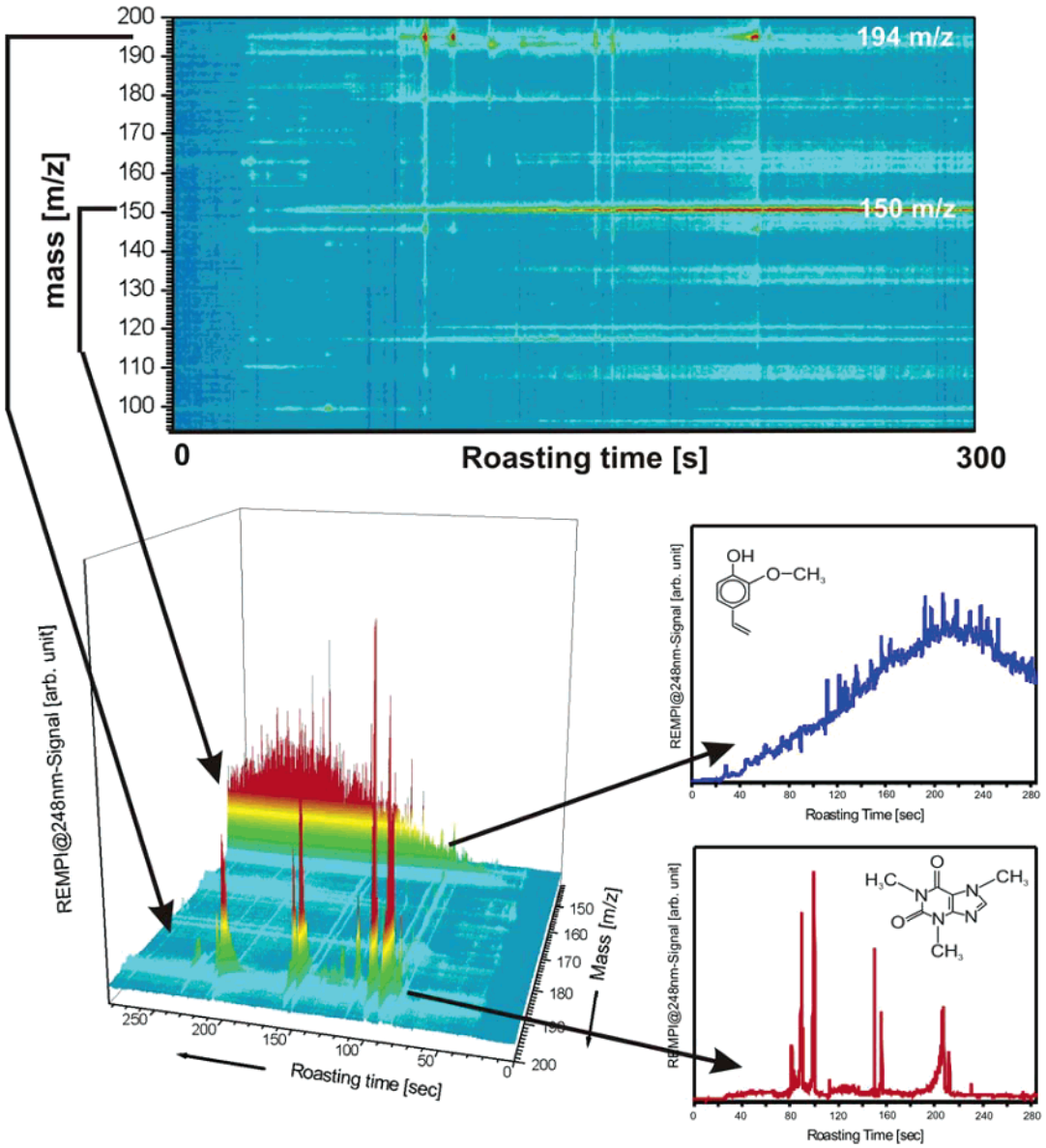

Figure 4. Effects of popping of coffee beans during the roasting process shown on REMPI at 248 nm TOFMS. Roasting of only a few green coffee beans (4−5 beans) was performed in a steel cylinder, at high temperature (400 °C): (a) 3D plot representation for the high-mass range *m*/*z* 140−200; (b) time profiles of the REMPI-TOFMS signal intensity of 4-vinylguaiacol (*m*/*z* 150) and caffeine (*m*/*z* 194), showing the burst emission of caffeine due to the rupture of the beans during popping.

RESULTS

(A) Roasting Simulations in the Heated Steel Cylinder. Figure 3a shows a full 3D representation—mass, time, intensity—of a typical roasting process at 200 °C, recorded at 10 Hz by REMPI at 248 nm. Characteristic cross sections through the 3D surface are given in Figure 3b and Figure 3c. Figure 3b gives a cross section of the roast gas composition at a fixed time (~12 min). In Figure 3c, two cross sections at fixed masses *m*/*z* 94 and 150 are shown, corresponding to *t*−*I* profiles of phenol and 4-vinylguaiacol. The assignment is based on the mass and optical absorption characteristics of the compounds.[17,28,30]

In a second set of experiments, just a few beans (4−5 beans) were roasted at high temperature (400 °C). Figure 4a shows a 3D plot of REMPI at 248 nm-TOFMS for the high mass range—*m*/*z* 140−200. Owing to the selectivity of the resonant ionization scheme, only two compounds appear in this mass range: 4-vinylguaiacol (*m*/*z* 150) and caffeine (*m*/*z* 194). Their *t*−*I* profiles are shown in Figure 4b.

(B) Roasting Experiments with the Laboratory-Scale Roaster. Figure 5a shows a typical REMPI at 266 nm mass spectrum while roasting at 225 °C. The laser power density is adjusted to 10^6−10^7 W/cm^2 to avoid nonresonant ionization processes or fragmentation. Figure 5b shows a SPI at 118 nm mass spectrum, recorded simultaneously with the data shown in Figure 5a (on alternating laser shots).

The assignment of the peaks is based on several criteria to ensure as far as possible correct identification of mass peaks. In the following, the single criteria are discussed in more detail:

Primarily, only compounds detected with conventional analytical methods are considered for peak assignment. Due to the soft and fragmentation-free ionization process, all mass peaks cor-

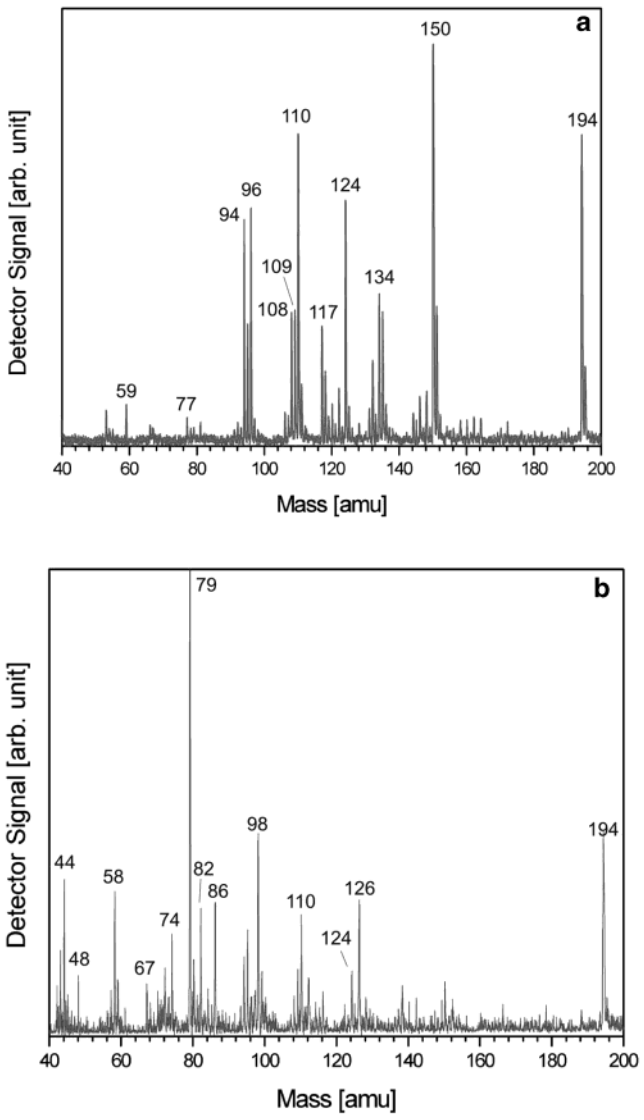

Figure 5. (a) REMPI-TOF (266 nm) mass spectrum of coffee roasting off-gas while roasting on the laboratory-scale coffee roasting unit. (b) SPI-TOF (118 nm) mass spectrum obtained on the same experiments as (a), by alternating the ionization laser between REMPI-TOF (266 nm) and SPI-TOF (118 nm).

respond to parent ions. The second step was the evaluation of the compound properties (ionization potentials and optical spectra) to verify whether the compound can be ionized with the applied technique. In the case of REMPI, for example, the ionization step is dependent on the optical properties of the compounds, meaning that only substances with suitable excited states can be ionized and readily be detected. Furthermore, data on the ionization efficiencies of compound classes were considered, as REMPI or SPI ionization efficiencies strongly vary for different substances. If there was more than one ionizable isobaric compound populating a nominal mass number in the mass spectrum, we used the data on the concentration of flavor compounds in coffee or coffee roasting gases one can find in the literature.[44] It came out that in most cases one single compound is responsible for the vast majority of the peak abundance at a given nominal mass, while other ionizable compounds are negligible. In this case, an assignation is justified. This procedure allows the determination of most of the peaks in the spectra. Accordingly, one has to admit that some mass peaks cannot be assigned to one single compound after this procedure. However, the main peaks present in the spectra, which are discussed according to formation pathways and are used for a statistical approach on determination of the roast degree can be assigned reliably due to the mentioned procedure and the comparison of their time behavior to data available in the literature (see Discussion).

Typical REMPI and VUV-SPI $t-I$ profiles are shown in Figure 6a and b, respectively. Furthermore, Figure 7 shows 3D plots of REMPI and SPI measurements to illustrate the differences between both measurement methods. Figure 6a shows the $t-I$ profiles of 4-vinylguaiacol (m/z 150), guaiacol (m/z 124), phenol (m/z 94), indole (m/z 117), furfural (m/z 96), and phenylacetaldehyde (m/z 120), ionized by REMPI at 266 nm, while Figure 6b presents methanethiol (m/z 48), 2-methylfuran (m/z 82), pyridine (m/z 79), and furfuryl alcohol (m/z 98), which were ionized by VUV-SPI at 118 nm.

Based on weight loss, color, and temperature measurements, the following calibration of the time axis in terms of roast degree (roasting at 225 °C) is obtained. At 200 s after the beginning of roasting, the beans reach ∼100 °C. The temperature does not increase appreciably until ∼300 s. During this initial stage of roasting, the coffee beans are mainly drying. The 10% moisture content of the green beans gradually reduces to ∼5%. At such low moisture contents, the temperature of the beans eventually takes off again. We see this happen at ∼300 s. After an additional 20 s, the beans reach a temperature of ∼170 °C. Pyrolysis reactions start, and the coffee roasting process becomes exothermic. A light roast is reached at ∼360 s. Extending the roasting beyond this point, a medium and a dark roast are reached at 400 and 450 s, respectively. Continuing the roasting even further, beans become overroasted.

(C) Principal Component Analysis for Process Control. The main objective of this research is to explore novel means for real-time process control of coffee roasting. For this purpose, we monitor the temporal evolution of a series of mass signals and analyze these via techniques for pattern recognition to track the progress of coffee roasting. In this work, multivariate statistics was applied for data reduction. This procedure is particularly appropriate when one aims at extracting and approximating relations and correlations included in large data sets. In many aspects PCA forms the basis for such multivariate data analysis.[45,46] In coffee research, PCA has been applied for several purposes. For example, different coffee varieties and blends could be distinguished based on their chemical composition (polyphenols, amino acids, caffeine, and several aroma components).[47,48]

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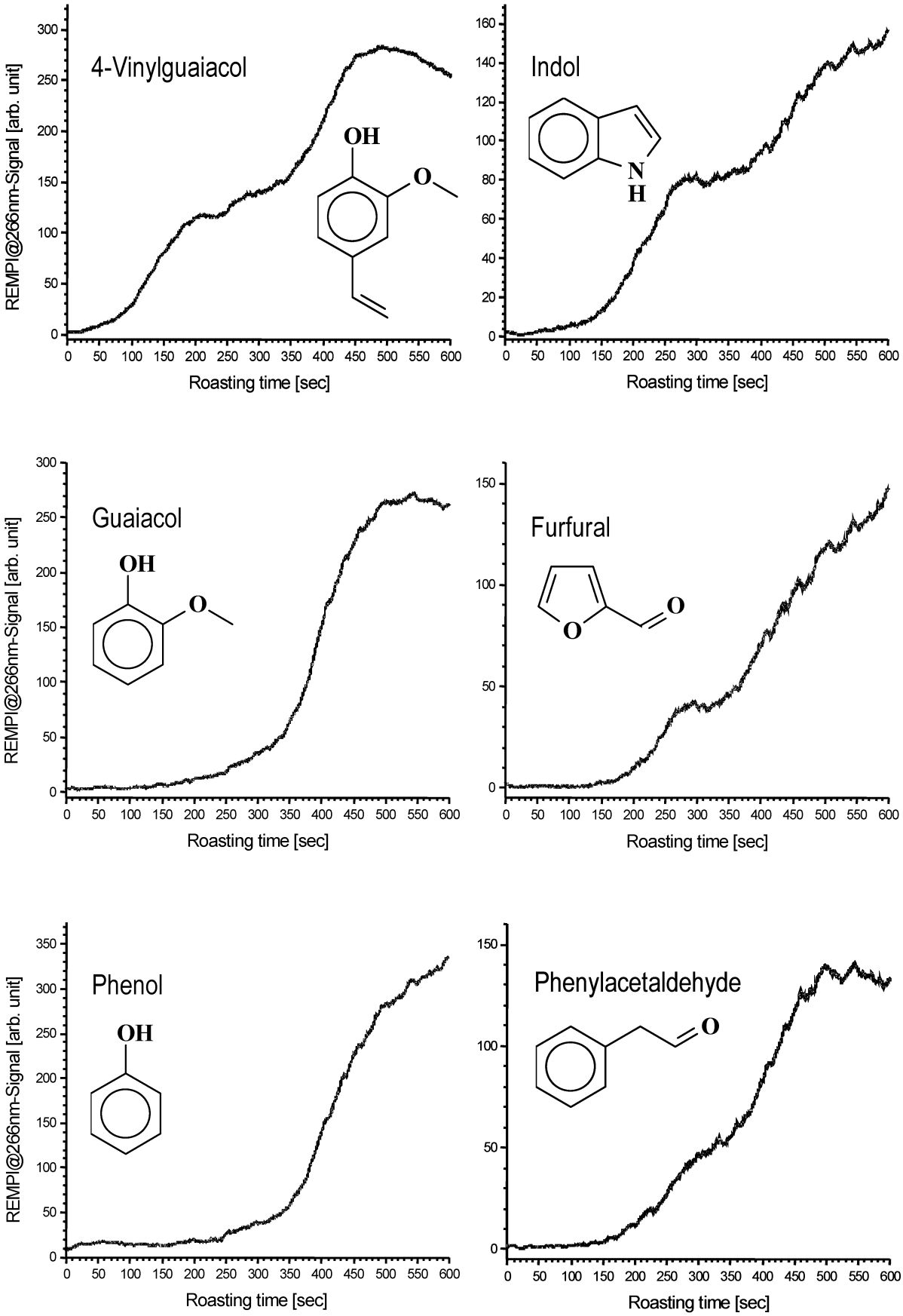
a


4-Vinylguaiacol
OH
O
Indol
N
H
Guaiacol
OH
O
Furfural
O
O
Phenol
OH
Phenylacetaldehyde
O
REMPI@266nm-Signal [arb. unit]
Roasting time [sec]

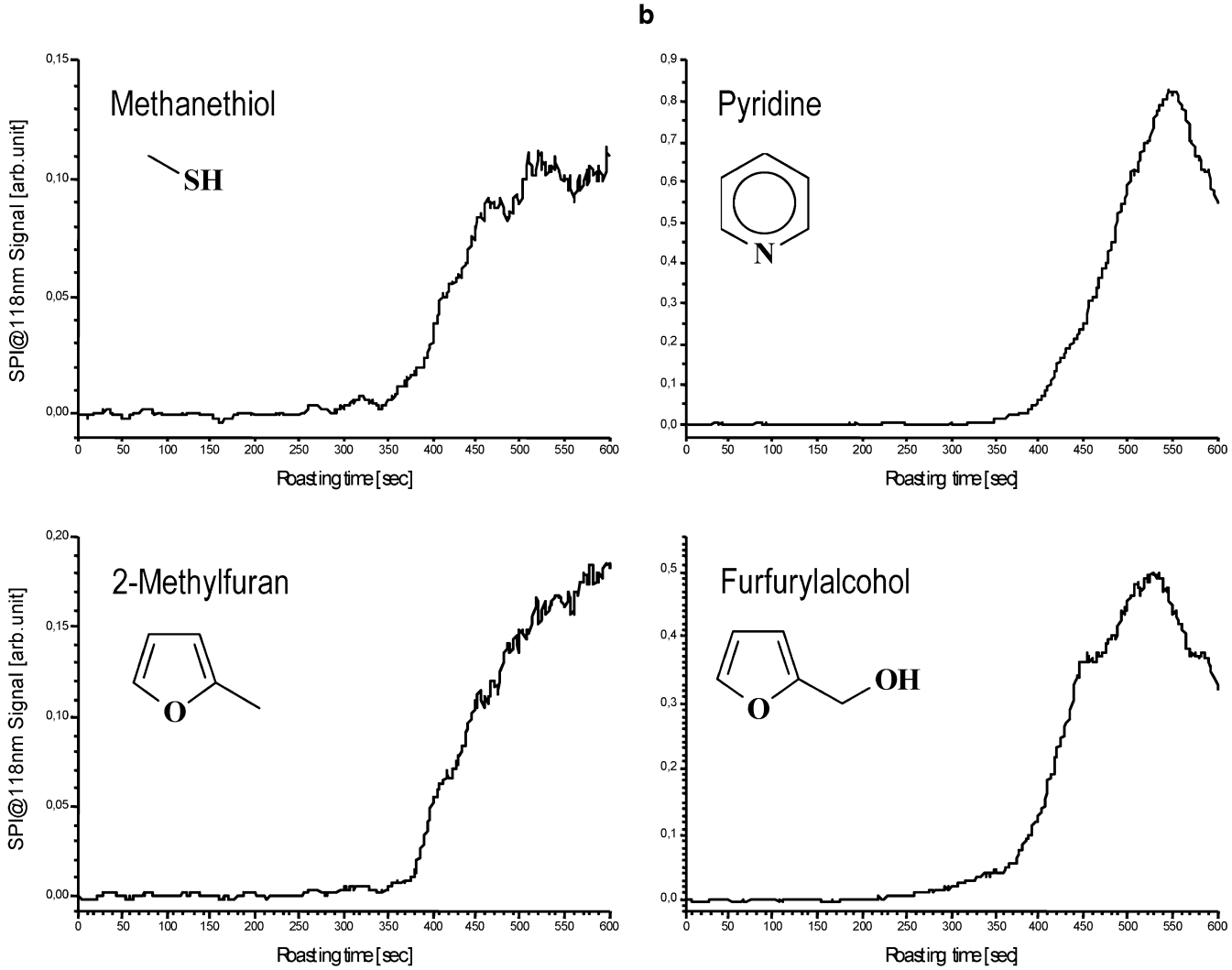


Figure 6. (a) REMPI at 266 nm TOFMS time profiles of six selected compounds: 4-vinylguaiacol (*m*/*z* 150), guaiacol (*m*/*z* 124), phenol (*m*/*z* 94), indol (*m*/*z* 117), furfural (*m*/*z* 96), and phenylacetaldehyde (*m*/*z* 120), during a roasting experiment on the laboratory-scale coffee roasting unit at 225 °C. (b) SPI at 118 nm TOFMS time profiles of four selected compounds: methanethiol (*m*/*z* 48), 2-methylfuran (*m*/*z* 82), pyridine (*m*/*z* 79), and furfural (*m*/*z* 96), during a roasting experiment on the laboratory-scale coffee roasting unit at 225 °C. The SPI profiles were recorded simultaneously with the REMPI profiles, by alternating the laser pulses during the same roasting trials.

Here we examine whether *real-time PCA* may apply to process monitoring and ultimately develop into a tool for process control.

In Figure 8, contour plots for three REMPI at 266 nm roasting experiments are shown, performed at three different temperatures; 200, 225, and 250 °C. While the mass range is identical for all three plots, the time axes have been adjusted to roughly reflect the respective roasting degrees. At 200 °C, a medium roast was reached after ~800 s. A similar roast degree was reached already after ~500 s for roasting at 225 °C and 400 s at 250 °C.

Contour plots give an overview of the 3D data space but are less suited for process control purposes. To monitor in real time the roasting process, a small number of mass traces were selected either because they show characteristic temporal profiles or because the corresponding compounds are known to be indicators of the roast degree. The PCA was carried out on REMPI at 266 nm data, based on 9 $t-I$ mass traces (see Table 3), and 13 roasting experiments at three different temperatures (6 experiments at 200 °C, 6 at 225 °C, and 1 at 250 °C), using the program package CharmWorks99 3.0 for Windows.

For PCA analysis, the $t-I$ profile at the nine selected masses were subjected to a data reduction and normalization procedure that allowed simplifying the data set and improving the resolving power of the results. The $t-I$ profiles of each of the 9 compounds listed in Table 3 (and the 13 roasting experiments) were subdivided into time intervals of 30 s to obtain a consistent time scale. For each of these time intervals, the average signal intensity was determined. As roasting time varied with roasting temperature (200, 225, and 250 °C), we obtained 30, 20, and 15 intervals of each 30 s, for the three different roasting temperatures.

To focus on deviations relative to the general trend of the $t-I$ curves, each average value was weighted statistically by taking the ratio of the measured average signal (30-s average) over the sum of the averaged signal of all nine mass variables of a given experiment. Therefore, for each compound i in the time interval j, a new variable was obtained according to

$$y_{i,j} = \mathrm{x}_{i,j} / \sum_i x_{i,j}$$

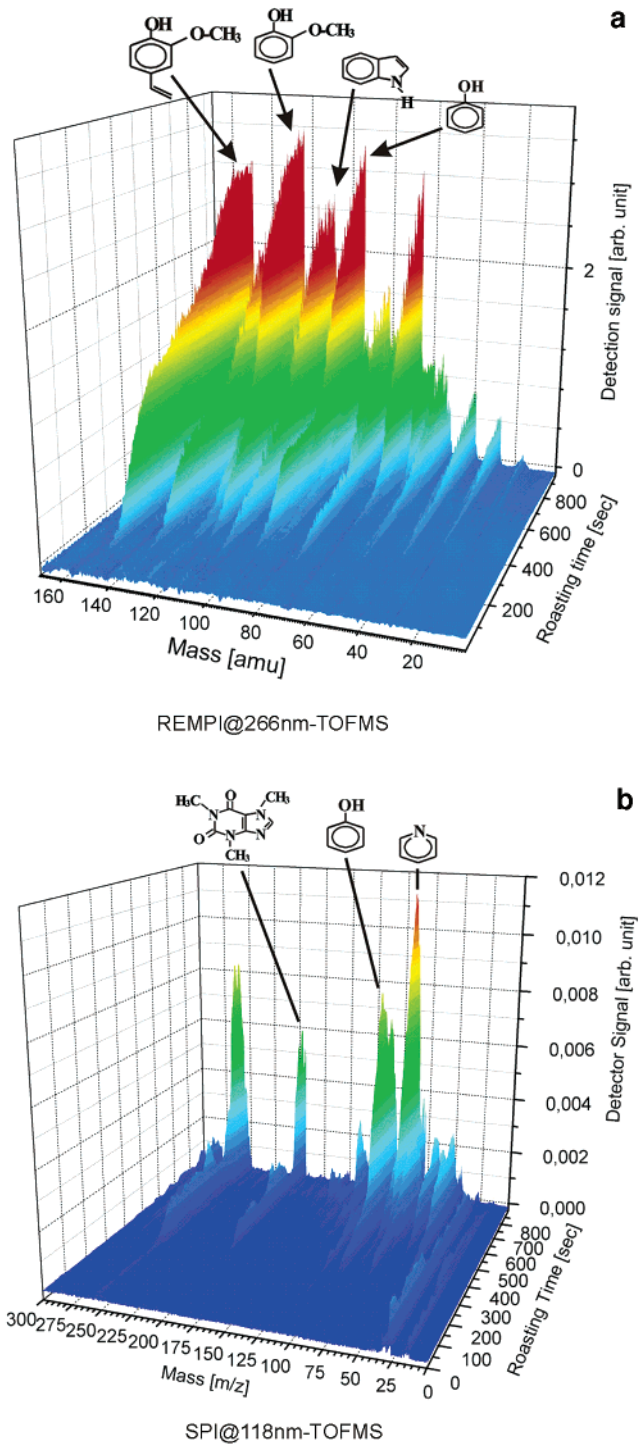


Figure 7. (a) 3D representation of the a REMPI at 266 nm TOFMS measurement sequence from a experiment with the laboratory-scale coffee roasting unit at 225 °C. (b) 3D representation of a SPI at 118 nm TOFMS measurement sequence from an experiment with the laboratory-scale coffee roasting unit at 225 °C.

where $y_{i,j}$ represents the new variable for each compound i in the time interval j and $x_{i,j}$ represents the averaged variables over the actual $t-I$ profiles. The number of variables corresponds to the number of chosen compounds as summarized in Table 3. The number of cases resulting in the scores on the score plot is derived from the sum of all time intervals derived from all measurements as is given in Table 4.

The loadings plot (Figure 9a) shows the different influence of the mass variables on the two first principal components, which account for 68% of the total variance of the data set. The nine selected compounds, identified by their respective masses, are projected onto the surface of the two most significant principal components PC1 and PC2. The fact that the nine compounds are well distributed over the PC1−PC2 surface denotes that they each have a different/complementary influence on the $t-I$ pattern of the roasting process and underlines their usefulness as indicators of the roast degree (nonredundant variable with high resolving power). While guaiacol (m/z 124) and 4-vinylguaiacol (m/z 150) have an (opposite) influence only on PC1, phenol (m/z 94), indol (m/z 117), and furfural (m/z 96) show a strong influence on PC2.

Figure 9b shows the score plot obtained for the first two principal components derived from the 13 roasting experiments. The scores belonging to roasting at 200 °C are marked as squares, those belonging to 225 and 250 °C, as circles and triangles, respectively. Thin lines connect scores belonging to the same roasting experiment. Taking this information in account, the score plot can be readily interpreted (see Discussion).

DISCUSSION

(A) Tuning the Selectivity in Fixed-Frequency Laser Ionization. The main objective of this work is to develop a method that allows monitoring on-line the flavor formation process of coffee during roasting. Ultimately this shall lead to an on-line process control tool to modulate and optimize the development and final quality of coffee flavor.

Since hundreds of VOCs are present in the headspace of coffee, selective laser ionization helps filtering specific VOCs out of the complex headspace distribution and identifying compounds by their optical absorptions and mass. The selectivity can be adjusted by varying the temperature of the molecules and tuning the laser wavelength. Here, the VOCs have the same temperature for all experiments (effusive inlet, room temperature). The selectivity was adjusted by ionizing at three different fixed wavelengths: 266, 248, and 118 nm.

Temperature. The molecule's temperature, which itself depends on the particularities of the inlet system, determines the ground-state population.[17;30] Here, an effusive molecular beam is used (no cooling) in all experiments, where a range of rotational and vibrational states are populated, resulting in broad absorption bands. Consequently, a whole substance class may be ionized at a given laser wavelength, due to overlapping absorption bands.

Wavelength. Three different ionization wavelengths were used. Comparing REMPI at 248 nm with REMPI at 266 nm, we see little differences in selectivity, although sensitivities (ionization cross sections) vary to some extent. In contrast, a different set of compounds is seen by SPI at 118 nm. To illustrate these differences, panels a and b in Figure 7 show 3D plots of REMPI at 266 nm and VUV-SPI at 118 nm of coffee roast-gas while roasting at 225 °C. In the following we discuss in more detail differences of ionization efficiencies at the three respective laser wavelengths.

248 nm. Figure 3a shows a REMPI at 248 nm TOFMS of coffee being roasted in a heated cylinder at 200 °C. Only aromatic and heterocyclic VOCs (mostly with molecular masses larger than m/z 100) are ionized at 248 nm. Nonsubstituted aromatic compounds dominate the spectrum (Table 1). In contrast, many

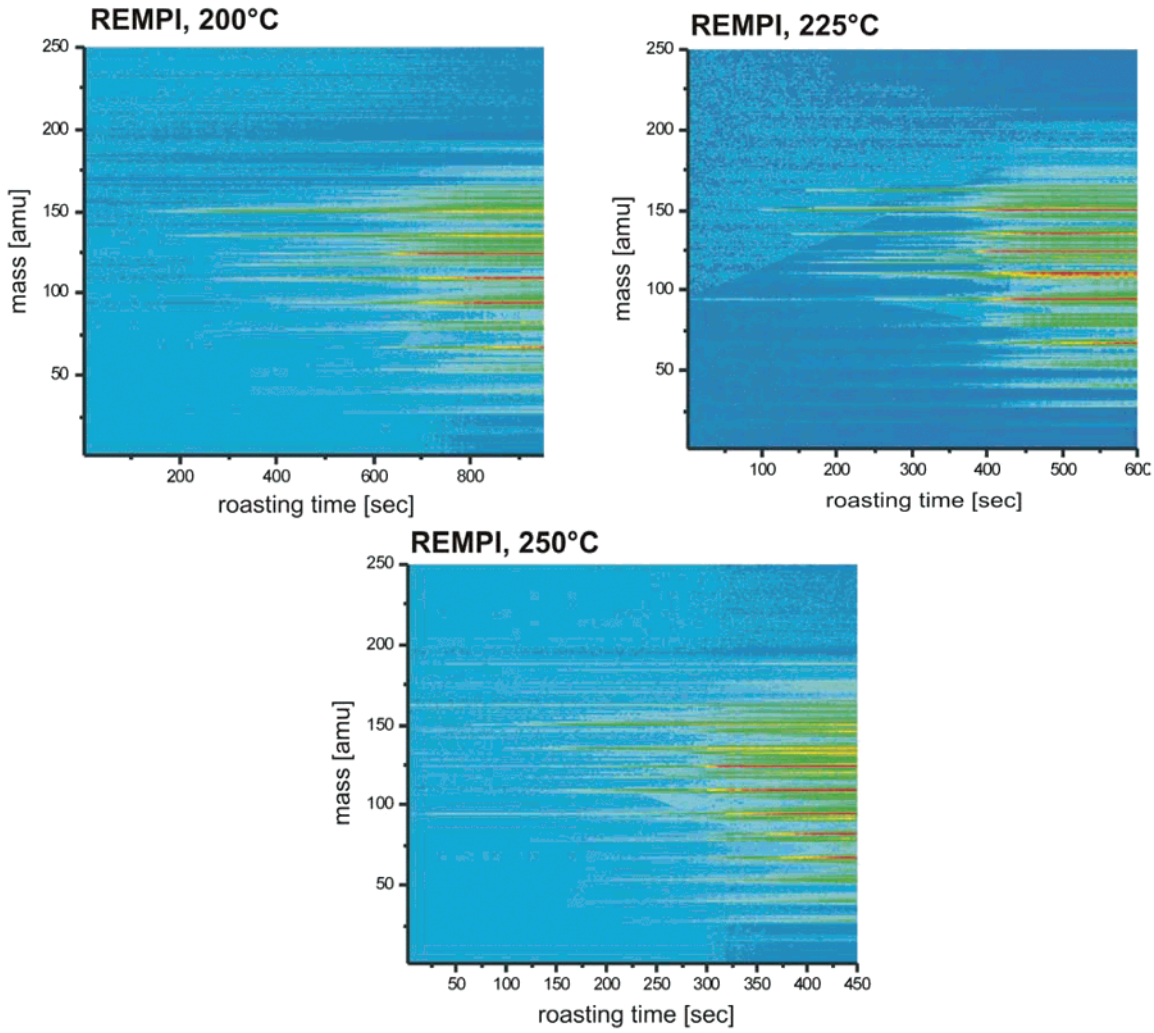


Figure 8. Contour plots of three REMPI-TOFMS experiment on the laboratory-scale coffee roasting unit, performed at different temperatures (200, 225, and 250°C). Note the different time scales for the plots.

substituted aromatics do not absorb and are hence absent from the spectrum. Several of these VOCs are known to contribute to coffee aroma or have formation pathways in common with aroma compounds.[15]

266 nm. Ionizing at 266 nm, we observe mostly the same compounds as at 248 nm, but relative intensities may vary between the two wavelengths. Figure 5a shows a REMPI at 266 nm TOFMS while roasting at 225 °C. As a general observation, we can state that phenolic compounds dominate. Some of these compounds are odor impact compounds of coffee, namely, guaiacol (m/z 124) and 4-vinylguiacol (150 m/z). Further, phenol (m/z 94), cresols (m/z 108), benzenediols (m/z 110), and dimethylphenols (m/z 122) are also detected. In addition to some styrene derivatives, heterocyclic compounds such as furfural (m/z 96) and indole (m/z 117) are detected. At some masses more than one aromatic/heterocyclic compound can potentially contribute to the MS signal. However, in most cases, one compound strongly dominates the mass spectral intensity. Compounds that can be assigned in the REMPI at 266 nm TOFMS are listed in Table 1.

118 nm. Figure 5b shows a SPI at 118 nm mass spectrum. The SPI spectrum contains, similar to the REMPI spectrum, predominately molecular mass peaks. Since many VOCs in the headspace of coffee have ionization thresholds below 118 nm, SPI at 118 nm shows limited selectivity. We mainly see the VOCs that are most abundant in the headspace. In addition to carboxylic compounds such as acetaldehyde (m/z 44), acetone (m/z 58), diacetyl (86 m/z), and pentanedione (m/z 100), nitrogen-containing heterocyclic compounds such as pyridine (m/z 79) and pyrrole (m/z 67) as well as alcohols (e.g., furfuryl alcohol, m/z 98) and methanthiol (m/z 48) are also observed. Table 1 gives the assignments of the compounds detected by VUV-SPI. Isobaric compounds, ionized at SPI at 118 nm are listed in the order of their expected abundances, according to literature. Clearly the VUV ionization scheme allows detecting a series of VOCs (mainly the most volatile and abundant compounds of molecular mass below m/z 100) that cannot be ionized by REMPI. Combining the compounds ionized by resonant and single-photon ionization, ~30 VOCs are monitored in real time.

(B) Time−Intensity Profile. Based on the VOCs listed in Table 1, we selected 10 compounds (listed in Table 2), whose $t-I$ profiles are shown in Figure 6. They represent molecules from different compound classes which are either directly related to the coffee aroma or have formation pathways believed to be analogous to flavor compounds.

Table 1. Assigned Compounds in Coffee Roasting Off-Gas from REMPI Spectra at 248 nm and at 266 nm and from SPI Spectra at 118 nm[a]

mass (m/z)	assignment for REMPI at 248 nm	assignment for REMPI at 266 nm	suggested assignment for SPI at 118 nm
44			acetaldehyde
48			methanthiol
58			acetone, propanal
59		propylamine	
67			pyrrole
72			butanone, butanal
74			butanol
79			pyridine
82			methylfuran
86			2,3-butadione, pentanone, pentanal
94	phenol	phenol	phenol, methylpyrazin
96	furfural	furfural	
98			furfuryl alcohol
100			2,3-pentanedione, hexanone, hexanal
108	cresols	cresols	
110	dihydroxybenzene	dihydroxybenzenes	dihydroxybenzenes
112			methylfurfural
117	indol	indol	
118		methylstyrenes	
120	2-phenylacetaldehyde	phenylacetaldehyde	
122		dimethylphenols	
124	guaiacol	guaiacol	
126			(dimethylfurfural and others)
131	skatol		
132		dimethylstyrene	
135		methyl-loss from 4-vinylguaiacol	
150	4-vinylguaiacol	4-vinylguaiacol	
152	4-ethylguaiacol		
194	caffeine	caffeine	caffeine

[a] Typical spectra are shown in Figure 5. The assignment in REMPI is based on the literature of volatile coffee compounds, their mass, and their optical absorption (when available). Assignment in SPI spectra is based on the literature of volatile coffee compounds, their mass, and the ionization potential (when available). Since optical absorption is a much stronger criterion for identification than ionization potential, we are confident about the assignments in REMPI, while assignments in SPI are considered as tentative.

Kinetic data on the evolution of odorous VOCs during roasting are rare. Some groups investigated the evolution of coffee VOCs during roasting by off-line GC analysis.[8,49,50] Recently we reported on the on-line analysis of coffee roasting by PTR-MS.[9,51] Finally, on-line experiments of coffee roasting using laser ionization were published.[17,28,30,34]

4-Vinylguaiacol, Guaiacol, and Phenol. The formation and chemistry during roasting of these three phenolic compounds was recently discussed in a separate paper, and only a brief account will be given here.

Chlorogenic acids (CQAs) degrade during roasting,[7,8,13,52−62] to form mainly nonvolatile compounds known as melanoidins, and to a minor fraction (1−5%), phenolic VOCs.[63,64] Model experiments by Tressl indicate that one particular group of CQA, the feruloyl quinic acids (FQA), leads to the formation of guaiacol and 4-vinylguaiacol.[7] FQA hydrolyses to form ferulic acid, which in turn decarboxylates to 4-vinylguiaicol. Oxidation of 4-vinylguaiacol leads to guaiacol, which can further react during roasting to form phenol and other phenolic VOCs.[13]

A few groups have reported kinetic data on the formation of 4-vinylguaiacol, guaiacol, and phenol.[8,17,34,34,49,50] In Figure 6a, we observe 4-vinylguaiacol already forming during the first 200 s of roasting at a relatively high rate, while guaiacol and phenol are hardly formed. During this phase, the bean temperature increases steadily from room temperature to ∼100 °C. The formation rate then slows down, reflecting the slower temperature increase during bean drying. At 300 s, the beans approach a moisture content of ∼5%,[4] and the bean temperature rises again, driving the formation rate of 4-vinylguaiacol. It is only once roasting enters the exothermic phase that guaiacol and phenol appear in ap-

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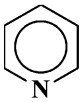
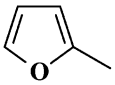
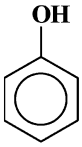
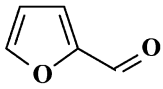
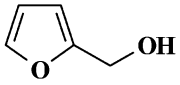
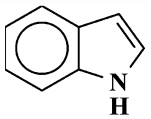
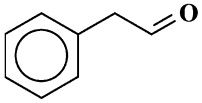
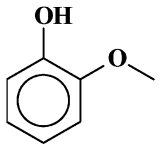
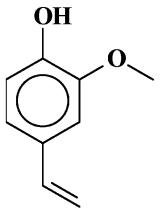
Table 2. List of Compounds from Which *t*−*I* Profiles Were Recorded Using Either REMPI (at 248 nm or at 266 nm) or SPI (at 118 nm)[a]

Name	Mass	Flavour description	Method	Formula
Methanethiol	48	strongly sulphurous, typical mercaptan, somewhat roasted on dilution, decomposing cabbage	Probat/SPI@118nm; 225°C	
Pyridine	79	putrid, narcotic, gasoline-like, somewhat fishy	Probat/SPI@118nm; 225°C	
2-Methylfuran	82	mild ethereal, somewhat gasoline and burnt	Probat/SPI@118nm; 225°C	
Phenol	94	strongly phenolic, medicinal, antiseptic	Cylinder/REMPI@248, 200°C & Probat/REMPI@266; 225°C	
Furfural	96	sweet caramel-like, nutty, baked bread, almond	Probat/REMPI@266; 225°C	
Furfuryl-alcohol	98	burnt, sweet, caramellic, warm oily, brown	Probat/SPI@118nm; 225°C	
Indol	117	animalic, cheese, slightly faecel on dilution, but also floral	Probat/REMPI@266; 225°C	
Phenylacet-aldehyde	120	Floral(hyacinth), honey-like with a sweet waxy nuance	Probat/REMPI@266; 225°C	
Guaiacol	124	aromatic, phenolic, burnt, sweet	Probat/REMPI@266; 225°C	
4-Vinylguaiacol	150	aromatic, spicy, somewhat phenolic	Cylinder/REMPI@248, 200°C & Probat/REMPI@266; 225°C	

[a] Roasting was performed either in a heated cylinder or a laboratory-scale Probat roaster. The experimental conditions are indicated in the "method" column. The corresponding data are shown in Figures 3 and 6. The flavor descriptors are from ref 73.

preciable amounts in the roaster off-gas. From a light to a dark roast, all three VOCs continue to increase. The compound that starts to decrease first is 4-vinylguaiacol. It reaches a maximum at a dark roast and falls off at longer roasting time. Next we

Table 3. Variables ($t-I$ Mass Profiles from the REMPI at 266 nm) Included in the Statistical Data Treatment by PCA

mass peak (m/z)	assignment
59	propylamine
94	phenol
96	furfural
110	benzenediol
117	indol
120	phenylacetaldehyde
124	guaiacaol
150	4-vinylguaiacol
164	dimethoxystyrene

Table 4. Number of Cases Included in the Statistical Data Treatment by PCA[68,69]

type of roasting expt (roasting temp) (°C)	no. of measrmnts (sample roastings)	no. of time intervals/ measurmnt	no. of cases/roasting temp (n sample roastings × m time intervals)
200	6	30	180
225	6	20	120
250	1	15	15
total case no.			315

observe guaiacol to level off and eventually start decreasing. In contrast, the phenol signal continues to increase until the end of the roasting experiment.

Referring to Dorfner et al.,[34] Figure 10 schematically depicts the main steps that are proposed to be involved in the formation of 4-vinylguaiacol, guaiacol, and phenol. Degradation of 5-FQA, which is partially derivatized to lactone by intramolecular esterification, proceeds via two connected reaction channels. We label the first the "low activation energy" channel (endothermic phase). It dominates in the early stages of roasting, where bean temperature is low (below 120 °C) and moisture content high. It consists of ester hydrolysis of 5-FQA, followed by decarboxylation of the ferulic acid to form 4-vinylguaiacol, and finally polymerization at the vinyl group to form partly insoluble polymers (melanoidins). Whether some transitory intramolecular esterification (lactone formation) on the 5-FQA or some esterification of the ferulic acid unit occurs is unclear. Yet, as long as the temperature is below ~170 °C, we believe that the "low activation energy" channel represents the main sequence of reactions.

Once the beans have dried, the bean temperature rises. On one hand, this increases the rate of 4-vinylguaiacol formation (and probably of its polymerization). On the other hand, a new "high activation energy" channel opens up, shown in the bottom frame of Figure 8, which sequentially leads to guaiacol and phenol.

Indol. Very scarce information is available on the formation pathway and kinetics of indol during coffee roasting. It is known that enzymatic degradation of tryptophan leads to indol (as well as skatol m/z 131), and it is speculated that it can be generated by an analogous route via nonenzymatic (thermal) processes.[14,15] Silwar and Lüllman[14] measured the formation of indol during coffee roasting and reported that it appears in considerable concentrations at 170 °C and increases with roasting time. Furthermore, Viani and Horman pyrolysed serotonin and found that indol was formed among a whole series of alkylindoles and alkylindanes.[65] From the $t-I$ curve in Figure 6a, we see that indol is generated already at an early stage of roasting, indicating that its formation can be induced at relatively low temperatures. Whether indol is indeed formed from degradation of the amino acids tryptophan and serotonin and whether other pathways are relevant remains to be answered. The bimodal shape of the $t-I$ curve can be explained along two lines. Either it reflects the time–temperature profile of the beans during roasting or two distinctively different formation channels are superimposed.

Methanethiol. Various volatiles derived from Strecker degradations are important odorants in roasted coffee. α-Dicarbonyls, which are highly reactive intermediates generated in the course of the Maillard reaction, condense with free amino groups and amino acids forming α-aminoketones and Strecker aldehydes via transamination and decarboxylation. From methionine as a precursor amino acid, methional is formed, which is essential for roasted coffee flavor.[10] β-Elimination of methional gives the highly volatile methanethiol, which contributes to the pleasant aroma of freshly roasted coffee. Subsequent oxidation of methanethiol leads to dimethyl disulfide, which itself may disproportionate into dimethyl sulfide and dimethyl trisulfide. Hence, methanethiol is a key flavor compound of coffee as well as part of chemical reaction pathways, which include several other coffee flavor compounds (methional and dimethyltrisulfide).

Holscher and Steinhart have observed a steady increase of methanethiol formation during roasting.[66] In Figure 6b, we see methanethiol forming only once the beans have reached the exothermic phase. Following a fast increase, the methanethiol concentration levels out at longer times, similar to observations of Holscher and Steinhart.

Phenylacetaldehyde.. For phenylacetaldehyde to form, α-dicarbonyl, generated in the course of Maillard reactions, condenses with the amino groups of phenylalanine, yielding a Strecker aldehyde.[10] Transamination and decarboxylation then lead to phenylacetaldehyde, a compound contributing to the flavor of coffee. From the $t-I$ profile, we see that it forms already early in the roasting process and exhibits a formation profile that resembles the temperature profile of the process.

Pyridine. Next to caffeine, trigonelline is the most abundant nonprotein nitrogen compound in coffee beans. As discussed by several authors, trigonelline decomposes during roasting and a series of compounds form during its decomposition.[66,67] The second most important thermal degradation product from trigonelline (in weight) is pyridine, after nicotinic acid. Pyridine, which has a smoke/ashy odor is not considered to be an impact compound of coffee.[15] Pyridine is known to gradually increase during roasting. It has been reported that high levels of pyridine are rather detrimental to the coffee quality, and its presence is often associated with overroasted coffee. Gianturco reported a late increase of pyridine after the commercial roast degree had been reached.[50] Figure 6b shows that the formation of pyridine starts late in the roasting process. Once pyrolysis reactions have set in (from 350 s on), the pyridine level in the roast gas increases steadily until ~550 s. At this point, the pyridine level decreases again. Since trigonelline is the unique precursor of pyridine, we

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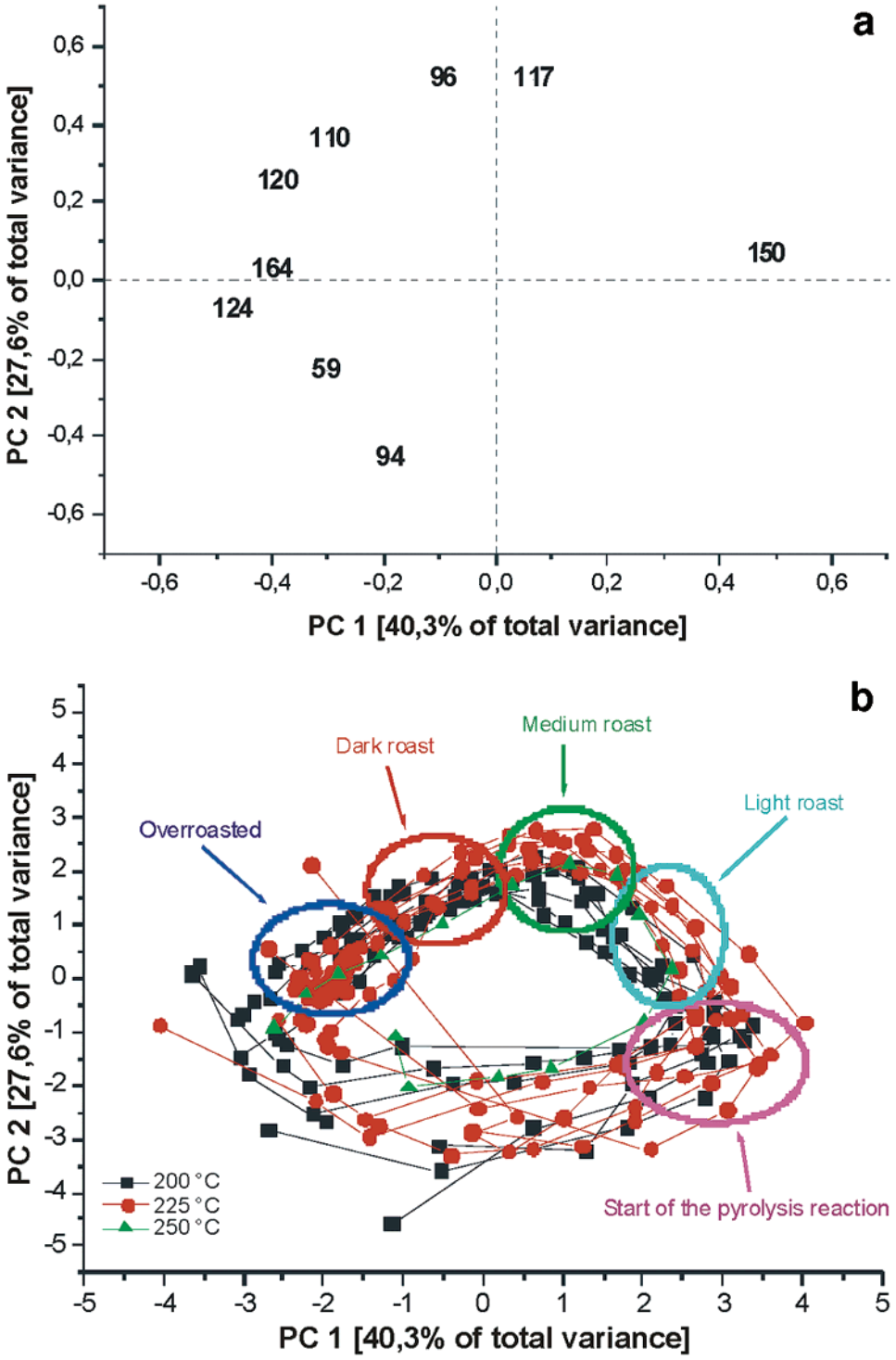

Figure 9. Statistical analysis of the *t*−*I* profiles of nine VOCs *m*/*z* 59, 94, 96, 110, 117, 120, 124, 150, and 164, from 13 roasting experiments with REMPI at 266 nm TOFMS. (a) PCA loading plot, showing the variance of the variables (i.e., the time behavior of the respective masses); (b) PCA score plot, showing the evolution of the roast degree as a circular trajectory on the PC1−PC2 surface.

may conclude that the decrease at dark roast indicates that the trigonelline pool has quantitatively reacted.

Methylfuran, Furfuryl Alcohol, and Furfural. Furans are among the most abundant VOCs of roasted coffee and are formed from decomposition and caramelization of monosaccharides and higher sugars. They have been quantified in coffee at a level of 100 ppm.[7,68−71] Furans per se are not considered coffee character compounds. Their significance stems from the fact that furans are involved in reactions that lead to the formation of several key coffee flavor compounds. For example, sulfur-containing amino acids react readily, forming sulfur derivatives of furans. Recently,

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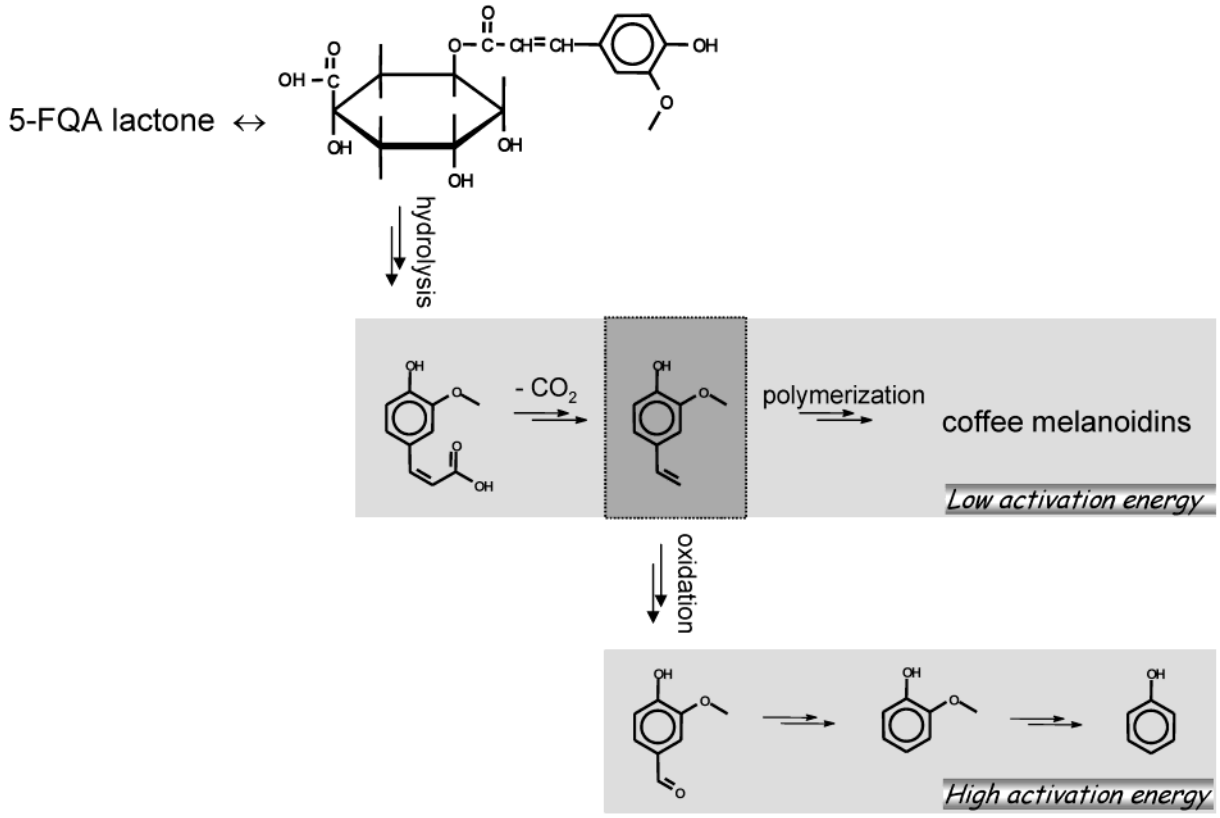

Figure 10. Postulated thermal degradation pathway of 5-feruloyl quinic acid and formation of phenolic compounds during roasting of coffee beans.

Hofmann and Schieberle postulated a formation pathway for furfurylthiol via furfural.[72]

The aforementioned results concerning concentration changes of several flavor compounds during coffee roasting in general agree with results found in the literature covering coffee flavor composition in dependence of the roast degree (see, for example, refs 50 and 54). Time profiles reported there, for example, for fufural, furfuryl alcohol, pyridine, and phenol as well as guaiacol and 4-vinylguaiacol, resemble the profiles we measured with on-line laser mass spectrometry. This shows that our technique is reliable in terms of the molecular information gained for distinct compounds. Furthermore, a much higher time resolution is achieved and thus the possibility to use this information for the purpose of an on-line process control.

(D) Popping of Caffeine in Single-Bean Experiments. Roasting just a few beans at elevated temperature (400 °C), we observed sporadic bursts of VOCs, which start ~100 s after begin of roasting. Bursts are accompanied by popping sounds. This is visualized in the REMPI at 266 nm 3D plot shown in Figure 4, where we focus on the high-mass range (m/z 140−200). Two compounds with strikingly different profiles dominate the 3D profile. These are 4-vinylguaiacol (m/z 150) and caffeine (m/z 194). While the $t-I$ profile of 4-vinylguaiacol is rather smooth, caffeine is sporadically released in short and intense bursts during individual popping (Figure 4b). Between the popping, caffeine is hardly detectable in the roast gas. The transient spikes in the caffeine signal have a width of only a few seconds, demonstrating the high time resolution of the REMPI-TOFMS method and in particular of the inlet system. Interestingly, these spikes are not visible on the 4-vinylguaiacol trace (m/z 150). For indol (m/z 117, not shown in Figure 4), some coincident spiking with caffeine is observed, thus being of considerably lower extent.

Popping is a consequence of the accumulation of mainly inorganic gases (CO_2, CO, N_2, H_2O) in closed voids inside the bean structure that are formed upon pyrolysis of organic green bean material. At high internal pressures, the bean structure ruptures, liberating abruptly entrapped gases. Owing to the high time resolution and sensitivity of REMPI-TOFMS, individual bursts of VOCs can be observed in real time. A similar observation was reported in on-line monitoring experiments of roast gas by PTR-MS, yet at a lower time-resolution.[51]

(E) Process Control via Real-Time Principal Component Analysis on a Set of Mass Traces. By monitoring several compounds that exhibit characteristic time−intensity profiles, it is possible to characterize the roasting process and to determine the roast degree of the beans. Due to individual reaction pathways and different time behavior of several compounds, the roast degrees can be distinguished according to the ratios of flavor-active compounds in the beans. For example, the ratio of phenol and 4-vinylguaiacol is discussed as marker for the roast degree.[7] With multivariate statistics, it is possible to extend this ratio information onto more flavor-active compounds and to achieve more precise information about the roasting degree.

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Due to the varying influence of the compounds/variables on the principal components, the roasting process shows a unique pattern in the PC1−PC2 plane. The progression of the scores on the score plot in a relatively narrow channel underlines these different influences of the indicator compounds. The early appearance of 4-vinylguaiacol in the roast off-gas (relative to other indicator compounds) shifts the scores to high values of PC1 (to the right on the PC1−PC2 plane). As roasting progresses, the relative weight of indole increases and shifts the scores back to the center of the PC1 axis. Later, guaiacol and even later phenol increase their respective weights, leading to a circular movement of the scores.

Since we can relate roasting time to roast level for all three roasting temperatures (see Experimental Section), it becomes possible to correlate the scores with the roast level. The different roast levels are grouped at different positions on the PC1−PC2 plane. The scores for light, medium, and dark roast can be distinguished as well as the area when the beans are burnt (overroasted). The roasting process follows a consistent path independent from the applied roasting conditions (temperature). At the very begin of the roasting process (still green beans), the scores show great variations. This is due to very weak signals at the beginning, when pyrolytic reactions begin. Therefore, small fluctuations in the signal intensities have a strong influence on the normalized variables. When roasting progresses and the signal intensities increase, the variability of the scores decreases and a clear path on the score plot appears.

Currently, only a rough subdivision of the roasting level is accomplished (light, medium, dark, overroasted). Yet, the resolution of the roast degree on the PC1−PC2 surface may be increased by adding more compounds from REMPI measurements as well as including VUV-SPI data (SPI data were not taken into account in this work). Note, that it is possible to record REMPI and SPI spectra simultaneously with one TOFMS instrument.[42] Also, one can define the roast degrees with higher precision by decreasing the time width of the time window for averaging the $t-I$ profile data (less than 30 s).

CONCLUSIONS

The objective of this work is to discuss a novel analytical approach that provides on-line, real-time information of the coffee roasting process. It is based on a primary quality criterion of coffee, the aroma, and takes into account the full time−temperature history of aroma formation during roasting.

We demonstrate that direct injection of roaster off-gas into a time-of-flight mass spectrometer, and ionization either by REMPI at 266 nm and at 248 nm or VUV-SPI at 118 nm, provide unique and complementary information on the progress of the roasting process. VUV-SPI ionizes the most abundant volatile compounds in the roast gas, mainly VOCs with molecular mass below m/z 100. In contrast, REMPI detects selectively aromatic compounds, most of which have molecular masses larger than m/z 100. Several of these compounds are important coffee aroma compounds.

While a total of 30 VOCs are detected by either resonant or single-photon ionization, the formation chemistry of 10 important coffee volatile compounds is discussed, based on measured time−intensity profiles.

For process control purposes, we apply PCA on the time−intensity traces of nine selected volatile coffee compounds and for a range of roasting temperatures (200−250 °C). The roasting degree can be traced as a consistent path on the score plot of the two most significant principle components (including 68% of the total variance).

Following up on these successful results on small-scale laboratory roasters, we recently performed successfully REMPI- and SPI-TOFMS measurements on large-scale, industrial coffee roasting facilities (capacity up to 1.5 t/h). The results of these measurements will be presented in a forthcoming publication.

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