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Monitoring of semi-volatile organic compounds release during coffee roasting by comprehensive two-dimensional gas chromatography

Fábio Junior Moreira Novaes[1], *Ademário Iris da Silva Junior*[2], *Chadin Kulsing*[3,4], *Yada Nolvachai*[4], *Humberto Ribeiro Bizzo*[5], *Francisco Radler de Aquino Neto*[6], *Claudia Moraes de Rezende*[1], *Philip John Marriott*[4]

[1]Universidade Federal do Rio de Janeiro, Laboratório de Análise de Aromas, Instituto de Química, Avenida Athos da Silveira Ramos, 149, Rio de Janeiro, RJ 21941-895, Brazil

[2]Instituto Federal do Rio de Janeiro, Rua Senador Furtado, 121/125, Rio de Janeiro, RJ20270-021, Brazil

[3]Department of Chemistry, Faculty of Science, Chulalongkorn University, 254 Phyathai Road, Patumwan, Bangkok 10330, Thailand

[4]Australian Centre for Research on Separation Science, School of Chemistry, Monash University, Wellington Road, Clayton, Victoria, 3800, Australia

[5]Empresa Agroindústria de Alimentos, Avenida das Américas, 29501, Rio de Janeiro, RJ23020-470, Brazil

[6]Universidade Federal do Rio de Janeiro, LADETEC, Instituto de Química, Avenida Horácio Macedo, 1281, Rio de Janeiro, RJ 21941-398, Brazil

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Corresponding Author:

E-mail: philip.marriott@monash.edu

Tel: +61-3-99059630

Fax: +61-3-99054597

Abbreviations

SVOC, semi-volatile organic compound; CSC, coconut shell charcoal; XAD-2 (styrene-divinylbenzene resin); FID, flame ionisation detector; GC, gas chromatography; GC×GC, comprehensive two dimensional gas chromatography; LMCS, longitudinally modulated cryogenic system.

Abstract

A novel dynamic approach to profile volatile organic compound (VOC) and semi-VOC (SVOC) emission during coffee roasting aimed at analysing components present in the roasting plume, and to monitor their evolution during the process. Two sorbents – coconut shell charcoal (CSC) and styrene-divinylbenzene resin (XAD-2) – helped collect substances in four sequential time intervals (0-3, 3-6, 6-9 and 9-12 min). Extracted VOCs (<200 Da) and SVOCs were analysed by gas chromatography (GC), and comprehensive two-dimensional gas chromatography (GC×GC) with flame ionisation (FID) and time-of-flight (ToFMS) detection. Results showed CSC extraction presented poor recovery of VOCs and SVOCs released during roasting. However, XAD-2 was able to collect both groups, including SVOCs of >400 Da. GC×GC resolved many co-eluting compounds observed in 1D GC and allowed chemical group type cluster analysis, revealing that many non-polar VOCs are observed within the 0-3 min interval, and that the release of polar and higher molar mass SVOCs were mostly found within the 3-6 min interval. These group-type cluster analyses offer a broad spectrum chemical profile of the released substances. It may also reveal detailed insights into the roast process evolution over time.

Keywords

Coffee bean cracking; SVOC; lipids; fatty acids; caffeine; sterols; solid phase XAD-2 extraction; GC×GC.

1. Introduction

More than 80% of the world's adult population appreciates coffee beverages (Sridevi, Giridhar & Ravishankar, 2011). The quality of coffee beverage correlates with its chemical composition after roasting. Coffee roasting elicits hundreds of different volatile and semi-volatile organic compounds (VOC and SVOC), and well controlled roasting will produce the most desirable coffee (Toledo, Pezza, Pezza & Toci, 2016). The roasting process is a critical and difficult step to control flavour enhancement (Gloess *et al.*, 2014; Chin, Eyres & Marriott, 2015), since its quality control involves monitoring a complex and evolving balance of changing substances, promoted by reactions that occur throughout the roasting process.

Commercial procedures for roasting control normally follow the personal evaluation of coffee masters, with their set of distinct and subjective assessments that involve colour, smell and sound (*e.g.* cracking; coffee bean explosive expansion). Colour alone is not a good general control (Wang & Lim, 2014), the high gas temperatures inside the roaster may interfere with and/or affect smell, and detecting the cracking sound without resorting to more sophisticated equipment can be imprecise (Wilson, 2014).

Direct roast sampling may help clarify the chemical profile and the dynamics of coffee transformation. Direct analysis based on high resolution mass spectrometry (MS) and proton transfer reaction generates chemical profiles during coffee roasting (Czech, Schepler, Klingbeil, Ehlert, Howell, & Zimmermann, 2016; Gloess *et al.*, 2014; Hertz-Schünemann *et al.*, 2013; Wieland, Gloess, Keller, Wetzel, Schenker & Yeretzian, 2012). The MS result may offer chemical identity (or at least empirical formula) of each ion, which may then be assigned to a specific compound– though without isomer-specific identification –using prior knowledge of coffee aroma (Hertz-Schünemann *et al.*, 2013). Thus, the complex mixture of structural and optical isomers in coffee volatiles needs a separation step prior to MS detection (Gloss *et al.*, 2014).

High resolution gas chromatography (GC) is effective for the determination of volatiles in coffee extracts that present a range of acids, alcohols, aldehydes, furans, indoles, ketones, phenolic compounds, pyrazines, pyridines and pyrroles (López-Galilea, Fournier, & Guichard, 2006; Franca, Oliveira, Oliveira, Agresti, & Augusti, 2009; Steiner & English, 2015; Sandron *et al.*, 2015). However, one-dimensional (1D) separation leads to substantial compound co-elution, limiting speciation and data analysis.

Comprehensive two-dimensional gas chromatography (GC×GC) offers better resolution, increased peak capacity, and improved limits of detection (Marriott, Chin, Maikhunthod, Schmarr, & Bieri, 2012). Modulation between a long first dimension (^{1}D) (*e.g.* 30 m) and a short ^{2}D (*e.g.* 1 m)

capillary column preserves the ^{1}D separation whilst providing focusing and further separation on the ^{2}D column (Khummueng, Harynuk, & Marriott, 2006). GC×GC is ideally suited to analysis of volatile compounds in complex samples, and its 2D structured chromatogram can provide support identification, since elution zones of classes of compounds depend on molecular physicochemical properties (Dalluge, Beens, & Brinkman, 2003).

GC×GC has been used for VOCs in coffee samples (Mondello *et al.*, 2004; Ryan, Shellie, Tranchida, Casilli, Mondello, & Marriott, 2004; Ryan & Marriott, 2006; Tranchida, Purcaro, Conte, Dugo, Dugo, & Mondello, 2009; Chin, Eyres, & Marriott, 2011; Chin et al., 2015), but to our knowledge has not been used to monitor the progression in roasting processes. Different column sets with polar ^{1}D column and non-polar ^{2}D columns (P-NP) may also provide good separation. However, polar column phases (e.g., wax phases) have T limits ≤ 260 °C, which promote extended elution times under isothermal operation to elute SVOCs (≥200 Da, and elution T ≥240 °C) (Hertz-Schünemann *et al.*, 2013; EPA, 2018). Ryan *et al.* (2004) used a medium polarity/non-polar combination (MP-NP) to analyse roasted coffee volatiles and observed a shorter total retention when compared with P-NP. Although MP-NP did not attain better separation, its use for SVOCs allows higher oven T (T_{max} ~350 °C) and can elute heavier and polar SVOCs in a more reasonable time.

Previous GC×GC analysis of coffee VOCs used solid phase micro-extraction (SPME) sampling with desorption in the GC inlet (Mondello *et al.*, 2004; Ryan *et al.*, 2004; Ryan & Marriott, 2006; Tranchida *et al.*, 2009; Chin *et al.*, 2011; Chin *et al.*, 2015). A SPME divinylbenzene fibre was able to extract abroad range of VOCs (Mondello *et al.*, 2004; Franca *et al.*, 2009). However, SPME fibres easily saturate with high abundance compounds and can also lose trapped substances, if their desorption in the GC injector is not conducted soon after adsorption (Pawliszyn, 2000).

Previous SVOC sampling studies for occupational exposure employs styrene-divinylbenzene copolymer (XAD-2) or coconut shell charcoal (CSC) (Okeme *et al.*, 2016; Amaral, Novaes, Ramos, Aquino Neto, & Gioda, 2016) in static/passive and flow-through/active sampling (Hayward, Lei, & Wania, 2011). XAD-2with up to 8 h exposure time can accumulate trace analytes on its large sorbent mass, even though the resin has less than half the SPME surface area. Additionally, sealing cartridges after trapping allows cold storage prior to thermal or solvent desorption (Supelco, 2018). These sorbents capture aromatic and polyaromatic hydrocarbons, pesticides, and polychlorinated biphenyls (Hayward *et al.*, 2011; Krugly *et al.*, 2014; Essumang, Dodoo, & Adjei, 2014).

In this work, XAD-2 and CSC sorbents were used to sample coffee VOCs and SVOCs from coffee roaster gas at different roasting intervals. Trapped components were subsequently analysed by 1D GC–FID, GC×GC–FID and GC×GC–TOFMS to study SVOCs distribution at a sequence of time

intervals of the same coffee roasting.

2. Experimental

2.1 Chemicals and Materials

Dichloromethane (DCM; HPLC grade) was from Merck Co. (Merck KGaA, Darmstadt, Germany). Normal alkane standards (C_8 to C_{22}, C_{24}, C_{28} and C_{30}) and saturated fatty acids (FA; 14:0, 16:0, and 18:0) were from Supelco (Bellefonte, PA; all 99% purity). Sterols (β-sitosterol, 40% and stigmasterol, 95%) were from Sigma–Aldrich (St. Louis, MO). CSC (20/40 mesh, 50/100 mg; type A; 226-01) and XAD-2 (40/80 mg, type B, 226-30) as sorbent sample tubes were from SKC Inc. (Eighty Four, PA).

2.2 Sample preparation

Seventy-five gram of green unroasted coffee beans (*Coffea arabica* L.) required 12 min of roasting at a maximum temperature of 230 °C to develop characteristic conditions associated with a light roast in acommercial benchtop air stream coffee bean roaster from Gene Café (model CBR-101, Gyeonggi - Do, Korea). The resulting coffee bean mass loss was 13.8%. The sorbents CSC and XAD-2 were used to trap exhaust roasting gases during four different time intervals (0-3, 3-6, 6-9 and 9-12 min) to track the evolution of roasting volatiles. Supporting Information **Fig S1A** shows the roaster and sampling tube locations. A vacuum pump pulled the roasting gases at 2.5 L min^{-1} through both sorbent tubes placed at the roaster gas outlet. Each experiment used four tubes for each sorbent. After trapping was completed for each sorbent, DCM (1 mL) at 25 °C eluted the trapped substances in each cartridge into a 2 mL vial with vortexing to settle any particulates (2 min). Sample extracts were analysed by 1D GC and GC×GC.

2.3 Analytical Instrumentation

2.3.1 GC and GC×GC–FID analysis

DCM sample extracts were injected (1 μL) at 300 °C in splitless mode (vent closed for 0.75 min) into an Agilent 6850 GC (Santa Clara, CA) with flame ionisation detection (GC–FID) and H_2 carrier gas at constant flow of 1.5 mL min^{-1}. Separation employed an Rxi-17Sil MS column (30 m × 0.25 mm I.D. × 0.25 μm film thickness (d_f); Restek, Bellefonte, PA). The GC×GC–FID column set comprised a mid-polarity Rxi-17Sil MS column (30 m × 0.25 mm I.D. × 0.25 μm d_f; Restek) ^{1}D column, and a non-polar BPX5 Fast column (1.0 m× 0.1 mm I.D. × 0.1 μm d_f; SGE Analytical Science Pty Ltd., Ringwood, Australia) ^{2}D column, connected by a deactivated Press-Tight connector (Restek). A longitudinal modulated cryogenic system (LMCS, Chromatography Concepts Ltd, Doncaster, Australia) used a constant modulation temperature (T_M) of 25 °C, and modulation

period (P_M) of 4 s. The oven temperature (T) program was 40 °C (3 min hold) to 300 °C (7 min hold) at 4 °C min^{-1}. Data collection frequency for the FID was 100 Hz for both 1D GC and GC×GC.

2.3.2 GC×GC–TOFMS analysis of SVOCs

An Agilent 7890A GC with a 7200 series Q-TOFMS (Agilent Technologies, Mulgrave, Australia) and an Everest model LMCS was used with the same column set as above. The GC×GC operation had various P_M as indicated by the ^2t_R scales in respective Figures. A cryotrap T of 80 °C less than the oven T throughout the run improved the remobilisation of polar components cryofocused in this cryotrap. The carrier gas was He (99.99% purity) at a constant flow of 1.5 mL min^{-1}. The Q-TOFMS has a quadrupole for MS/MS operation, but the MS was operated in total transfer ion mode throughout the quadrupole sector. Other conditions were: ion source T at 230 °C; transfer line T at 300 °C; ionisation energy of 70 eV; mass range of 50-500 Da; and TOF mass resolution of 2 GHz in extended dynamic range. Data acquisition was at the highest nominal rate of ca. 50 Hz.

2.4 Data processing

ChemStation software (Agilent) helped acquire and process data acquisition/processing, and Microsoft Excel 2010 and Fortner Transform 3.3 (Fortner, Inc., Savoy, IL) helped data processing and visualization.

For group type analysis (group classification), data analysis was performed according to the previously reported approach (Kulsing, Rawson, Webster, Evans, & Marriott, 2017). For GC×GC–TOFMS analysis, the GC×GC result for each compound class was obtained by analysing extract ion chromatograms (EIC) according to a mass error within ±10 ppm of the exact mass values of all the related analytes in each group. A^1t_R vs. ^2t_R plot for each group was then generated according to the positions of all the peaks within each group.

3. Results and discussion

3.1 Coffee SVOCs separation in 1D GC

The evaluation of CSC and XAD-2 sorbents aimed at finding the best trapping of coffee SVOCs during roasting. Both sorbents were set parallel to the coffee roaster exhaust (Fig. S1A) under the same vacuum flow (2.5 L min^{-1} for each tube) for each time interval (0-3, 3-6, 6-9, and 9-12 min) to monitor the evolution of organic compounds during roasting. Roasting and gas exhaust temperatures started at room temperature and reached 57 °C in 1 min, 229 °C and 146 °C in 2 min, and 230 °C and 154 °C in 3 min. Afterwards, the roasting temperature remained constant and

exhaust temperature raised at 2 – 3 °C min^{-1} (Fig. S1B). Since temperatures over 150 °C in the exhaust do not favour VOC extraction, the focus of this work was SVOCs (Hertz-Schünemann *et al.*, 2013; EPA, 2018). **Fig. 1** shows 1D GC-FID analyses of extracts for each time interval.

Although GC data showed similar profiles in their early parts, XAD-2 extraction presented improved recovery of high molar mass SVOCs along the whole roasting process. Both extractions showed the highest intensity within the 3-6 min time interval. Thus, although CSC and XAD-2 sorbents have similar surface area (Okeme *et al.*, 2016), XAD-2 showed better performance for coffee SVOCs. XAD-2 styrene-divinylbenzene polymer is more hydrophobic, and likely resulted in higher efficiency when compared to CSC.

Figure 1

3.2 Separation of coffee SVOCs using GC×GC-FID

In order to improve resolution, the samples were also analysed by GC×GC–FID. Results confirmed that CSC was not able to trap higher mass coffee SVOCs in reasonable concentrations (Supporting Information **Fig. S2**). On the other hand, XAD-2 presented chromatograms that comprised high mass SVOC, with good coverage of the GC×GC 2D separation space, and the display of structured retentions (**Fig. 2**) that resembled others described in the literature for coffee VOCs with GC×GC (Mondello *et al.*, 2004; Ryan *et al.*, 2004; Dalluge *et al.*, 2003). These results confirm the improved resolution of GC×GC to evaluate coffee SVOCs, showing narrow and higher intensity peaks, higher peak capacity, and better sensitivity than 1D GC.

Four peaks with excessive peak tailing were observed in the GC×GC cryogenic system for chromatograms of XAD-2 extracted samples beyond 3-6 min roasting interval (Fig. 2B-D). In previous work investigating Arabica green coffee oil constituents by GC×GC, the separation of FA without derivatisation revealed similar peak shapes, when a ^{1}D mid-polarity column was also used (Novaes, Kulsing, Bizzo, Aquino Neto, Rezende, & Marriott, 2018). Peak tailing in GC×GC can be indicative of either strong interaction with active silanol groups present either in the capillary tube wall or in the stationary phase, or inefficient substance release during modulation (Ramos & Sanz, 2009). A standard mix of saturated FA containing myristic ($FA_{14:0}$), palmitic ($FA_{16:0}$), and stearic ($FA_{18:0}$) acids was injected under the same chromatographic conditions and showed identical retention times, accompanied by equivalent peak tailing, which indicated the presence of all three FA as coffee SVOC components (Supporting Information **Fig. S3**).

Figure 2

3.4 Group class identification of coffee SVOC XAD-2 extracts by GC×GC–TOFMS

Samples were analysed using GC×GC–TOFMS to propose group class identities. An exhaustive identification of every substance was not the purpose of this work, but rather an overview of chemical class identification to assist group classification. Minor compounds (signal-to-noise ratio S/N <100) were not identified, since they generally had poor library match scores. Ryan *et al.* (2004) found similar difficulty; although the authors detected 1000 peaks, they identified only 17 VOCs in volatiles of roasted coffee beans by GC×GC–TOFMS using SPME with headspace extraction. In this work, the first time span of 0-3 min showed 376 peaks, the second span of 3-6 min showed the highest number, of 741 peaks, the third span of 6-9 min indicated 515 peaks and the last span, 9-12 min, 597 peaks by GC×GC-FID. Twenty-two VOCs that appear in the last three time intervals were subsequently chosen for identification.

Identification of SVOCs (**Table 1**) followed approaches developed by Jiang, Kulsing, Nolvachai & Marriott (2015). The method consists of three steps: (1) comparison of the experimental mass spectrum with the NIST library with match scores ≥750 as an acceptance criterion, (2) calculation of mass accuracy being <20 ppm, and (3) comparison of the experimental retention index (*I*) with literature. In general, step (3) is relevant when the *I* value is available for the same stationary phase. Even though this study employed a mid-polar column with *I* data not available in the NIST library, its experimental *I* data were calculated, since the calculated value must be between the *I* data for non-polar and polar phase columns, both of which are available in the NIST library. Thus, the *I* data reported here can be used to reject unreasonable values. The agreement of all these data filters is required for tentative identification; further positive identification requires injection of authentic standards and comparison with mass accuracy and retention time in ^{1}D (Table 1). The injection of *n*-alkane standards also indicated that no wrap-around existed under these chromatographic conditions.

Table 1

Alkanes, FA, caffeine and sterols are green coffee oil components (Novaes et al., 2017) that are also present in roasted beans (Speer & Kölling-Speer, 2006). Zimmermann and his group monitored the coffee roasting process by photoionisation (PI) and TOFMS, and published three papers. Herz-Schunemann *et al.* (2013) monitored 18 VOCs, Fisher *et al.* (2014) monitored 17 VOC and Czech

et al. (2016) monitored 30 compounds. In the latter case, five chosen SVOCs were fatty acids (16:0, 18:0, 18:2, 20:0, and 22:0). None of these works could determine whether several structures were in fact isomers. Fischer *et al.* (2014) also found caffeine in the gas phase released during coffee roasting using thermogravimetry coupled to PI-TOFMS. Czech *et al.*(2016) found caffeine and several FA (16:0, 18:0, 18:2, 20:0, and 22:0) in coffee roasting off-gas analysis. The release of these compounds in roasting probably occurs during coffee bean cracking, when the beans outpour water, CO_2, VOCs and other SVOCs (Rosa et al., 2016). Alkenes, alcohols and methyl esters are pyrolysis products of FA (Fabbri, Baravelli, Chiavari, Prati, 2005).

In Table 1, masses *m/z* 270 and 282 refer to more than one substance for each fragment ion. Mass spectrometry alone would not distinguish between isopropyl myristate and methyl palmitate (molar mass 270). For the same reason, eicosane, 2-nonadecanone and oleic acid give the same *m/z* 282 ion. The use of GC×GC allowed the independent characterization of these molecules. GC×GC helps systematise component identification, since it produces a chemical profile of isolated substances, and provides the relative abundance of different chemical groups. This can give a broad idea of roasting gas chemical composition, that cannot be otherwise easily obtained, *e.g.*, from MS with soft ionisation based on proton transfer reactions, since these previous works were restricted to low *m/z* compounds (≤300 Da), targeted substances, or do not offer molecular separation (Hertz-Schünemann *et al.*, 2013; Fischer *et al.*, 2014; Gloess *et al.*, 2014; Czech *et al.*, 2016).

TOFMS results helped clarify group classification of GC×GC. **Fig. 3** shows ${}^{1}t_R$ vs.${}^{2}t_R$ plots for the extracted ion chromatograms (EIC) of compounds in different groups that were obtained according to accurate mass analysis with the tolerance for mass accuracy set at 10 ppm. For example, the EIC for C_{14}-C_{24} saturated FA included *m/z* 228.2085, 242.2241, 256.2397, 270.2553, 284.2709, 298.2865, 312.3021, 326.3177, 340.3333, 354.3489 and 368.3645, respectively. Fragment ions of high intensity, characteristic of the class of compounds as well as being present in more than one chromatographic peak, guided the confirmation or discovery of chemical groups and their positioning in the 2D space. This procedure helped define homologous series with the roof tile effect or structured retentions typical of GC×GC. The NIST library also indicated the possibility of homologous compounds from the same class. The use of standards of alkanes, FAMEs and free fatty acids further confirmed this trend (Fig. S3). Another guidance for group classification was the compliance with volatility and polarity orders of substances (Nolvachai, Kulsing, & Marriott, 2017). Wraparound can disturb, but they also help identify, the distribution pattern. Locating these class distributions does not require the identification of every substance, although the selectivity of the styrene-divinylbenzene resin in the cartridges may alter the 'true' distribution of compounds – some substances may have lesser extraction yields, for example.

Figure3

Although there was no specific identification of individual substances in Fig. 3, this classification generally confirms the coffee volatiles already present in the literature. For example, $C_nH_{2n+2}O$ can refer to saturated methylated alcohols; $C_nH_{2n}O$ to mono-unsaturated alcohols, aldehydes and ketones; $C_nH_{2n-2}O$ to mono-unsaturated aldehydes and ketones; $C_nH_{2n-4}O$ to alkylated furans and cyclic ketones; and $C_nH_{2n-6}O$ to benzyl alcohol and vinyl-furanols (Ryan *et al.*, 2004; Cordero *et al.*, 2008; Mondello *et al.*, 2004 and 2009; Chin *et al.*, 2011 and 2015; Amaral *et al.*, 2017).

3.3 Group type analysis in the coffee XAD-2 extracts by GC×GC–FID

GC×GC-FID analysis revealed variation of total composition of VOCs and SVOCs from XAD-2 extraction (**Fig. 4**). The greatest total SVOC amount occurred within the 3-6 min time interval, and this time and temperature (about 180 °C) is expected to correspond to the first crack of the coffee beans (Gloess *et al.*, 2014) (see hood roaster T curve, Supporting Information Fig. S1B for further details). The next two time intervals showed a reduced SVOC level (Fig. 4A), and one might anticipate some thermal-induced change. This behaviour is consistent with observations made by other authors for some specific substances (Gloess *et al.*, 2014; Hertz-Schünemann *et al.*, 2013; Fischer *et al.*, 2014).

Fig. 4B shows a group-type data analysis – replicated for each monitored time interval– that divided the 2D chromatograms into four sectors: lighter/non-polar (LN – upper left corner), lighter/polar (LP – lower left corner), heavier/non-polar (HN – top right corner), and heavier/polar compounds (HP – lower right corner). The horizontal division between polar and non-polar placed caffeine, a water-soluble compound, in the polar region, and fatty acids, immiscible in water, in the non-polar region. The placement of the vertical division at C_{20} resulted from the emphasis on SVOCs and the search for a division more pertinent to their study. According to EPA (2018), SVOCs classification ranges from boiling points (B.P.) 240-260 °C to 380-400 °C, which would roughly span between *n*-alkanes C_{14} and C_{25} – with B.P.'s of 253 °C and 402 °C, respectively.

The comparison with the corresponding separation patterns obtained with GC×GC-TOFMS shown in Fig. 3 helped the identification of compound classes within each sector in GC×GC-FID analysis. Possible compounds in the LN sector included alkanes, alkenes/cycloalkanes, dialkenes/cycloalkenes and $C_nH_{2n-8}O$. LP contained $C_nH_{2n-8}O$, alkylbenzenes, $C_nH_{2n-6}O$, $C_nH_{2n-6}O_2$ and trialkenes/cyclodialkenes. Possible compounds in HN were saturated FA, unsaturated FA with

1-3 double bonds, FAME, $C_nH_{2n}O$, $C_nH_{2n-2}O$, $C_nH_{2n-4}O$ and $C_nH_{2n-6}O$. HP consisted of $C_nH_{2n+2}O$, $C_nH_{2n}O$, $C_nH_{2n-2}O$, $C_nH_{2n-4}O$, $C_nH_{2n-6}O$, $C_nH_{2n-8}O$, caffeine, alkylbenzenes and trialkenes/cyclodialkenes. This division – although possibly resembling the true apportion – is just an arbitrary guidance to help classify the distribution. This approach provided an indicative distribution of SVOCs in each time interval along the roasting axis (Fig. 4A), and showed clear decrease in the release of lighter and non-polar compounds with increased roasting T.

In the first three min, the coffee bean roaster reached 230 °C (see hood roaster T curve, Supporting Information Fig. S1B). At this temperature, free water in the coffee evaporates, sucrose caramelises, aroma formation begins, with the release of more volatile compounds, and coffee beans become brown and swell, as a consequence of Maillard and Strecker reactions (Farah, 2012; Hertz-Schünemann *et al.*, 2013). All these events explain the increasing intensity of LN compounds in the 3-6 min interval, followed by a considerable drop in LN along the roasting time axis (Fig. 4A). In the roaster hood, the roasting T started at 25 °C and rose to 154 °C in 2 min. After that, its temperature rose approximately 2.4 °C min^{-1} until completion of the roasting process at 12 min and 173 °C (Supporting Information Fig. S1). At 3 min, the roaster source is at 230 °C (Supporting Information Fig. S1). At this temperature, the light brown beans darken because of Maillard and Strecker reactions of low- and high-molar-mass compounds such as carbohydrates, proteins, with simultaneous melanoidin production and its thermal degradation (Farah, 2012). This explains the release of light and heavy polar compounds including SVOCs, which normally includes compounds with ≥200 Da (Hertz-Schünemann *et al.*, 2013) (*e.g.* FAs and sterols) or classified in relation to their B.P. from 240-260 ºC to 380-400 ºC (EPA, 2018).

However, the SVOC label may be extended to compounds with lower mass but with higher polarity (which elute relatively later on polar columns), since both physical and chemical characteristics have to be considered to classify this group of compounds. Caffeine is a good example for this exception, since it has a mass of 194 Da and B.P. of 178 ºC, but elutes after stearic acid (284 Da, B.P. 361 ºC) and linoleic acid (280 Da, B.P. 230 ºC) using the investigated column set (elution order shown in Table 1).

The two heavier groups – HN and HP – were the most abundant, comprising more than 80% of the total area of trapped SVOCs. Whilst caffeine is a major component of the HP group, the HN group contains mostly FA (Fig. 4A, values in parenthesis). After 6 min, these two groups seem to have a slight increase in their abundance that could correspond to a second coffee bean cracking process, which would then be characterised by a new, second expansion of the bean internal volume and another release of compounds still retained in the bean matrix (Gloess *et al.*, 2014). This explanation requires testing in further studies.

Figure4

Conclusion

Combining vacuum pump sampling with an XAD-2 sorbent was an efficient, easy and simple system to trap coffee SVOCs during the roasting process. GC×GC analysis presented an informative result and allowed group-type chemical analysis to elucidate the chemical distribution, and monitor coffee roasting. The GC×GC retention of standard compounds using XAD-2 sorbent sampling confirmed the trapping of SVOCs *n*-alkanes, fatty acids (14:0, 16:0, 18:0, 18:1, and 18:2), caffeine, stigmasterol and β-sitosterol – which are green coffee oil components – with all having a surge in abundance in the volatile plume during coffee bean cracking in the3-6 min time interval. Long chain alkenes, alcohols and methyl esters were also found, and they are probably formed by the thermal degradation of fatty acids constituents. After this time, the amount of trapped components extracted from the exhaust plume decreased. The developed method gave an insight into the dynamics of SVOC formation in the roasting of coffee beans. Detection and identification of these compounds along the roasting evolution trajectory opens new possibilities for the study of coffee roasting and the chemical profiling of the roasting process. For further application, the use of a cryofocusing method– for the sampling and rapid introduction into the GC – could be applied to improve the trapping of more volatile compounds and the focusing of all substances. It would enhance the resolution of the earliest eluting peaks and identification of classes and individual compounds in the GC×GC-MS system.

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Supplementary data

The online version includes supplementary data associated with this article.

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Figure Captions

Fig. 1. 1D GC chromatograms for VOCs and SVOCs volatile substances during coffee roasting, with XAD-2 (blue) and CSC (red) sorbent trapping for intervals (A): 0-3 min; (B): 3-6 min; (C): 6-9 min; and (D): 9-12 min. The squares highlight differences between XAD-2 and CSC for SVOCs.

Fig. 2. GC×GC results for SVOC extraction of the coffee roasting process using XAD-2 adsorbents for different time intervals: (A) 0-3 min, (B) 3-6 min, (C) 6-9 min, and (D) 9-12 min. The squares highlight SVOC elution regions.

Fig. 3. Chemical group class distributions from analysis of results of the GC×GC-TOFMS chromatogram for the 3-6 min roasting time interval.

Fig. 4. (A) SVOC distribution obtained from group analysis of the coffee roasting process based on GC×GC-FID results, with an example of arbitrary assignment of 2D chromatogram divisions shown in (B). Bold values for each bar represent the percentage of each group within each time interval, in relation to the total area. Values in parentheses represent the percentage of fatty acids and caffeine in the total SVOC composition, which are present in HN and HP groups, respectively.

Table 1. Identified coffee SVOCs in the roasting atmosphere by GC×GC-TOFMS based on matching the MS NIST library with retention index (*I*) and accurate mass (ppm) equivalence with authentic standards as well as literature data.

^1t_R (min)	Compound Name	CAS Number	Molecular Formula	Match / Rel. Match	*I* NIST (NP)[a]	*I* NIST (P)[a]	*I* Experimental (MP)[a]	Fragment Exact Mass	Fragment Experimental Mass	Mass Accuracy (ppm)
34.14	Hexadecane*	544-76-3	$C_{16}H_{34}$ 226 Da 287 ºC	959/975	1600	1600	1600	226.2655 119.0855(C_9H_{11}) 105.0699(C_8H_9) 55.0542(C_4H_7)	226.2628 119.0841 105.0695 55.0544	11.94 11.98 3.59 -3.15
34.32	1-Hexadecene	629-73-2	$C_{16}H_{32}$ 224 Da 284 ºC	902/919	1587	1648	1616	224.2499 125.1325(C_9H_{17}) 97.1012(C_7H_{13}) 85.1012(C_6H_{13})	224.2499 125.1326 97.1010 85.1009	-0.21 -0.98 1.82 3.25
35.36	Methyl Laurate	111-82-0	$C_{13}H_{26}O_2$ 214 Da 267 ºC	707/811	1481	1803	1648	214.1927 143.1067($C_8H_{15}O_2$) 87.0441($C_4H_7O_2$) 74.0362($C_3H_6O_2$)	214.1917 143.1060 87.0440 74.0360	4.82 4.59 0.64 3.12
37.17	Heptadecane	629-78-7	$C_{17}H_{36}$ 240 Da 303 ºC	874/924	1700	1700	1700	240.2812 210.2342($C_{15}H_{30}$) 182.2029($C_{13}H_{26}$) 155.1794($C_{11}H_{23}$)	240.2798 210.2335 182.2026 155.1787	5.63 3.34 1.66 4.69
39.87	Octadecane*	593-45-3	$C_{18}H_{38}$ 254 Da 316 ºC	865/925	1800	1800	1800	254.2968 225.2577($C_{16}H_{33}$) 183.2107($C_{13}H_{27}$) 169.1951($C_{12}H_{25}$)	254.2955 225.2578 183.2097 169.1934	5.12 -0.54 5.61 9.91
42.27	Myristic Acid*	544-63-8	$C_{14}H_{28}O_2$ 228 Da 251 ºC	709/847	1769	2697	1900	228.2084 185.1536($C_{11}H_{21}O_2$) 129.0910($C_7H_{13}O_2$) 73.0284($C_3H_5O_2$)	228.2077 185.1535 129.0903 73.0289	2.99 0.57 5.47 -6.77
42.71	Isopropyl Myristate	110-27-0	$C_{17}H_{34}O_2$ 270 Da 315 ºC	725/815	1814	2027	1918	270.2553 228.2084($C_{14}H_{28}O_2$) 185.1536($C_{11}H_{21}O_2$) 129.0910($C_7H_{13}O_2$)	270.2534 228.2076 185.1532 129.0903	7.15 3.42 2.19 5.47
43.46	Palmitoleyl Alcohol	10378-01-5	$C_{16}H_{32}O$ 240 Da 389 °C	693/752	1863	2413	1948	240.2448 194.2029($C_{14}H_{26}$) 165.1638($C_{12}H_{21}$)	240.2438 194.2022 165.1633	4.03 3.62 2.89

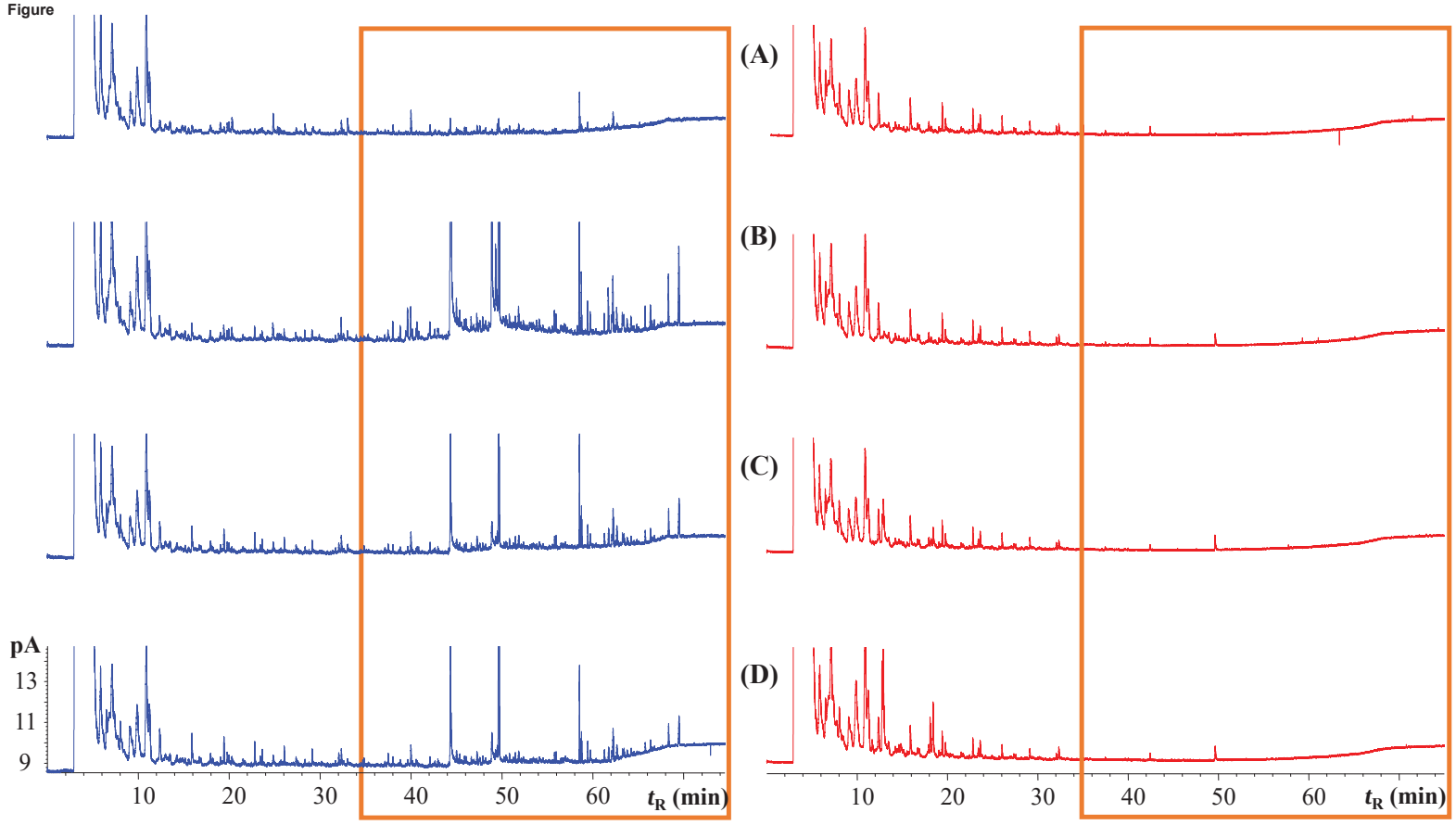
								109.1012(C_8H_{13})	109.1011	0.70
45.71	Methyl Palmitate	112-39-0	$C_{17}H_{34}O_2$ 270 Da 417 °C	651/784	1878	2210	2040	270.2553 227.2006($C_{14}H_{27}O_2$) 143.1062($C_8H_{15}O_2$) 87.0441($C_4H_7O_2$)	270.2537 227.2001 143.1062 87.0440	6.04 2.01 3.19 0.64
47.38	Palmitic Acid*	57-10-3	$C_{16}H_{32}O_2$ 256 Da 351 °C	890/905	1968	2908	2110	256.2397 213.1849 ($C_{13}H_{25}O_2$) 185.1536 ($C_{11}H_{21}O_2$) 129.0910 ($C_7H_{13}O_2$)	256.2382 213.1851 185.1539 129.0914	5.63 -0.81 -1.53 -3.36
48.26	Oleyl Alcohol	143-28-2	$C_{18}H_{36}O$ 269 Da 330-360 °C	818/850	2061	-	2149	250.2655($C_{18}H_{34}$) 222.2342($C_{16}H_{30}$) 152.1560($C_{11}H_{20}$) 124.1247(C_9H_{16})	250.2655 222.2337 152.1564 12.1247	0.01 2.26 -2.94 0.42
49.48	Eicosane*	112-95-8	$C_{20}H_{42}$ 282 Da 344 °C	849/891	2000	2000	2000	282.3281 238.2655($C_{17}H_{34}$) 183.2107($C_{13}H_{27}$) 99.1168(C_7H_{15})	282.3306 238.2656 183.2111 99.1169	-8.85 -0.41 -2.03 -0.74
50.07	2-Nonadecanone	629-66-3	$C_{19}H_{38}O$ 282 Da 344 °C	727/890	2106	-	2230	282.2917 180.1873 ($C_{13}H_{24}$) 127.1117 ($C_8H_{15}O$) 71.0491 (C_4H_7O)	282.2906 180.1878 127.1113 71.0492	3.96 -3.04 3.47 -0.83
50.37	Methyl Stearate	12-61-8	$C_{19}H_{38}O_2$ 299 Da 443 °C	658/726	2077	2418	2245	298.2866 143.1067 ($C_8H_{15}O_2$) 87.0441 ($C_4H_7O_2$) 74.0362 ($C_3H_6O_2$)	298.2851 143.1062 87.0440 74.0362	5.14 3.19 0.64 0.42
51.87	Stearic Acid*	57-11-4	$C_{18}H_{36}O_2$ 284 Da 361 °C	875/903	2167	3159	2316	284.2710 241.2168 ($C_{15}H_{29}O_2$) 185.1536 ($C_{11}H_{21}O_2$) 129.0910 ($C_7H_{13}O_2$)	284.2688 241.2145 185.1534 129.0903	7.43 0.94 1.22 5.78
52.02	Oleic Acid	112-80-1	$C_{18}H_{34}O_2$ 282 Da 360 °C	813/872	2145	3179	2323	282.2547 264.2448($C_{18}H_{32}O$) 213.1849($C_{13}H_{25}O_2$) 185.1536($C_{11}H_{21}O_2$)	282.2553 264.2439 213.1852 185.1535	2.24 3.28 -1.38 0.57
52.77	Linoleic Acid	60-33-3	$C_{18}H_{32}O_2$ 280 Da 230 °C	834/839	2095	3192	2358	280.2397 209.1536($C_{13}H_{21}O_2$) 182.1301($C_{11}H_{18}O_2$) 124.1247(C_9H_{16})	280.2385 209.1559 182.1310 124.1240	4.22 -10.97 -4.77 5.25
52.90	(9Z)-9,17-Octadecadienal	56554-35-9	$C_{18}H_{32}O$ 264 Da 360 °C	454/770	1997	2372	2363	264.2448 109.0648 (C_7H_9O) 95.0855 (C_7H_{11})	264.2475 109.0633 95.0851	-10.34 13.67 4.49

								81.0699 (C_6H_9)	81.0698	0.95
53.20	Caffeine*	58-08-2	$C_8H_{10}N_4O_2$ 194 Da 178 ºC	859/868	1795	-	2378	194.0798 165.0771($C_7H_9N_4O_2$) 109.0634($C_5H_7N_3$) 82.0525($C_4H_6N_2$)	194.0808 165.0764 109.0642 82.0531	-5.01 4.16 -6.89 -6.71
62.84	Nonacosane	630-03-5	$C_{29}H_{60}$ 409 Da 443 ºC	823/883	2900	2900	2900	408.4690 211.2420($C_{15}H_{31}$) 155.1794($C_{11}H_{23}$) 99.1168(C_7H_{15})	408.4694 211.2422 155.1796 99.1168	-1.09 -0.82 -1.11 0.27
76.66	Stigmasterol*	83-48-7	$C_{29}H_{48}O$ 412 Da 490 ºC	725/818	3168	-	>3000	412.3700 394.3594 ($C_{29}H_{46}$) 271.2056 ($C_{19}H_{27}O$) 255.2107 ($C_{19}H_{27}$)	412.3693 394.3578 271.2041 255.2095	1.62 4.06 5.69 4.81
78.31	β-Sitosterol*	83-46-5	$C_{29}H_{50}O$ 414 Da 502 ºC	813/884	3204	-	>3000	414.3856 329.3203 ($C_{24}H_{41}$) 213.1638 ($C_{16}H_{21}$) 145.1012 ($C_{11}H_{13}$)	414.3851 329.3195 213.1636 145.1008	1.25 2.36 0.83 2.60

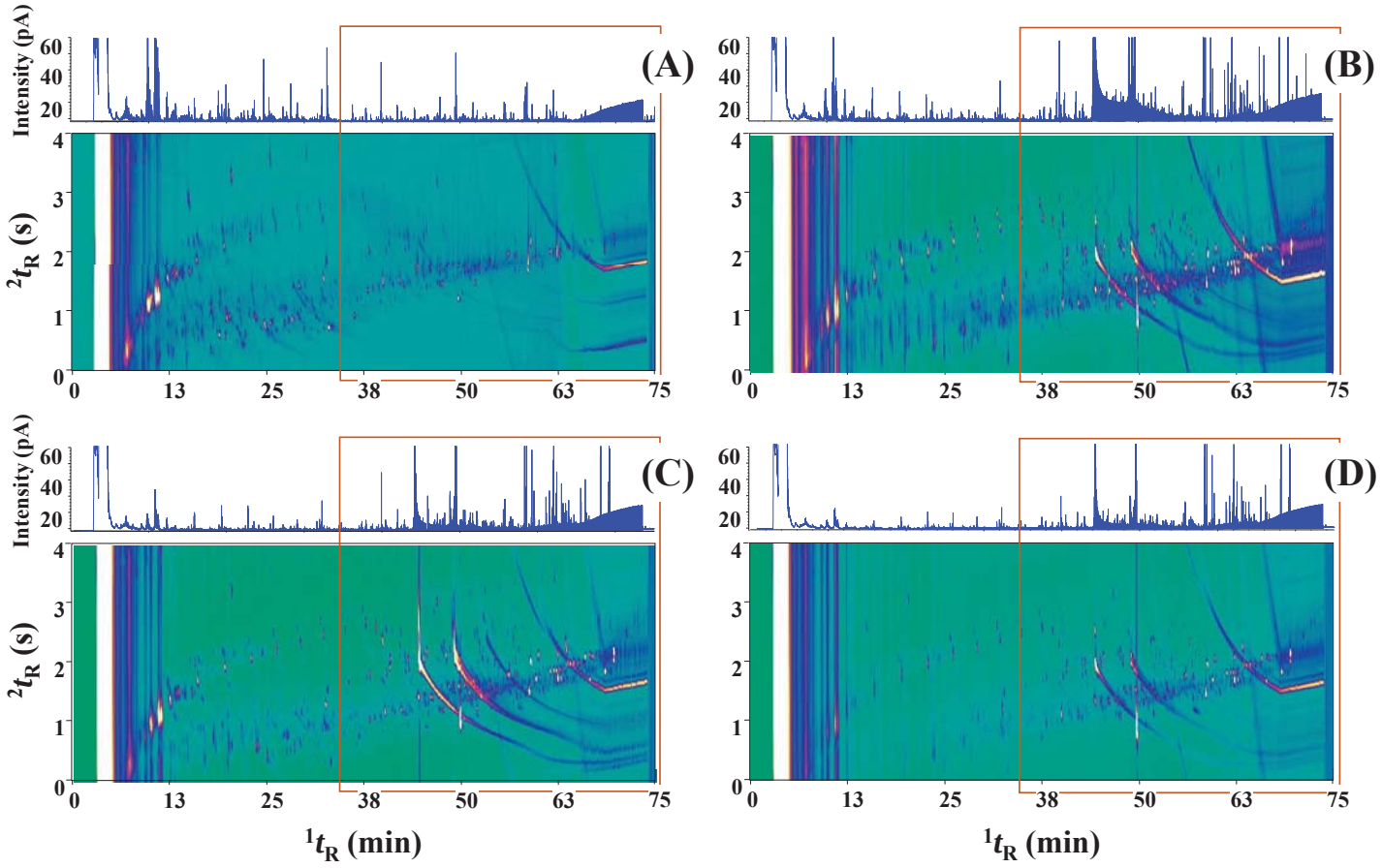
*Authentic Standards (Section 2.1); Mass spectra of compounds present in Supplementary Information, Fig. S4-S6.

[a] *I* data on non-polar (NP), polar (P) and mid-polarity (MP) columns respectively.

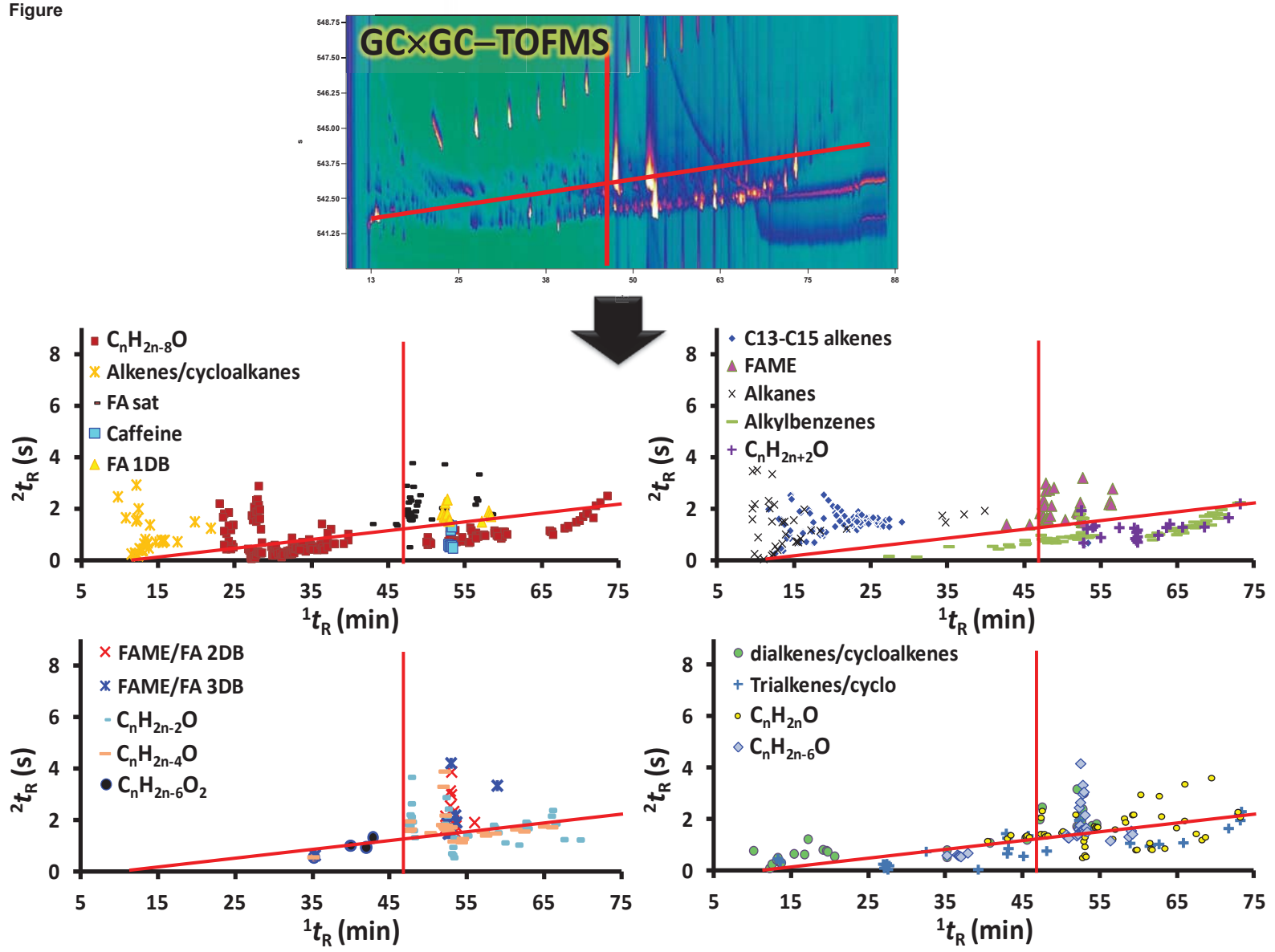
Figure



Figure



Figure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FA sat
Caffeine
FA 1DB
C13-C15 alkenes
FAME
Alkanes
Alkylbenzenes
$C_nH_{2n+2}O$
FAME/FA 2DB
FAME/FA 3DB
$C_nH_{2n-2}O$
$C_nH_{2n-4}O$
$C_nH_{2n-6}O_2$
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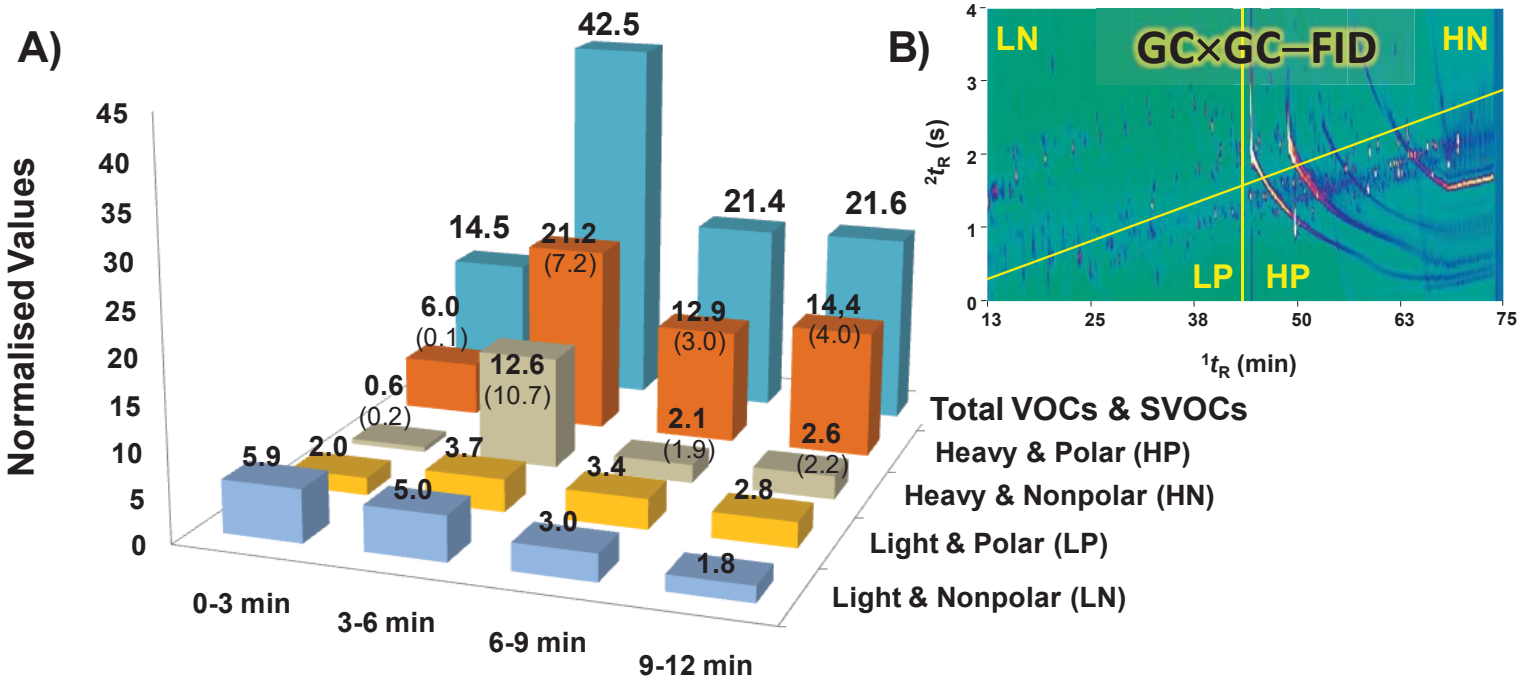
Figure


A)
Normalised Values
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14.5
21.2
(7.2)
21.4
21.6
6.0
(0.1)
12.9
(3.0)
14,4
(4.0)
12.6
(10.7)
0.6
(0.2)
2.1
(1.9)
2.6
(2.2)
5.9
2.0
3.7
5.0
3.4
2.8
3.0
1.8
0-3 min
3-6 min
6-9 min
9-12 min
Total VOCs & SVOCs
Heavy & Polar (HP)
Heavy & Nonpolar (HN)
Light & Polar (LP)
Light & Nonpolar (LN)
B)
LN
GC×GC–FID
HN
LP
HP
^2t_R (s)
^1t_R (min)
4
3
2
1
0
13
25
38
50
63
75