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Evidence of different flavour formation dynamics by roasting coffee from different origins: On-line analysis with PTR-ToF-MS

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ABSTRACT

Coffees from different origins were roasted to different roast degrees and along varying time temperature roasting profiles. The formation of volatile organic compounds (VOCs) during roasting was analyzed on-line by proton-transfer-reaction time-of-flight mass-spectrometry (PTR-ToF-MS). Coffee samples were *Coffea arabica* from Colombia, Guatemala (Antigua La Ceiba), Ethiopia (Yirga Cheffe, Djimmah) and *Coffea canephora* var. *robusta* from Indonesia (Malangsari). The roasting profiles ranged from high temperature short time (HTST) to low temperature long time (LTLT) roasting, and from medium to dark roast degree. The release dynamics of the on-line monitored VOCs differed for the different coffees and showed a strong modulation with the time–temperature roasting profile. While for Guatemalan coffee the formation of VOCs started relatively early in the roasting process, the VOC formation started much later in the case of Yirga Cheffe and Malangsari. Off-line analysis of the coffee brew augmented the measurements. These included headspace solid phase micro extraction gas chromatography mass spectrometry (HS SPME GC/MS), content of total solids, chlorogenic acids, caffeine, total polyphenols (Folin Ciocalteu), organic acids (ion chromatography), titratable acidity and pH. Some general trends, irrespective of the coffee origin, were observed, such as an increase in pH when going from an HTST to an LTLT profile or from a medium to dark roast degree. Furthermore, a decrease of total headspace intensity was observed from an HTST to an LTLT roasting profile. In general, the changes of the time temperature roasting profiles and/or the roast degree influenced the intensity of the respective coffee constituents as well as their relative composition differently for different coffee origins.

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1. Introduction

For more than 300 years, coffee has been making steady inroads throughout the world and its popularity in new markets is growing. Nevertheless, efforts to improve and refine this much-loved beverage continue. One of the crucial steps towards a good cup of coffee is the roasting process, where various physical and chemical changes lead to the formation of the desired coffee aroma molecules. During the initial endothermic phase of roasting, the green beans dry, reducing the water content from about 8–12% to a few percent. Further heating of the beans initiates the exothermic pyrolysis reactions. This can be perceived as a popping sound, called the first crack (at about 175–185 °C). If one continues roasting to a very dark roast degree, at higher temperatures (above 200 °C) the second crack can be heard. At the end of the roasting process the beans are cooled quickly, either by spraying water on the beans (quenching) before removing them from the roasting drum or by cooling with air after removing the beans from the roaster. Mainly between the first and the second crack, the typical coffee aroma compounds are formed in chemical reactions. Several pyrazines, e.g., are produced in Maillard reactions, whereas pyridines are obtained mainly by the degradation of trigonellines. Thermal decomposition of ferulic acid leads,

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among other things, to the key coffee aroma compound 4-vinylguaiacol. Besides aroma compounds, melanoidines are also formed, giving roasted coffee its characteristic brown colour.

Several chemical reaction mechanisms of coffee aroma formation are still not well understood. Some of the chemical reactions depend strongly on moisture content, temperature and pressure, or, in short, on the equilibrium conditions they are exposed to. Since during the roasting of coffee the chemical reactions take place in small micro reactors, i.e., the individual coffee beans, the equilibrium conditions may vary from bean to bean and/or from coffee type to type. Hence, analysis of the roasting of different coffees along different time–temperature roasting profiles might give an insight into the effect of the type of micro reactor on the aroma formation.

One possibility of studying the formation of volatile organic compounds (VOCs) during roasting is taking samples at specified stages of the roasting process and analysing them off-line. Such an analysis can be performed on extracts of the ground powder, the headspace of the ground powder or the headspace above the coffee brew [1–7]. Although this analysis is usually performed with gas chromatography, even nuclear magnetic resonance (NMR) has been performed at-line of the roasting process [8]. However, all these techniques are not only time-consuming, but also need further sample preparation before analysing the VOC composition, even if this is only a matter of grinding the roasted beans. In contrast, direct on-line analysis of the roasting of different coffees might give an insight into the dynamics of VOC formation. An already well-proven tool for on-line analysis of coffee roasting is proton-transfer-reaction mass-spectrometry (PTR-MS). Yeretzian and co-workers monitored on-line and in real-time the roasting process of small batches of beans with PTR-quadrupole-MS at different temperatures [9–11]. The roasting was performed isothermally, keeping the roaster gas at a fixed temperature during the whole process. Individual aroma bursts were observed at each bean's crack. In collaboration with Zimmermann et al., a different technique was used, which is more selective and based on resonant laser ionization coupled to time-of-flight mass analysis [11–16], or ion trap mass spectrometry [17]. With single-photon ionization time-of-flight mass spectrometry (SPI-ToF-MS), even single bean roasting was performed on Arabica as well as Robusta beans [18].

Combining soft ionization via proton-transfer reaction with high mass resolution of a time-of-flight instrument (PTR-ToF-MS) [19] provides the advantage of a fast analytical technique to record all the information about volatile organic compounds (VOCs) formed during roasting in just one single mass spectrum. On-line monitoring of coffee roasting with PTR-ToF-MS allows the formation dynamics of numerous VOCs to be followed in real-time [20–23].

All these studies gave progressively more insight into the dynamics of VOC formation during coffee roasting, but were often restricted to just one coffee type, one roasting profile or a specific roast degree. Here, we extended the on-line coffee roasting studies to compare the formation dynamic of VOCs of coffee from different origins. In the first series of experiments, the time–temperature roasting profile, as well as the roast degree, were maintained constant to monitor the differences in VOC formation dynamics for different coffees varieties. In a second step, the roast degree was varied from medium to dark. Thirdly, the time–temperature roasting profile was changed in the range from high temperature short time (HTST) to medium temperature medium time (MTMT) up to a low temperature long time roasting (LTLT).

To support the on-line analysis, a cup of coffee was prepared from the roasted coffees and evaluated with a number of off-line techniques. In an earlier study on the influence of the coffee extraction method (French Press, mocha, filter coffee, semi or fully automatic coffee machine etc.) on the cup of coffee [24], we were able to show several correlations of analytical measurements with sensory aspects: total solids – texture/body, headspace intensity – perceived aroma intensity, concentrations of caffeine/chlorogenic acids – bitterness and astringency (although different compounds are responsible for bitterness [25–27]). Hence, in this study, we analyzed the total solids gravimetrically, the aroma was measured with HS SPME GC/MS and the concentrations of 3-CQA, 4-CQA and 5-CQA as well as caffeine were analyzed with HPLC. A direct correlation of the sensory attribute acidity with the pH and the titratable acidity of the coffee brew was not observed in the earlier study, most probably because the differences were too small. Nevertheless, these parameters were included in this study as the acidity is an important characteristic of a cup of coffee. To get a full overview of the coffee, we complemented the analytical characterization by the analysis of the composition of the organic acids with ion chromatography, as well as the determination of the content of total polyphenols with flow injection analysis applying the Folin Ciocalteu assay on the brew [28].

2. Experimental details

2.1. Coffee

The following green coffees were analyzed: *Coffea arabica*: Colombia, Guatemala (Antigua La Ceiba), Yirga Cheffe (Ethiopia), Djimmah (Ethiopia); *Coffea canephora* var. *robusta*: Malangsari (Indonesia). Coffee from Colombia was provided by Probat Werke, Germany, the other coffee beans were from Rast Kaffee AG, Switzerland.

2.2. Coffee roasting

All experiments were performed using a Probatino drum roaster (PROBAT, 2008, heating gas: propane, PanGas, Winterthur). For all trials, 1 kg batches of green beans were roasted. The different roasting profiles were achieved by varying the heating intensity of the Probatino. The respective time–temperature profiles are shown in Fig. 1. For all experiments, the roasting was stopped by removing the beans from the roasting drum and cooling them with air. For Colombian coffee, the following time temperature roasting profiles were performed: high temperature short time (HTST) to medium and dark roast degree, medium temperature medium time (MTMT) to medium and dark roast degree, low temperature long time (LTLT) to medium roast degree. For Guatemala and Yirga Cheffe, an MTMT profile to medium and dark roast degree and an LTLT to medium roast degree were performed. Djimmah and Malangsari were roasted according to an MTMT profile to a medium and dark roast degree. The roast degree was measured by Colorette 3b (Probat Werke, Germany). The details of the roast batches are shown in Table 1. All roastings were performed in triplicate at least. The roasted beans were filled in bags (WICOVALVE PET/ALU/PE 12-8-75 80 mm × 50 mm × 280 mm silver) of 250 g and stored at −22 °C until further analysis.

2.3. On-line monitoring with PTR-ToF-MS

The VOCs, and therefore the aroma profile of the coffee beans, were monitored on-line during roasting with PTR-ToF-MS (PTR-ToF-MS, Ionicon Analytik GmbH, Austria). The experimental setup is shown schematically in Fig. 2. The roasting gas from the Probatino was withdrawn from the exhaust gas outlet with a vacuum membrane pump (Typ N86 KN.18, KNF Neuberger AG, Switzerland) through deactivated stainless steel tubes (BGB Analytik AG, Switzerland). To prevent condensation of the VOCs, the roasting gas was diluted with activated carbon-filtered prewarmed compressed air, and the stainless steel tubes were heated to 80 °C. A constant flow of 100 ml/min of the diluted roasting gas

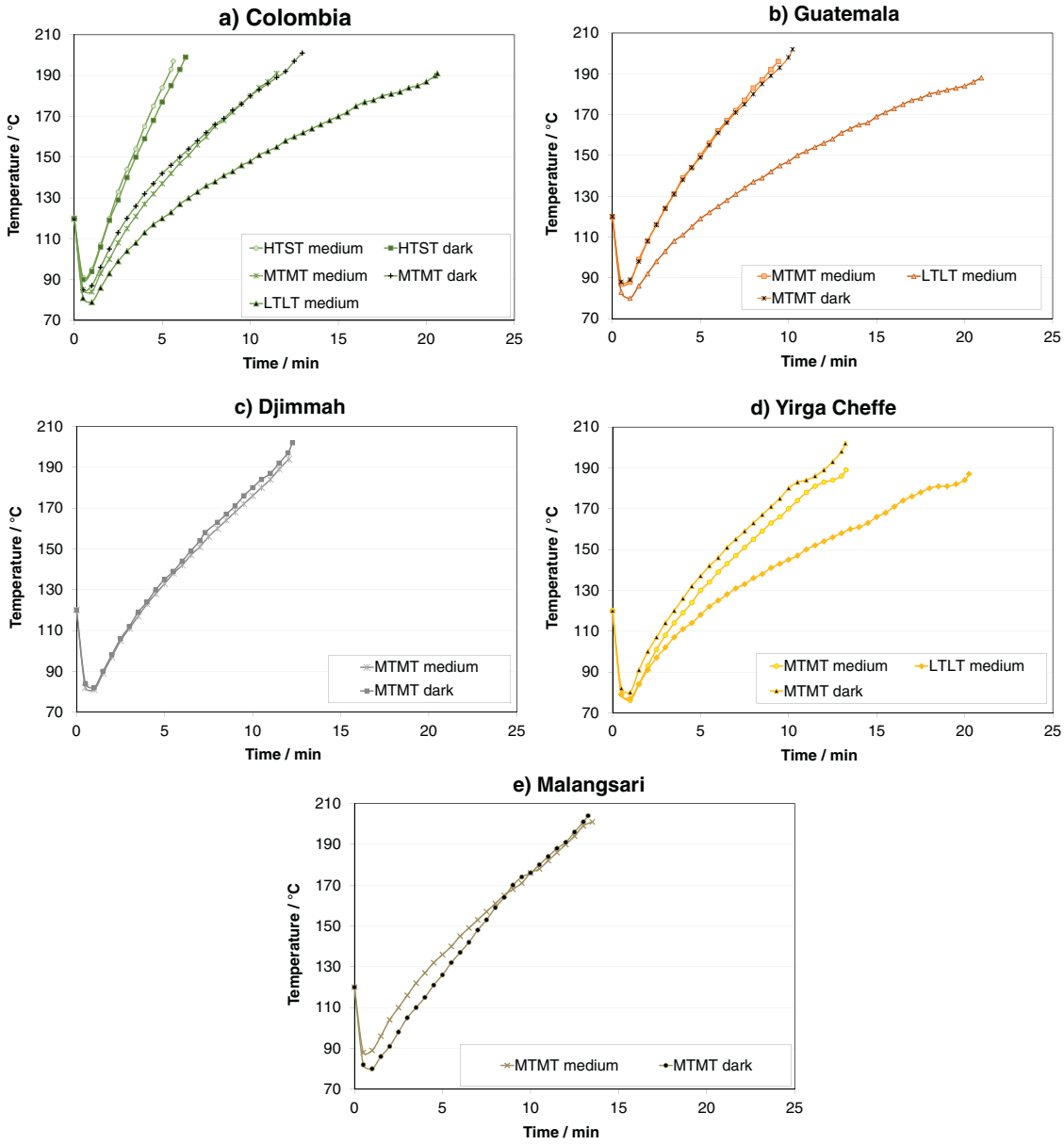

Fig. 1. Time–temperature roasting profiles of (a) Colombian coffee, (b) Guatemalan coffee, (c) Djimmah, (d) Yirga Cheffe and (e) Malangsari.

was transferred to the PTR-ToF-MS. The transfer line was 1.2 m long and had an inner diameter of 1 mm (PEEK tubing, BGB Analytik AG, Switzerland). The estimated residence time in the sampling line was circa 600 ms. The PTR settings were as follows: p (drift): 2.13 mbar, U (drift): 600 V, T (drift): 80 °C. Mass spectra were recorded in the mass-to-charge (m/z) range of 0–310 a.m.u. with a time resolution of one second. The mass resolution of the PTR-ToF-MS changed slightly from 4500 to circa 4200 for increasing m/z values. Mass calibration was performed on $[H_3{}^{18}O]^+$, $[H_5O_2]^+$ and $[C_8H_{11}N_4O_2]^+$. All peaks above a maximum intensity of a signal-to-noise ratio of 5:1 in the individual mass spectra were integrated; the respective intensities were normalized to the primary ion intensity. As no calibration was performed with an internal or external standard, the absolute intensities between different runs sometimes varied due to e.g., small differences in the gas flows. For better comparison of the relative intensities between the different roastings, the intensity of the VOCs is given in relation to the maximum intensity of the ion $[C_2H_5O_2]^+$ within the respective roasting trial. This VOC corresponds most probably to the protonated acetic acid. In general, one has to consider that in the PTR-ToF-MS spectra, no pre-separation of the analyzed gas mixture is performed, and all ions are measured within one mass spectrum. Based on the sum formula of the respective VOCs, a peak can be tentatively assigned to a specific compound based on the knowledge of the aroma compounds in coffee. However, it is impossible to distinguish between isomers like 2- and 3-methyl butanal, although a differentiation between isobaric compounds containing oxygen and pure hydrocarbons might be possible based on the isotopic pattern of the molecules. In the following, we characterize each ion by its sum formula, complemented in a few cases by a tentative assignment of the molecules.

2.4. Off-line analysis

2.4.1. Coffee brew

Coffee brew was prepared with 12 g roasted and ground coffee (espresso grinder KED 640, Ditting, grinding degree 8) per 200 ml of water (Evian, France) at 90 °C, the extraction time was 4 min. The

Table 1
Experimental results for the respective roast batches for the following time–temperature roasting profiles: Colombian HTST (medium, dark), MTMT (medium, dark), LTLT; Yirga Cheffe MTMT (medium, dark), LTLT; Djimmah MTMT (medium, dark); Guatemalan MTMT (medium, dark), LTLT; Malangsari MTMT (medium, dark). Given is the weight loss after roasting in percent, the gain in volume in percent, the roasting time in minutes, the end temperature of the roasting process in °C, and the roast degree in Pt (Colorette 3b).

	Colombia				
	HTST medium	HTST dark	MTMT medium	MTMT dark	LTLT medium
Weight loss/%	−13.4 ± 0.5	−14.0 ± 0.3	−13.5 ± 0.4	−15.5 ± 0.7	−13.3 ± 0.2
Gain in volume/%	81 ± 2	81 ± 2	73 ± 2	82 ± 0	64.3 ± 0.0
Roasting time/min	5.7 ± 0.2	5.8 ± 0.4	11.4 ± 0.1	12.4 ± 1.1	20.8 ± 0.9
End temperature	196.3 ± 0.7	198 ± 4	193.3 ± 0.7	201.5 ± 1.0	190 ± 3
Roast degree/Pt	102 ± 1	94 ± 2	104 ± 3	77 ± 1	102 ± 3
	Yirga Cheffe			Djimmah	
	MTMT medium	MTMT dark	LTLT medium	MTMT medium	MTMT dark
Weight loss/%	−13.2 ± 0.2	−15.9 ± 0.3	−13.4 ± 0.1	−13.8 ± 0.1	−16.3 ± 0.3
Gain in volume/%	55 ± 4	71.4 ± 0.0	42.9 ± 0.0	71.4 ± 0.0	82.1 ± 0.0
Roasting time/min	13.1 ± 0.4	13.2 ± 0.0	19.9 ± 0.5	13 ± 1	12.2 ± 0.1
End temperature	190 ± 2	202.0 ± 0.0	186 ± 1	194 ± 1	202.0 ± 0.0
Roast degree/Pt	103 ± 4	78 ± 1	105 ± 12	106 ± 6	77 ± 1
	Guatemala			Malangsari	
	MTMT medium	MTMT dark	LTLT medium	MTMT medium	MTMT dark
Weight loss/%	−12.7 ± 0.1	−14.8 ± 0.6	−12.4 ± 0.2	−15.0 ± 0.3	−16.2 ± 0.1
Gain in volume/%	69 ± 2	73 ± 4	61 ± 4	64 ± 4	65.4 ± 0.0
Roasting time/min	9.7 ± 0.8	9.8 ± 0.7	21 ± 1	12.8 ± 0.6	12.8 ± 0.8
End temperature	194 ± 2	203 ± 2	187.3 ± 0.7	202 ± 1	205 ± 2
Roast degree/Pt	106 ± 6	79 ± 2	106 ± 4	100 ± 4	89 ± 2

brew was filtered with a ceramic filter (Bayreuth coffee machine, Erste Bayreuther Porzellanfabrik Walküre Siegmund Paul Meyer GmbH, Germany) before further analysis.

2.4.2. Total solids

10 g of coffee extract was dried at 105 °C until reaching a constant weight (less than ± 0.5 mg).

2.4.3. pH, titratable acidity

The pH of each sample was measured at 20 °C. 40 ml of coffee brew was titrated with 0.1 M NaOH at 20 °C to (i) a pH of 6.6 and (ii) a pH of 8.0 (Titrando 809, Metrohm, Switzerland).

2.4.4. Organic acids

The following organic acids were determined by ion chromatography (IC 761 compact with suppression, conductivity detector, Metrohm, Switzerland): citric, malic, quinic, lactic, formic and acetic acid with a Metrosep Organic Acids column (Metrohm, Switzerland), eluent: 0.5 mmol/l H_2SO_4/15% acetone, flow: 0.5 ml/min, injection volume: 20 μL of 10-fold diluted coffee extract, suppression: 10 mmol/l LiCl, 20 °C.

2.4.5. Caffeine, chlorogenic acids

2 g of coffee brew was mixed with 500 μL Carrez I (30% aqueous $ZnSO_4$ solution), 500 μL Carrez II (15% aqueous potassium hexacyano (II) ferrate trihydrate) and 500 μL of methanol to precipitate high molecular weight compounds. The obtained solution was diluted with distilled water up to 25 ml and filtered with filter paper (Faltenfilter LS 171/2, *D* = 150 mm, Schleicher & Schuell, Germany) and a syringe filter (Chromafil Xtra PET-45/25, Macherey-Nagel, Switzerland). Quantitative analysis was performed using an Agilent Series 1200 HPLC, equipped with an Agilent Eclipse Plus C18 1.8μ Column (100 mm × 2.1 mm i.d., thermostat at 20 °C) and a diode array detector. Mobile phase A was water (containing 0.1% formic acid) and mobile phase B was acetonitrile (containing 0.1% formic acid). The gradient mode was 1 min with 5% mobile phase B, then 10 min with 25% of B and finally 50% of B for 20 min. The flow rate was 0.35 ml/min. The detector was set at 325 nm for chlorogenic acids and 272 nm for caffeine. The injection volume was 3 μL. Substances were identified by comparing their retention times to those of the respective standards. Concentrations of 3-CQA, 4-CQA, 5-CQA and caffeine were calculated using the regression equation of external standards and corrected with the recovery rate. All measurements were performed in triplicate.

5-*O*-caffeoyl quinic acid (5-CQA) was obtained from Acros Chemicals, Switzerland; caffeine, 3-*O*-caffeoyl quinic acid (3-CQA) and 4-*O*-caffeoyl quinic acid (4-CQA) are from Sigma–Aldrich Chemie, Switzerland.

2.4.6. HS SPME GC/MS

10 ml of coffee extract were analyzed immediately after preparation with headspace solid phase micro extraction gas chromatography/mass spectrometry (HS SPME GC/MS). A Polydimethylsiloxan/Divinylbenzen (PDMS/DVB) SPME fibre with a 65 μm thick film (Supelco, Sigma–Aldrich Chemie GmbH, Switzerland) and a DB-WAX (30 m × 250 μm × 0.25 μm) column (Agilent Technologies, Switzerland) were used. *SPME parameters* (*Gerstel, Switzerland*): Incubation: 4 min at 50 °C, agitating at 250 rpm; extraction time: 7 min at 50 °C, agitating at 250 rpm; desorption time: 5 min at 240 °C; *GC/MS parameters* (*7890/5975N, Agilent Technologies, Switzerland*): 35 °C for 1 min; then 4 °C/min to 100 °C for 10 min; then 30 °C/min to 130 °C for 8 min; then 6 °C/min to 220 °C for 5 min; splitless mode; flow 1 ml/min; EI source 70 eV, 230 °C; detector 150 °C. For data analysis, the software MSD Chemstation (Version G1701 EA E.02.00.493, Agilent Technologies, Switzerland) and the database NIST08 was used. Chemical identification was performed via the respective mass spectrum and retention time. From more than 100 compounds that could be identified, 57 molecules contributing to the aroma of coffee were chosen for evaluating the headspace of the respective coffee brew extraction methods (see Supp. Table 2). Total headspace intensity was calculated by adding up the HS SPME GC/MS intensities of the chosen compounds.

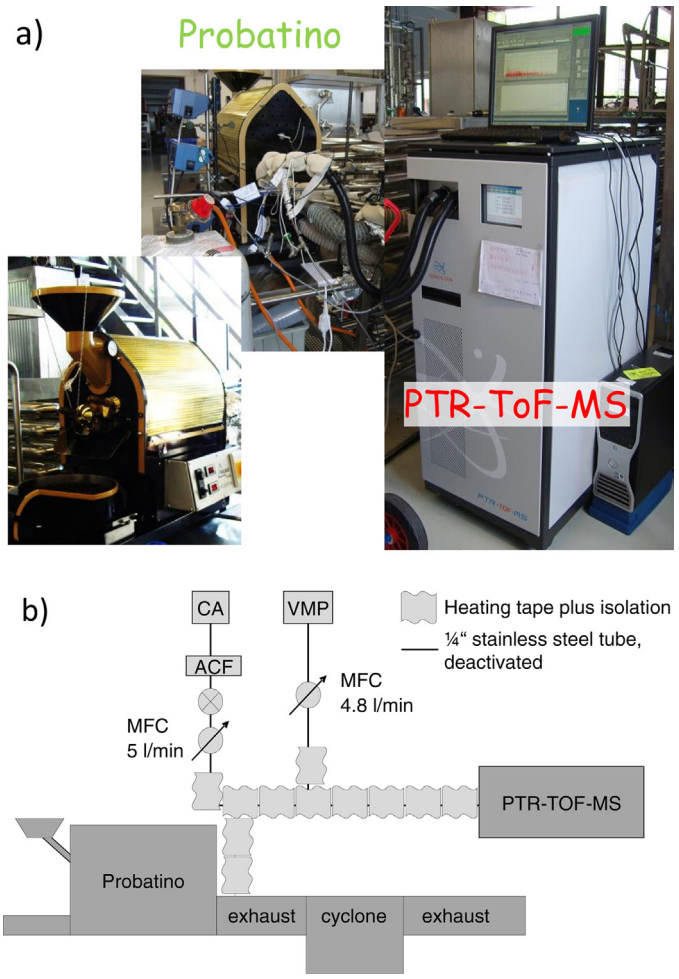

Fig. 2. (a) Left: front view of the Probatino, middle: rear view of the Probatino coupled to the PTR-ToF-MS (right) and (b) schematics of the experimental setup. CA, compressed air; ACF, active carbon filter; VMP, vacuum membrane pump; MFC, mass flow controller.

2.4.7. Total content of polyphenols

The total polyphenol content was measured with flow injection analysis using the Folin Ciocalteu reagent as described by Petrozzi et al. [28]. In short, the reagent solution (tenfold diluted Folin Ciocalteu's phenol reagent solution, Sigma–Aldrich, Switzerland), the diluted coffee brew (25 °C) as well as an alkaline NaOH solution (10 g/L NaOH, Sigma–Aldrich, Switzerland) were mixed in a mixing coil. The flow rate was 2 ml/min, the introduced sample volume was 100 μL, the reaction coil had a length of 100 cm. The reaction product was analyzed with a UV/VIS Perkin Elmer Lambda 1 spectrophotometer at a wavelength of λ = 765 nm. Freshly prepared gallic acid solution was used as standard.

3. Results and discussion

3.1. Time–temperature roasting profiles

The coffee beans were roasted to a medium (circa 103 Pt) and dark (circa 80 Pt) roast degree along different time–temperature roasting profiles, ranging from high temperature short time (HTST, circa 5 min) over a medium temperature medium time (MTMT, circa 11 min) up to a low temperature long time profile (LTLT, circa 21 min). The details are given in Fig. 1 and Table 1. The weight loss of the coffee beans ranged from 12% to 16%, being higher for darker roast degrees. The gain in volume of the beans ranged from 43% to 82%, being higher for darker roast degrees and lower for longer roasting times.

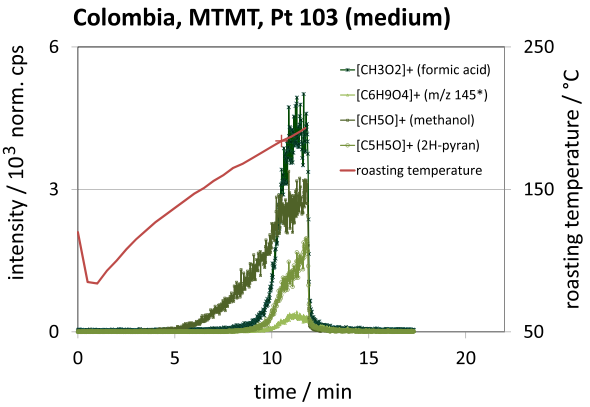

Fig. 3. Formation dynamics of four different VOCs (sum formula + tentative assignment) during the MTMT roasting of Colombian coffee to a medium roast degree of Pt 103 (Colorette 3b), plotted together with the time–temperature profile inside the roasting drum. The red cross marks the point of the first crack. *The VOC $[C_6H_9O_4]^+$ at m/z 145 can be tentatively assigned to 5,6-dihydro-5-hydroxymaltol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.2. MTMT – medium roast degree – different coffees

3.2.1. On-line monitoring with PTR-ToF-MS

The roasting process was analyzed on-line via PTR-ToF-MS allowing for real-time monitoring of the development of the volatile organic compounds of coffee with time.

In Figs. 3–5, the time–intensity profiles of selected ions are shown. First, it must be mentioned that when roasting a specific coffee along a specific roasting profile, different VOCs are formed differently. In Fig. 3, the formation dynamics of four VOCs during

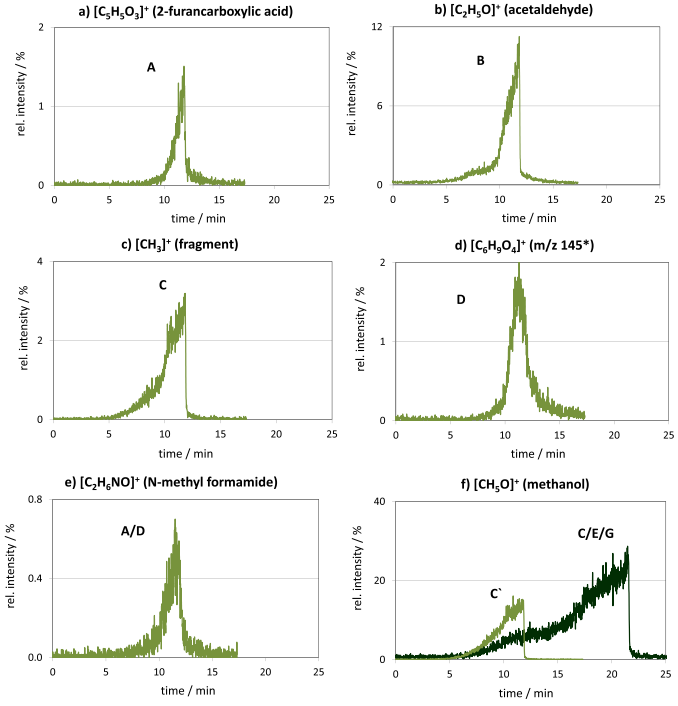

Fig. 4. Time intensity profiles of VOCs monitored during MTMT medium and LTLT medium (only in (f)) roasting of Colombian coffee as examples of the different VOC formation families. *The VOC $[C_6H_9O_4]^+$ at m/z 145 can be tentatively assigned to 5,6-dihydro-5-hydroxymaltol.

the MTMT medium roasting profile are shown for Colombian coffee. The VOC $[CH_5O]^+$, for example, is generated very early in the roasting process, and the intensity rises more or less continuously until a roasting time of roughly 10 min, before the formation rate slows down (family C′ in Table 2). The compound $[CH_3O_2]^+$, however, appears at a later time and reaches a plateau in intensity after about ten minutes of roasting (family F′ in Table 2). Because within one roasting profile the VOCs are formed differently, they can be grouped into families according to their formation dynamics (families A, B, C, etc.), as shown in Table 2 and Fig. 4 for the MTMT-medium roasting profile of Colombian coffee. VOCs from family A are characterized by a straight rise in intensity, family B shows a slight decrease in formation after the first crack while family C shows a distinct decrease in formation (plateau) after the first crack. Family D includes VOCs with intensity profiles showing a symmetric peak. Family F is similar to family C, but shows a dip in intensity in the plateau. C′ is like C and F′ is like F, but without a rise after the plateau. Families A/D, B/D, C/D are like A, B, and C without a sharp drop off at the end. Families A/E/G, B/E/G, C/E/G show intensity profiles like A, B, and C, however with an early plateau in addition. VOCs in family J show an asymmetric peak with a tailing towards longer roasting time. The information for the VOC grouping of all other roasting profiles and coffees is given in Supp. Table 1 and the supplementary material.

A special formation pathway was observed for the compounds $[C_6H_9O_4]^+$ and $[C_6H_7O_3]^+$. They were formed quite early in the roasting process, and the intensity dropped before the roasting process was completed without any further rise, even at darker roast degrees. This decrease has also been observed by others [8,20–23,29–31]. Both VOCs could be tentatively assigned to common compounds in heat-treated food ($[C_6H_9O_4]^+$: 5-dihydrohydroxymaltol, $[C_6H_7O_3]^+$: 5-hydroxymethylfurfural, maltol, or isomaltol). Since their intensity decreased with ongoing roasting, these compounds seemed to be precursors for other aroma compounds. Whether or not 5-hydroxymethylfurfural has a negative effect on human health has been under discussion [32,33], but due to the rapid decrease of its intensity during roasting, little is left in roasted coffee, even at a light roast degree.

For most VOCs, these results are in agreement with those of Zimmermann et al. [13–15], who analyzed the coffee roasting gases with resonant photo ionization mass spectrometry on a sample drum roaster (100 g batch size). Of course, the ionization efficiencies for the various VOCs in the roaster off gas are different when applying resonant laser ionization compared to proton transfer reaction ionization, due to the different ionization mechanisms. Some molecules, like the guaiacol group (guaiacol, 4-vinylguaiacol, 4-ethyl guaiacol), are ionized better by REMPI. The degradation pathway of 5-feruloyl quinic acid over 4-vinyl guaiacol to phenol ("high activation energy channel") or to melanoidines ("low activation energy channel"), for example, can be monitored better with REMPI-ToF-MS than with PTR-MS [14].

Chemical reactions are, in general, based on an equilibrium process, being very sensitive to changes in pressure, temperature, and, in some cases, humidity. During the coffee roasting process, these reactions are believed to occur under high pressure conditions until the first crack, in closed cavities inside the coffee bean structure, inside the individual small micro reactors. The pressure release during the first crack might lead to changes in the chemical reactions/equilibrium processes. This can be seen for the time intensity profile of the VOCs $[CH_5O]^+$ and $[CH_3O_2]^+$, where the formation dynamics changed after the first crack (red cross in Fig. 3). In contrast, some other VOCs were generated more or less continuously until the end of the roasting process (family A) and any first crack effect was not evident.

By changing the coffee variety, the impact of the micro-environment on the VOC formation can be explored, as the characteristics of the coffee bean, which is the micro reactor where the chemical reactions occur, are being *de facto* changed. To do this, different varieties of coffee were roasted under the same time temperature roasting conditions and the differences in the flavour formation were monitored on-line by PTR-ToF-MS. The result is given in Fig. 5 for the MTMT-medium roasting profile for the five coffees Colombia, Guatemala, Djimmah, Yirga Cheffe and Malangsari.

In Fig. 5(a), the time intensity profile of the VOC $[C_5H_5O]^+$ is shown, which was clearly affected by the first crack for the Colombian MTMT medium roasting profile. A comparison of the formation dynamics for the different coffees clearly revealed the influence of the properties of the micro reactor: the VOC was formed differently for every single coffee. Whether this is due to a difference in the structure of the micro reactor or in the chemical composition thereof cannot be answered at this point. For the coffee from Colombia, the intensity of the VOC increased strongly until the first crack. After the first crack, the intensity kept on rising, but more slowly. For the Guatemaltecan coffee, the step at the first crack was almost not visible, as well as for the Djimmah. For the latter, however, the VOC formation started much later in the roasting process. For the Ethiopian Yirga Cheffe, it took even longer for the onset of the formation of $[C_5H_5O]^+$. The intensity rose until the first crack, but afterwards, it reached a plateau and remained constant until the beans were removed from the roaster. In contrast, for the Malangsari, the intensity started to rise at a similar time as for the Yirga Cheffe, but it increased more or less continuously until the end of the roasting process, without any step at the first crack. The chemical reaction leading to this VOC seemed to be strongly influenced by the chemical composition and/or the structure of the coffee beans.

In 2002, Yeretzian et al. [11] performed an on-line analysis with PTR-MS on roasting of a small amount of coffee beans (Arabica and Robusta). For some compounds, such as VOCs with a mass-to-charge ratio (m/z) of 45 for the protonated ion (most probably acetaldehyde) or m/z 83 (most probably methyl furan), a sharp burst of VOC release was observed, coming from single bean popping. For other compounds, however, the observed formation was continuous during the whole roasting process. It would be of interest to know whether the VOCs which showed popping in single bean experiments exhibit a larger difference in formation dynamics between the different coffees, as the chemical reactions leading to their formation might be more influenced by the structure of the coffee bean. With respect to m/z 45 ($[C_2H_5O]^+$) and 83 ($[C_5H_7O]^+$), differences in the formation of the VOCs were observed between different coffees. However, changes in the formation dynamics for different coffees were also observed for m/z 81 ($[C_5H_5O]^+$), although this compound did not show a burst of VOC during popping of single beans.

For the compounds $[CH_5O]^+$, $[C_6H_9O_4]^+$, and $[CH_3O_2]^+$ (Fig. 5(b–d)), the differences in the formation dynamics of the VOCs were not as pronounced as they were between the different coffees for $[C_5H_5O]^+$. Still, the time intensity profiles of the VOCs for the Malangsari (Robusta) differed from the other formation dynamics: the formation of VOCs started later and rose more or less continuously for all compounds. For the Yirga Cheffe, the intensity rose until the first crack and reached either a plateau afterwards or decreased again (families B, C′, D, F′, B/D).

The two coffees from Central and South America showed the most similar formation dynamics in this study, although the time when the VOCs started to form was different. The second Ethiopian coffee, Djimmah, was sometimes similar to the first Ethiopian coffee, the Yirga Cheffe, and sometimes similar to the Central and South American coffees.

Mayer et al. [3] analyzed the aroma profiles for coffees of different origins. They also found similarities between two South

Table 2
Grouping of the formation dynamics of the monitored VOCs for the roasting profile Colombian MTMT-medium.

Colombian MTMT medium									
A	B	C	C′	D	F′	A/D	B/D	C/D	J
CH_3O (formaldehyde)	C_3H_3 (fragment)	CH_3 (fragment)	C_2H_5 (fragment)	$C_6H_5O_2$ (1,4-benzo-quinone)	CH_3O_2 (formic acid)	C_2H_6NO (N-methyl formamide; 2-amino-acet-aldehyde)	$C_5H_7O_3$ (4-hydroxy-5-methyl-2H-furan-3-one; etc.)	$C_4H_7O_3$ (acetyl acetate; methylpyruvate)	$C_6H_7O_3$ (5-(hydroxy-methyl) furfural; isomaltol; maltol)
CH_5S (methane thiol)	C_3H_5 (fragment)	$C_4H_7O_2$ (butane dione)	CH_5O (methanol)	$C_5H_9O_3$ (acetonyl acetate)		C_5H_6N (pyridine)		$C_3H_7N_2S$ (dihydro-thiazol-amine; dihydro-1H-imidazole-thiol; 2-imidazolidinethione)	
C_4H_7 (butadiene; fragment)	C_2H_3O (ketene)	$C_6H_9O_2$ (5-methylfurfuryl alcohol, dimethyl-3(2H)-furanone)	C_2H_2O (fragment)	$C_6H_9O_4$ (5,6-dihydro-5-hydroxy-maltol)				$C_6H_5O_3$ (furandicarbox-aldehyde; 2-hydroxy-1,4-benzoquinone)	
C_4H_6N (pyrrole)	C_2H_5O (acetaldehyde)		C_4H_5 (fragment)					$C_6H_9O_3$ (furaneol)	
C_4H_7O (2-methyl-propenal)	C_3H_7O (acetone/propanal)		C_3H_5O (2-propenal; prop-1-en-1-one)						
$C_6H_7O_2$ (5-methyl furfural)	$C_2H_4O_2$ (fragment)		C_4H_9O (isobutanal, methyl propanal)						
$C_5H_5O_3$ (2-furan carboxylic acid)	$C_2H_5O_2$ (acetic acid)		$C_3H_7O_2$ (propanoic acid, propionic acid)						
	C_4H_5O (furan)		C_5H_5O (2H-pyran)						
	$C_3H_5O_2$ (2-oxopropanal, pyruvaldehyde)		$C_4H_9O_2$ (butanoic acid, butyric acid)						
	C_5H_7O (methyl furan)		$C_2H_7N_3O$ (2-azido ethanol)						
	$C_4H_5O_2$ (2(5H)-furanone)		$C_5H_3O_2$ (fragment)						
	110.04 (n.d.)		C_6H_7O (phenol)						
			$C_5H_7N_2$ (methyl-pyrazine)						
			C_5H_6NO (2-pyrrolecarb-aldehyde, 2-formyl-pyrrole)						
			$C_5H_5O_2$ (furfural)						
			$C_5H_7O_2$ (2-furan-methanol)						
			$C_5H_9O_2$ (pentane dione)						
			$C_5H_{11}O_2$ (2-hydroxy-3-pentanone, 2-methyl-butanoic acid)						
			$C_7H_9O_2$ (2-methoxy-phenol)						

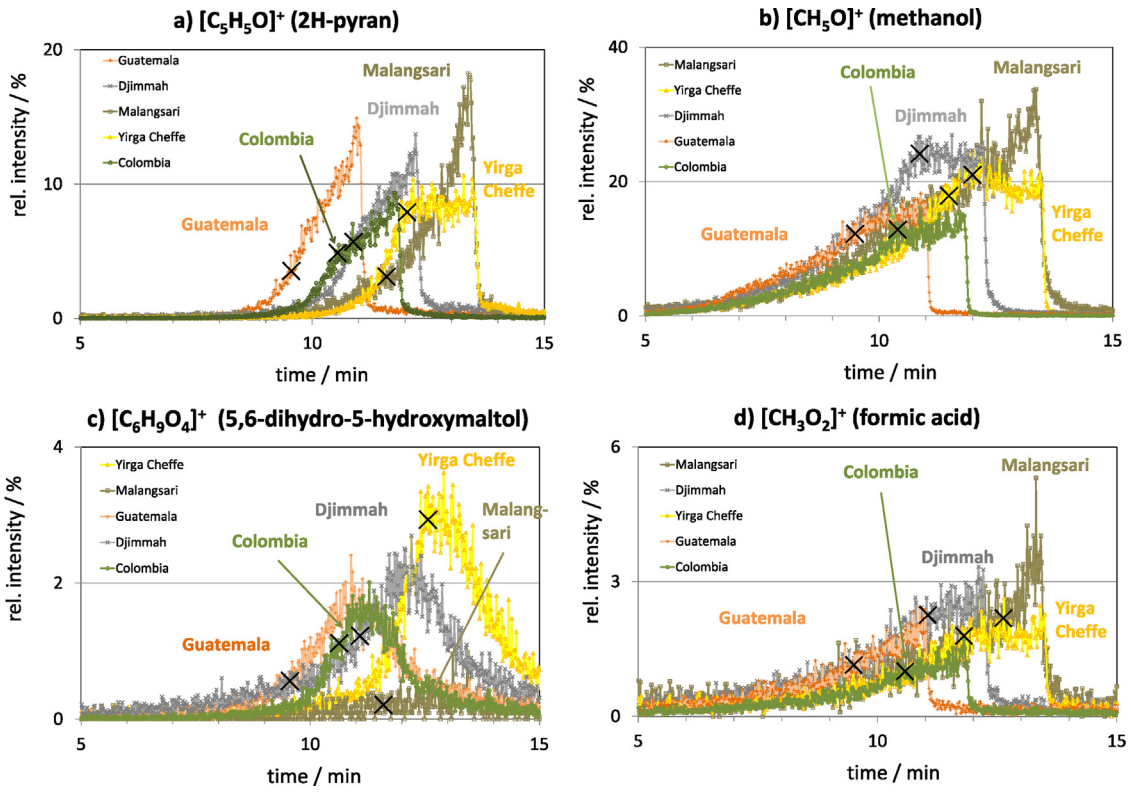

Fig. 5. Time intensity profiles for the MTMT medium roasting profile for the coffees Colombia, Yirga Cheffe, Malangsari, Djimmah and Guatemala, for the VOCs (a) $[C_5H_5O]^+$, (b) $[CH_5O]^+$, (c) $[C_6H_9O_4]^+$, and (d) $[CH_3O_2]^+$. The cross marks the respective time of the first crack (at a roasting temperature of 184 °C).

American coffees, Colombian and Brazilian, whereas the coffee from Kenya showed differences in the intensity of several compounds. However, not all coffees from South and Central America showed similar profiles in their studies. So, not only the global region where coffee is grown influences the aroma profile, but also the variety of the coffee plant and the regional conditions, like soil or climate where the coffee is grown, have an impact on the aroma profile.

For all coffees studied here, the time when the VOC formation in the roasting started was different, although the energy input from the gas burner of the drum roaster was the same for all roasting trials. It seemed that the form and composition of the micro reactor, the green bean, not only affected the formation dynamics of the VOCs, but also the time when the reactions set in. This time shift could not be explained by the initial humidity of the samples, as this did not differ significantly between different coffees. It might be explained by the structure or size of the beans leading to different kinetics in drying during the coffee roasting. As no microscopic studies were performed on the bean structure, this question cannot be answered conclusively.

The time shift in aroma formation for different coffees might have a huge influence on coffee blends. A roast master must always decide whether the respective coffees for a blend are mixed before (pre-) or after (post-blending) the roasting, based on, among other things, organizational or economic reasons. In the case of post-blending, the roasting profile can be optimized for every single coffee. In the case of pre-blending, all ingredients have to be roasted along the same roasting profile. Taking into account the results presented here, pre-blending of Yirga Cheffe and Guatemala, for example, might lead to a very inhomogeneous roast result when roasting according to the MTMT profile; at the time when the VOC formation set in for Yirga Cheffe, the Guatemala coffee would have already been burned. However, it is not clear if the heat transfer to the coffee beans would be altered when roasting a pre-blended mixture.

3.2.2. *Off-line analysis*

The time intensity profiles of VOCs varied significantly depending on the type of coffee being roasted. To elucidate the influence of these different formation dynamics on the final end product, the cup of coffee, the brews based on these roasted coffees (along the same roasting profile to the same roast degree), were analyzed analytically with different techniques. The results are given in Fig. 6 for Colombia, Guatemala, Djimmah, Yirga Cheffe and Malangsari for the MTMT medium roasting profile. Every type of coffee showed a different picture of its composition. The Malangsari was more pronounced in the content of total solids, headspace intensity of the aroma, polyphenols, quinic acid and caffeine (highest content for all coffees) and showed the highest pH value, which was also reflected in the lowest titratable acidity to pH 6.6. This is consistent with results of Bicho et al. [34], who analyzed the pH and caffeine content of Arabica and Robusta coffees. Interestingly, the content of chlorogenic acids for Malangsari was also the lowest, although it is a *C. canephora var. robusta*. Studying the content of phenolics for different coffees (Arabica and Robusta), Alves et al. [31] also found higher total phenolic contents for Robusta coffees. In the case of chlorogenic acids, they did not find a significant difference between Arabica and Robusta coffee.

The Yirga Cheffe had the lowest pH value (as expected for an Ethiopian coffee), a high titratable acidity to pH 6.6, a slightly lower total headspace intensity and a low titratable acidity to pH 8. The Ethiopian Djimmah was high in polyphenols and showed a high titratable acidity to pH 8. In general, there was a trend towards higher contents of total polyphenols with a higher titratable acidity to pH 8, except for Malangsari. There was no correlation observed between a higher titratable acidity to pH 8 and the content of

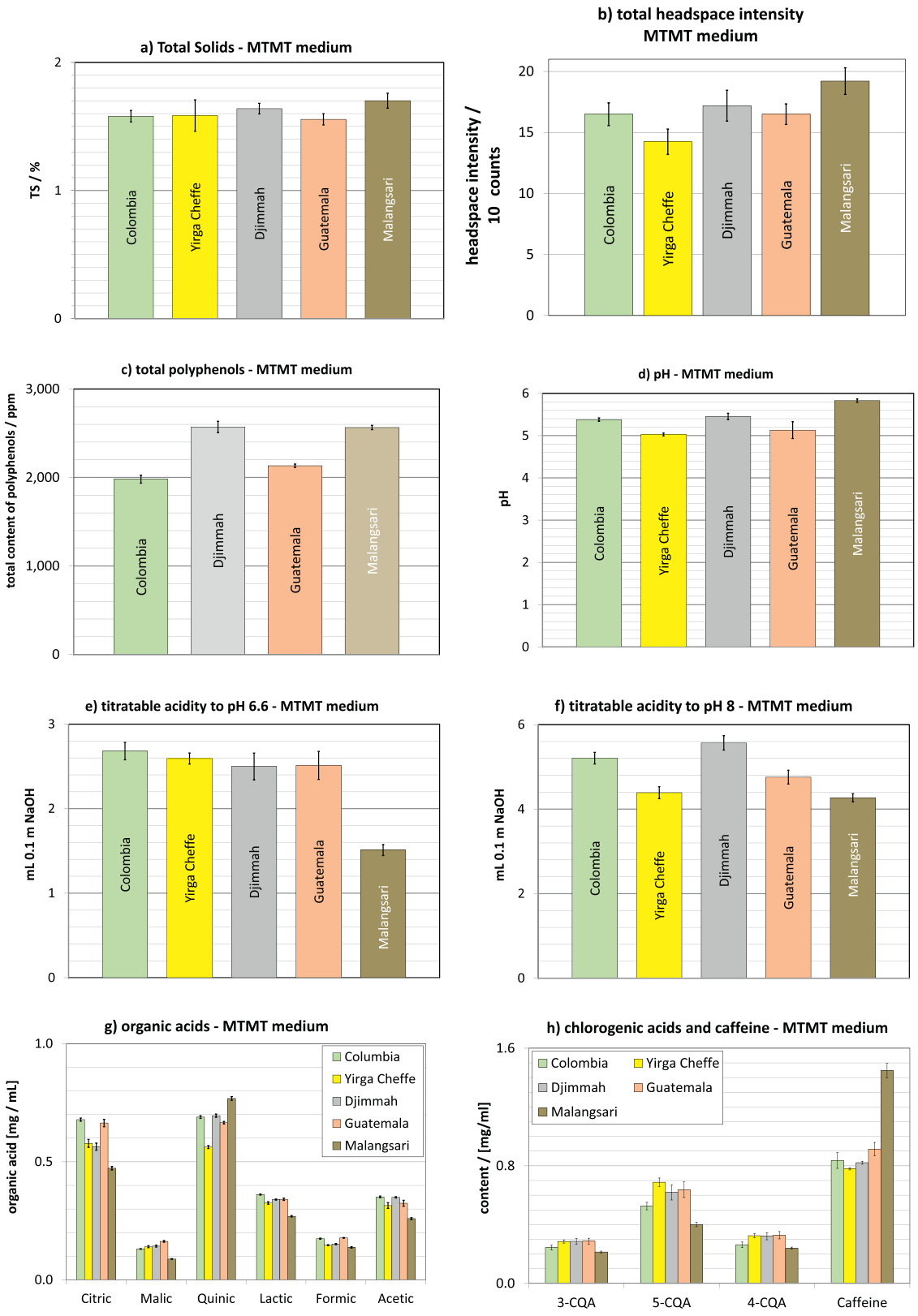

Fig. 6. Analytical results for the off-line characterization of the coffee brews based on the MTMT medium roasting profile. Given are (a) the content of total solids, (b) the total headspace intensity, (c) the content of total polyphenols, (d) the pH of the brew, (e) the titratable acidity to pH 6.6, (f) the titratable acidity to pH 8, (g) the content of organic acids (citric, malic, quinic, lactic, formic and acetic acid), as well as (h) the content of the chlorogenic acids 3-CQA, 5-CQA and 4-CQA and caffeine.

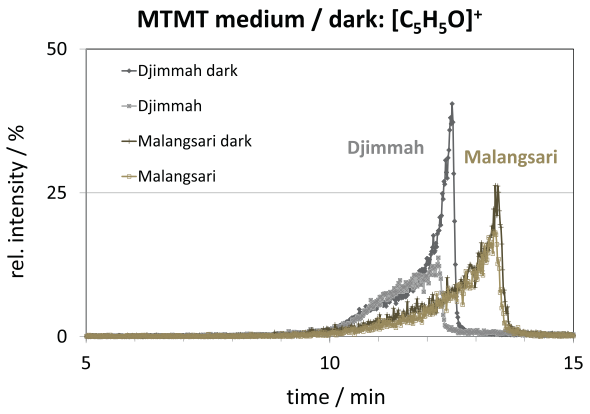

Fig. 7. Time intensity profile of $[C_5H_5O]^+$ (2H-pyran) for Djimmah and Malangsari for the roasting profiles MTMT medium and MTMT dark.

chlorogenic acids, nor between the content of total polyphenols and chlorogenic acids. The coffees from Colombia and Guatemala showed a well-balanced profile with a lower content of total polyphenols than the other coffees.

The intensities of the VOCs observed in the on-line analysis with PTR-ToF-MS were not directly reflected in the HS SPME GC/MS analysis of the coffee brew. This was due to the fact that during roasting, the VOC release inside the roaster was analyzed, but for off-line analysis, the VOC release above the cup of coffee brew was analyzed. It has already been shown by Grosch and co-workers that during coffee brewing, the composition and intensity of the VOCs change when going from coffee powder to coffee brew [35–39].

To summarize, on-line monitoring with PTR-ToF-MS of roasting different coffees along the same time temperature roasting profile (MTMT) to the same medium roast degree showed differences in the formation dynamics of the VOCs between the different coffees. Although the energy input during roasting and the initial humidity of the beans were the same for all coffees, the starting time of VOC formation differed from coffee to coffee. The cup of coffee brewed from these roastings differed in all analyzed parameters except the content of total solids. The differences in acidity, for example, were reflected in the pH and the titratable acidity as well as in the amount and composition of organic acids. This study confirmed the expected higher acidity of a Yirga Cheffe, but also showed that a Robusta coffee brew does not necessarily has a higher content of chlorogenic acids, showing once more that coffees differ significantly from each other.

3.3. MTMT – different roast degrees – different coffees

3.3.1. On-line monitoring with PTR-ToF-MS

Roasting along only one roasting profile to a single roast degree gives just a small snapshot on what is going on when transforming green, hard and dense coffee beans into brownish, brittle and nice-smelling roasted coffee beans. To enlarge this picture, we continued roasting to a darker roast degree (espresso type), while keeping the roasting profile constant (MTMT dark). The influence of the roast degree on the formation dynamics of the VOCs in the on-line analysis is shown in Fig. 7 for the roasting profiles MTMT medium and dark for Djimmah and Malangsari. Roasting to a darker roast degree led first of all to a prolongation of the roasting. In addition, the intensity of almost all VOCs increased strongly when reaching the second crack towards the end of the roasting process at about 200 °C. In the case of the Malangsari coffee, this was not as obvious, as the intensity was already continuously rising with roasting time, but it was clearly noticeable for the Djimmah coffee.

Schenker et al. [1] observed for some compounds an increase in VOC intensity with darker roast degrees, for others a decrease in VOC concentration. As they roasted with a fluidized bed roaster at much higher temperatures (240–260 °C versus 200 °C), the comparability with this study is limited. The decrease of 2,3-pentanedione for darker roast degrees, for example, which was observed by several authors [1–3], was not found in this study. Instead, the intensity rose continuously.

For $[C_5H_6N]^+$ (pyridine), the formation started late in the roasting process, and its intensity increased continuously until the end of the roasting process for all coffees analyzed, which is consistent with observations made by other authors [4,5]. The intensity of pyridine in the on-line analysis was higher for Robusta coffee than for Arabica, which is in contrast to Franca et al. [5]. In addition, they observed a decrease in intensity in the headspace of ground coffee powder for several VOCs with increasing roast degree, which was not observed here. This can again be explained by a completely different roaster setup.

3.3.2. Off-line analysis

The influence of the roast degree on the final end product, the cup of coffee, was expected to be clearly noticeable, as a coffee roasted for filter coffee was being compared to an espresso type roast. The trends are given in Fig. 8. The respective graphs for the specific data like total solids, pH, total headspace intensity etc. are given in the supplementary material in Supp. Figs. 1–6. The most pronounced differences when going from a medium to a dark roast degree for the same coffee and the same roasting profile (MTMT) were a decrease in the titratable acidity, as the citric and malic acid as well as the chlorogenic acids were degraded at this roasting step. The decrease of chlorogenic acids with increasing roast degree was described by others, too [8,31,34,40–47]. Bicho et al. [34] analyzed the composition of coffee brew as a function of the roast degree, and found similar results, like an increase in pH and total solids as well as a decrease in chlorogenic acids for darker roasts, both for Arabica and Robusta coffees.

The total content of polyphenols decreased for Guatemala and Djimmah. A decrease of total polyphenols for Guatemalan coffee with increasing roast degree was also observed by Smrke et al. [46], analysing the influence of roast degree on the antioxidants of coffee by comparing different antioxidant assays coupled with size exclusion chromatography.

The Colombian coffee showed no significant difference in polyphenols going from medium to dark roast degree. For Malangsari, the darker roast showed a higher content of total polyphenols, which is in contrast to the results of Vignoli et al. [30] and Alves et al. [31], who reported a decrease of total polyphenol content measured with the Folin-Ciocalteu reagent for most of the studied Robusta coffees with increasing roast degree. This again shows the diversity in composition among coffees from different origins.

The content of quinic and lactic acid in the coffee brew in the case of Guatemala and Djimmah increased with darker roast degree. The change of acid composition in coffees with increasing roast degree was also followed by Wei et al. [8] with nuclear magnetic resonance analysis (NMR). The decrease of citric, malic and formic acid as well as the increase of quinic and lactic acid are consistent with the results of this study.

The total headspace intensity increased with darker roast degree, except for the HTST roasting of Colombian coffee. Hence, a medium roast is characterized by a higher acidity and a higher content of chlorogenic acids, while a darker roast has a higher aroma intensity above the cup and a higher content of total solids, representing a higher body.

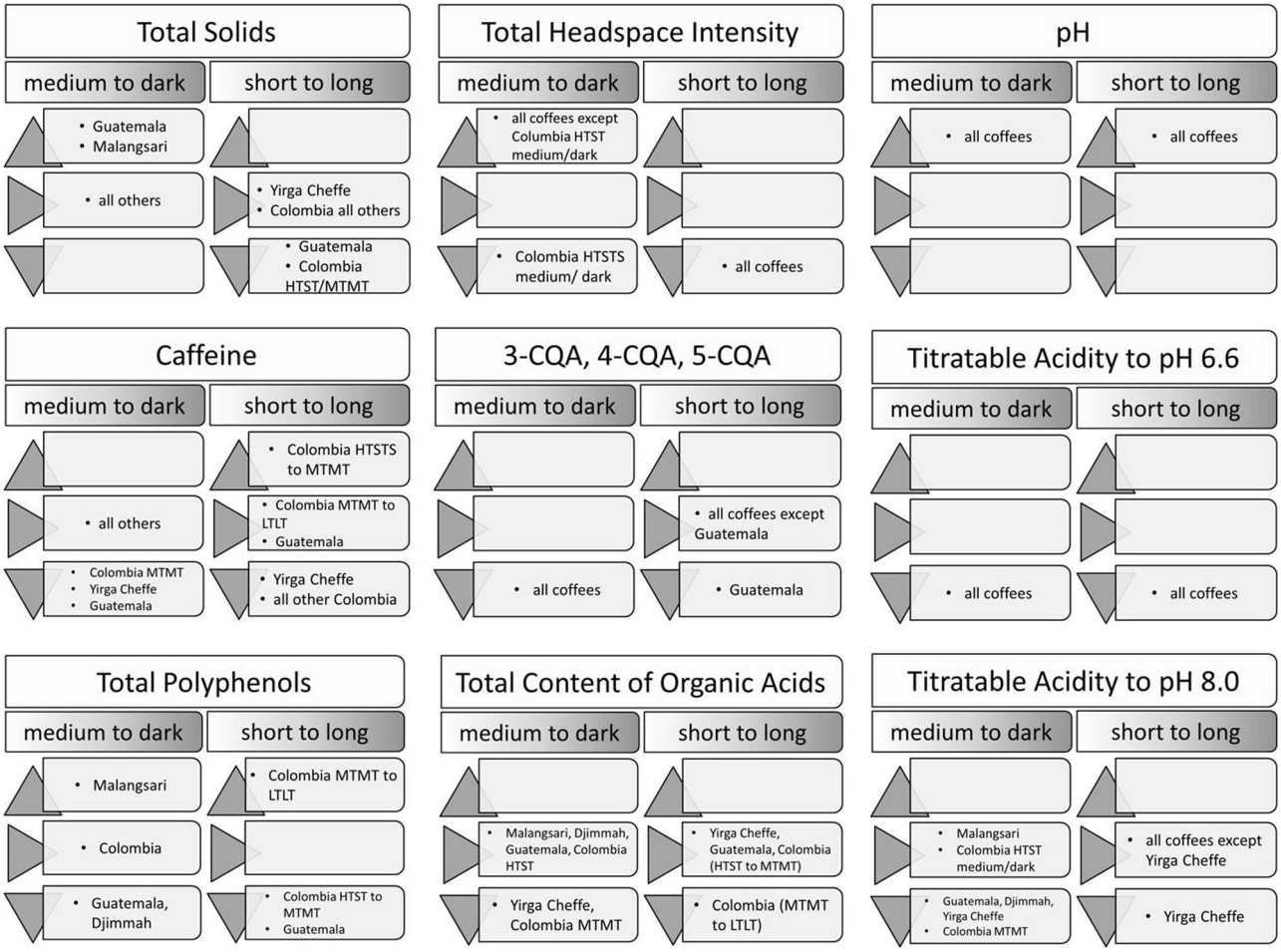

Fig. 8. Influence of the time–temperature roasting profile and the roast degree on the chemical composition of the coffee brew.

To summarize, roasting to a darker roast degree along the MTMT roasting profile lead to a sharp increase in VOC formation in the on-line analysis towards the 2nd crack for almost all VOCs. The resulting cups of coffee were characterized by a higher content of total solids, a higher pH and therefore a lower titratable acidity, as well as a lower content of chlorogenic acids. The total content of organic acids remained more or less constant, whereas the composition in organic acids changed from medium to dark roast degree. The content of total polyphenols changed differently from medium to dark roast degree for the different coffees. Thus, a darker roast degree not only changes the amount of components in a cup of coffee, but also the relative composition thereof.

3.4. Different time temperature roasting profiles – medium roast degree – different coffees

3.4.1. On-line monitoring with PTR-ToF-MS

The overall picture of the formation dynamics when roasting different coffees is still limited when looking on the MTMT roasting profile to a medium and dark roast degree. In earlier studies we showed that changing the time temperature roasting profiles changed the time intensity profiles for some VOCs [20–23]. To complete the picture of roasting different coffees, the roasting profile was changed from MTMT to low temperature long time roasting (LTLT) for the coffees Colombia, Guatemala and Yirga Cheffe. In the case of Colombian coffee, a high temperature short time roasting (HTST) was performed in addition. This allowed differences in the formation dynamics when changing the time temperature roasting profiles to be seen, as given in Figs. 9 and 10, as well as differences in the final cup of coffee (Fig. 8). The most pronounced changes in the on-line analysis were, on the one hand, the change of the formation dynamics towards a more pronounced plateau in the VOC intensity after the first crack with longer roasting profiles. This was valid for all analyzed coffees of this study. On the other hand, the roasting times, needed to reach a specific roast degree, were becoming more similar for all three coffees within the LTLT profile. Prolonging the roasting profile seemed to level out the differences in bean properties which led to different roasting times to reach the same roast degree within the MTMT profile. Interestingly, it did not level out the differences in the formation dynamics between the different coffees. Still, the VOCs are formed differently for the respective coffees.

A change in formation dynamics of VOCs when changing the time temperature roasting profile was also observed by Schenker et al. [1]: “The formation of most compounds was found to be dependent on the temperature conditions during roasting.” Again, as they used a fluidized bed roaster, a direct comparison of time intensity profiles is not possible, as they vary when going from one roaster to another. This was shown for example by Baggenstoss et al. [4], comparing different roasting profiles on a fluidized bed roaster and a drum roaster. Similar to Schenker et al. [1], we do not see a common trend of formation for specific compound classes like aldehydes, ketones, alcohols, sulfur-containing molecules when varying the roasting conditions. No classification according VOC formation via Strecker, Maillard reaction or thermal degradation was found either.

Changing the roasting profiles in a more drastic way, from HTST over MTMT to LTLT, as shown in Fig. 10 for Colombian coffee,

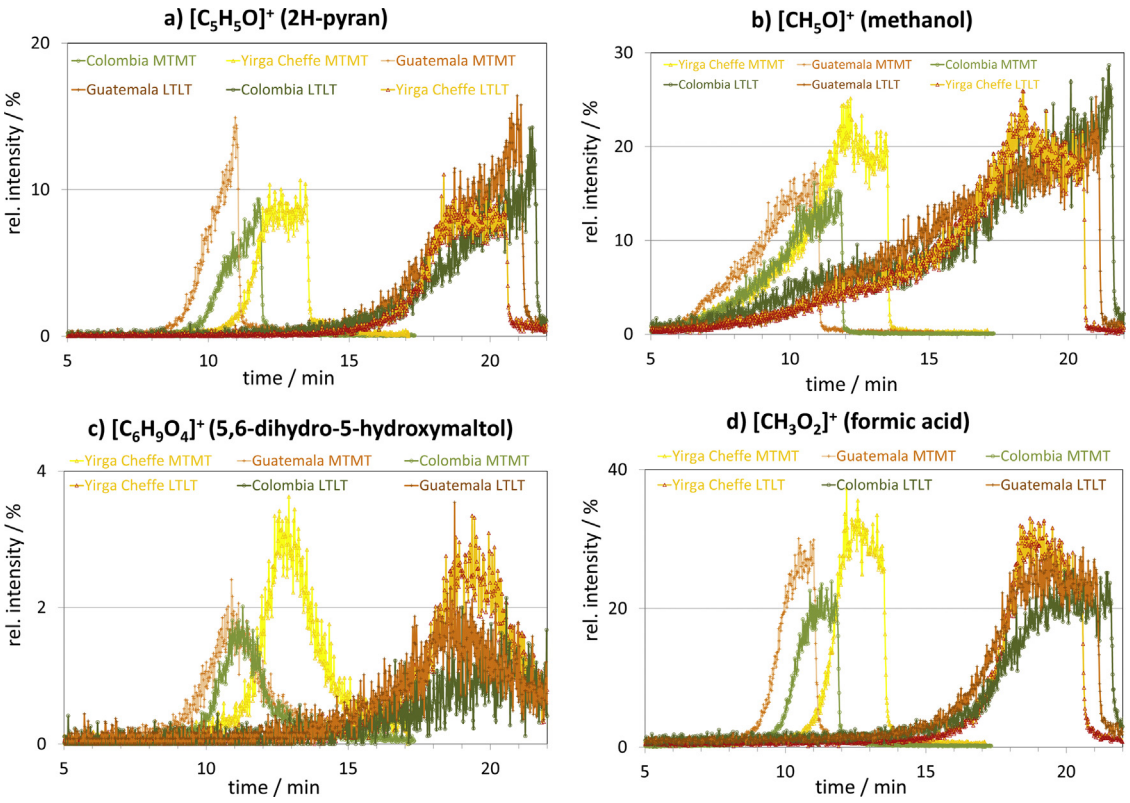

Fig. 9. Influence of the time–temperature roasting profile on the formation pathway of (a) $[C_5H_5O]^+$, (b) $[CH_5O]^+$, (c) $[C_6H_9O_4]^+$ and (d) $[CH_3O_2]^+$ for the coffees Colombia, Yirga Cheffe and Guatemala.

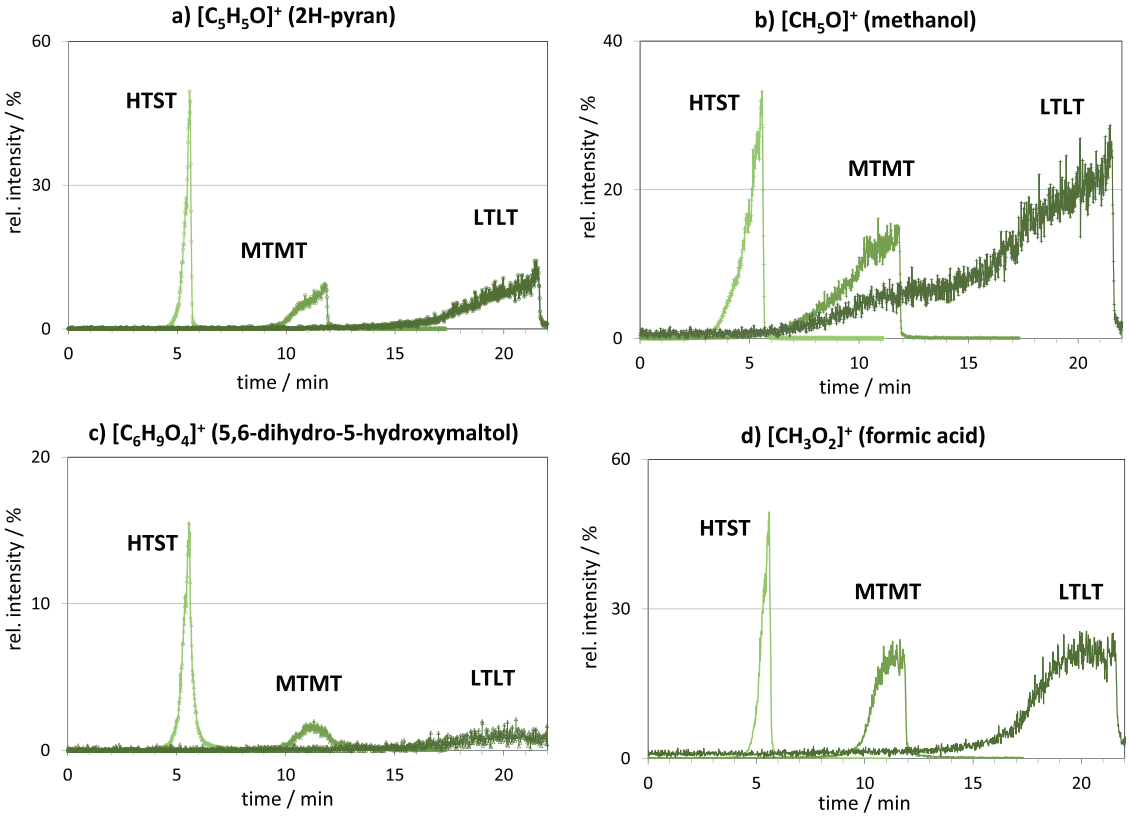

Fig. 10. Influence of the time–temperature roasting profile on the formation dynamics of (a) $[C_5H_5O]^+$, (b) $[CH_5O]^+$, (c) $[C_6H_9O_4]^+$ and (d) $[CH_3O_2]^+$ for Colombian coffee (HTST, MTMT and LTLT roasting profile).

the change in the formation dynamics with changing the roasting profiles became even more pronounced. For the HTST profile, the intensity for all VOCs rose continuously and quickly with roasting time. When going to the MTMT profile, the differences in the formation dynamics of the different VOCs started to become apparent. This reflects how, in longer roasting profiles, a small variation of the roasting time or profile can already change the coffee flavour profile, as different compounds might be produced more or less intensively within this time frame (some rise continuously, others show a plateau, etc.). This opens the opportunity to the roast master to realize specialty aroma profiles with only small changes in the roasting time or roast degree.

3.4.2. Off-line analysis

In the off-line analysis, the elongation of the time temperature roasting profile led to changes in the characteristics of the cup of coffee. An increase with a longer roasting profile was observed for the pH. In contrast, the total headspace intensity decreased when going from MTMT to LTLT, as did the titratable acidity to pH 6.6 and the content of total polyphenols. The titratable acidity to pH 8 did not change significantly, except for the Yirga Cheffe, where it decreased for the LTLT profile. Regarding the composition of the organic acids, there was no change with prolonging the roasting profile from MTMT to LTLT except a decrease of formic acid for Guatemala and Yirga Cheffe. Colombia showed a significant decrease from MTMT to LTLT for citric, malic, lactic and formic acid. Quinic acid content decreased significantly from HTST to LTLT. The content of acetic acid was significantly different for all time temperature roasting profiles of Colombia coffee, with maximum intensity for MTMT.

The content of chlorogenic acids did not change significantly either, except for the Guatemala coffee (decrease from MTMT to LTLT). For the content of total solids and caffeine, there was no general trend for all coffees when prolonging the roasting profile. For Guatemaltecan coffee, the total solids content decreased, for Yirga Cheffe it stayed constant, and for Colombian coffee it decreased from HTST to MTMT, showing no significant difference for the LTLT profile.

Fernandes [48] studied the influence of the roasting profile on the coffee brew as well, roasting coffee blends from an HTST to an LTLT profile to always the same roast degree. They also observed a decrease in titratable acidity and an increase in pH. In addition, they reported a decrease in chlorogenic acid content, as did Lang et al. [47], roasting *C. arabica* from Brazil, Guatemala and Colombia and *C. canephora* var. *robusta* from India. This shows once more the differences between roasting different coffees.

Hence, roasting coffee along an LTLT profile reduced the total headspace intensity and led to a coffee brew of less acidity. One has to keep in mind that in this study, the HTST and LTLT roasting profiles were the shortest and longest time temperature roasting profiles feasible on the Probatino drum roaster, to gather as much information as possible about reducing or prolonging the roasting time. Both roasting profiles are beyond the commercial range of roastings in a drum roaster.

To summarize, the formation dynamics of VOCs in roasting one type of coffee changed when the time temperature roasting profile was prolonged from HTST over MTMT to LTLT. Comparing the roasting of different coffees, the differences in the formation dynamics of the respective VOCs were obvious for the MTMT as well as for the LTLT roasting. The differences in the timing of VOC formation for the respective coffees observed in the MTMT roasting decreased in the LTLT profile. The characteristics of the respective cup of coffee changed, too. Some parameters changed in the same direction for all analyzed types of coffee (decrease of total headspace intensity and titratable acidity to pH 6.6, increase of pH). Others, however, changed differently for different coffees. The titratable acidity to pH 8, for example, only decreased for the Yirga Cheffe coffee when prolonging the time temperature roasting profile from MTMT to LTLT. The content of chlorogenic acids was only reduced for Guatemala coffee. It can be concluded that prolonging the roasting by reducing the energy input in the beans, while keeping constant the roast degree altered the different types of coffee in different ways.

4. Conclusion

The profile of a cup of coffee can be modulated by the choice of the coffee, the roast degree and the time temperature roasting profile. The different coffees Guatemala, Colombia, Djimmah, Yirga Cheffe and Malangsari were affected differently by changing these parameters. The formation dynamics of VOCs were different between these five coffees. In addition, the time when the VOC formation started during roasting differed for each of the coffees when roasting along the same time temperature roasting profile, especially in the case of the MTMT roasting. The earliest VOC formation was observed for Guatemala coffee (Arabica), the latest in case of the Malangsari (Robusta) and Yirga Cheffe (Arabica). Whether this is influenced by the structure (like hardness, compactness) of the green bean or not, cannot be answered conclusively at this point. A detailed analysis of the coffee beans during the roasting process is planned for further experiments.

The changes of the time temperature roasting profile and/or the roast degree were reflected in the characteristics of the cup of coffee brewed from the respectively roasted beans. The roasting parameters did not only affect the intensity of the components, but also their relative composition among the different coffees. The Guatemalan coffee, for example, had a reduced content of chlorogenic acids and total polyphenols for an LTLT roasting to a dark roast degree, whereas a Colombian coffee roasted according to an LTLT profile was characterized by a higher content of polyphenols and a lower total content of organic acids, compared to an MTMT roasted coffee. The HTST roasting profile to a medium roast degree led to a Colombian coffee with a higher content of total polyphenols than an MTMT roasting, and a higher total headspace intensity than a dark HTST roasted coffee.

To conclude, on-line analysis with proton transfer reaction time-of-flight mass spectrometry accompanied by off-line analysis is a powerful tool for gaining a deeper understanding of how a specific profile of a cup of coffee can be generated, based on the choice of coffee and the way of roasting it.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijms.2014.02.010.

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