On-line coffee flavour formation analysis using PTR-ToF-MS during roasting under different atmospheres

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Abstract

The impact of the atmosphere on the flavour formation of coffee aroma during roasting was investigated by means of on-line proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS). Roasting under inert atmosphere (nitrogen) was compared to roasting under oxidative conditions (air). Roasting under air has resulted in overall higher intensities of PTR-ToF-MS time-intensity profiles for seven mass peaks, which were significantly higher in intensity for ≥30 % of the roasting duration. Conversely, to the coffee roasted in air, coffee roasted under nitrogen had an unpleasant smell and lacked the distinctive coffee aroma. The results show clear differences between the flavour formation during coffee roasting in different atmospheres and provide evidence that a certain degree of oxidation during roasting is essential to formation of coffee aroma.

Introduction

Coffee roasting contributes most significantly to coffee aroma by transforming the green coffee beans both physically and chemically into its characteristic end-product. Thermally induced pathways, including the Maillard reaction, generate a plethora of volatile organic compounds (VOCs) that contribute to the coffee's characteristic aroma. During coffee roasting, these reactions occur throughout the bean, resulting in a portion of the volatiles being released into the roaster exhaust while the rest remains trapped within the bean matrix. Roaster exhaust is primarily composed of water vapour, driven off the beans through air convection. This study aims to investigate the influence of oxidative flushing of the roasting chamber during roasting on the VOC composition of the roaster exhaust gas. Previous EPR studies suggest that oxygen does not contribute to radically driven pathways during roasting [1]; however, this does not exclude it from being essential in non-radical pathways.

Traditionally studied using static measurement techniques, such as gas chromatography mass spectroscopy (GC/MS), coffee aroma analysis has recently adopted more dynamic approaches, for example PTR-ToF-MS. Several groups have used PTR-ToF-MS to monitor the exhaust gas of coffee roasters. Wieland and associates [2] used this highly sensitive, time resolved technique to predict the coffee roast degree based on the evolution of the exhaust gas composition. Whereas Gloess and colleagues [3] found that the exhaust gas composition was coffee origin dependent, providing evidence that different VOC pathways were occurring. The sensitivity of PTR-ToF-MS was a key feature in the present study to investigate the impact of anaerobic and oxidative conditions on the roaster exhaust gas VOC composition.

Experimental

Coffee roasting

Arabica coffee beans from Guatemala were used for roasting experiments. The coffee was conditioned before experiments for 20 min at 105 °C and roasted in 10 g batches. A modified pilot plant type 4E Reactor vessel (Büchi, Uster, Switzerland) was

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used for roasting. The reactor was set horizontally and consisted of an internal fan, rotating sample basket and two heaters (internal and in the vessel jacket). The inlet to the reactor vessel was connected to air or nitrogen supply for purging the reactor at approximately 20 L_N/min (normal litre per minute). The outlet of the reactor was left open. Coffee was roasted 20 min to reach a set point of 180 °C at the sensor in the reaction vessel.

PTR-ToF-MS

The PTR-ToF-MS was interfaced directly to the inside gas of the reaction vessel using a custom built dilution system. The experimental setup is shown schematically in Figure 1. The outlet of the dilution system was actively pumped and nitrogen was introduced to the dilution stream at 3.9 L_N/min. The sampling flow rate was set to 24.0 ± 0.4 mL_N/min (mean ± SD) from the roasting chamber, to achieve dilution of about 160-fold. The gas lines were heated to 90 °C and the dilution system was heated to 120 °C. A PTR-ToF-MS 8000 mass spectrometer (Ionicon) was used. The PTR drift tube was operated at 80 °C and 140 Td. The mass axis calibration was performed on $[H_3{}^{18}O]^+$, acetone ($[C_3H_7O]^+$) and caffeine ($[C_8H_{11}N_4O_2]^+$).

Gas chromatography

Headspace GC/MS (system with cryogenic CO_2 oven cooling) was performed on roasted and ground coffee beans. Two grams of coffee powder were transferred into vials and analysed with HS GC/MS based on a previously published method [4]. Peak identification was based on comparing the mass spectra with the NIST08 database. In total, 58 peaks were evaluated.

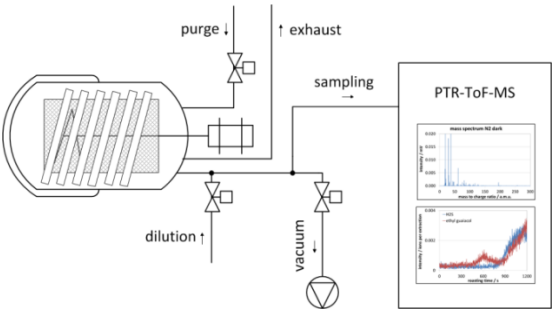

Figure 1: Schematics of the coupling of the PTR-ToF-MS to the reaction vessel for on-line PTR-ToF-MS analysis of the exhaust gas during roasting under controlled atmosphere.

Results and Discussion

The aerobic conditions realised by flushing the roasting chamber with air were found to have a significant influence on the coffee aroma. Sensory observations parallel to those made by Tai and Ho's [4] for cysteine model systems, suggesting that cysteine's oxidative state plays an essential role in the development of coffee's aroma profile. These observations are further supported by differences observed, using PTR-ToF-MS, in the exhaust gas composition.

Roasting under inert atmosphere increased the intensity of m/z 34.996, tentatively assigned to dihydrogen sulphide (H_2S). The increased intensity of H_2S (Figure 2a) was accompanied with an unpleasant aroma, a similar unpleasant aroma was observed by Tai and Ho [4]. These authors observed that when cysteine's sulphur group was reduced sulphur containing molecules were dominant within the product profile [4].

Roasting under oxidative conditions generated characteristic differences within the PTR-ToF-MS profile and restored the characteristic coffee aroma. Tai and Ho [4] observed an absence in sulphur containing compounds as well as, "a strong coffee note" when the sulphur side chain of cysteine was oxidized to cysteinesulfinic acid.

Aerobic roasting increased the intensities and shape of several VOC PTR-ToF-MS profiles (Table 1) demonstrating the influence of oxygen on the evolution of coffee aroma formation pathways. Amongst the most prominent differences was the higher intensity observed for m/z 153.0910, tentatively assigned to 4-ethylguaiacol (Figure 2b).

Table 1: Compounds of significantly higher intensities generated during coffee roasting in either air or inert (nitrogen) atmosphere.

Atmosphere	*On-line PTR-ToF-MS*[a]	*Headspace GC/MS*[b]
Nitrogen	m/z 34.996 (H_2S)	Methanethiol, dimethyl sulfide
Air	m/z 31.0178 (CH_2O, formaldehyde), m/z 44.0174 (CH_2NO^+), m/z 55.0542 (C_4H_6, butadiene), m/z 67.0542 (C_5H_6), m/z 107.0491 (C_7H_6O, benzaldehyde), m/z 135.1 (unresolved), m/z 153.0910 ($C_9H_{12}O_2$, 4-ethylguaiacol)	Dimethyl disulphide

[a] PTR-ToF-MS: mean intensities (n=4) differ for at least 2 SD for >30% of roasting time, compounds were tentatively assigned based on molecular mass.

[b] HS GC/MS: t-test, $P < 0.1$

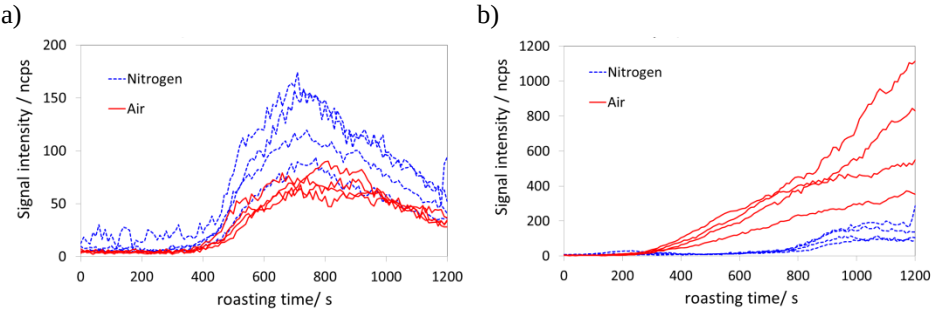

Figure 2: Time-intensity profiles of (two samples: air and nitrogen, each four repetitions) (a) a VOC of mass-to-charge-ratio (m/z) 34.996 (tentatively assigned to protonated H_2S) and (b) m/z 153.091 (tentatively assigned to protonated 4-ethyl guaiacol) of roasting in air and nitrogen.

PTR-ToF-MS time-intensity profile of m/z 107.049 (tentatively assigned to protonated benzaldehyde) was observed at higher intensity when roasting in air (Figure 3a), but no difference in the shape of the profile was seen. Despite no obvious difference in profile, the larger amount of benzaldehyde formed during aerobic roasting is consistent with studies on model systems [5], where oxidative degradation of phenylalanine at high temperatures was studied. Phenylacetaldehyde, the Strecker aldehyde of phenylalanine has been suggested as an intermediate for benzaldehyde formation, but it does not show a significant difference between air and nitrogen roasting (Figure 3b). This could be caused by less reproducible signal for phenylacetaldehyde, or alternatively that oxidative

formation of benzaldehyde in coffee matrix does not go through a phenylacetaldehyde intermediate.

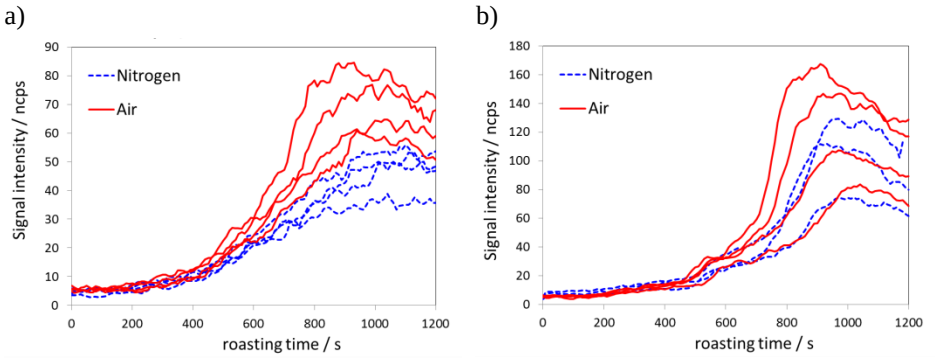

Figure 3: Time-intensity profiles of (two samples: air and nitrogen, each four repetitions) (a) m/z 107.049 (tentatively assigned to protonated benzaldehyde) and of (b) m/z 121.067 (tentatively assigned to phenylacetaldehyde) of roasting in *air* and *nitrogen*.

The GC/MS analysis was performed seven days after coffee roasting. The higher intensity of methanethiol in samples roasted in nitrogen indicated that there is less oxidative degradation during storage. This is consistent with higher amounts of dimethyl disulphide in the samples roasted in air. Dimethyl disulphide is a product of methanethiol oxidation and is used as an indicator of coffee freshness in its ratio against methanethiol [6].

The aerobic conditions in the roaster play an essential role in the development of characteristic coffee aroma. Under anaerobic conditions dihydrogen sulphide (H_2S) serves as the dominant nucleophile leading to high concentrations of primarily sulphur containing VOCs, which unbalances coffees aroma profile leading to an undesirable sensory experience. Oxidative conditions suppress the formation of H_2S by oxidizing coffee's sulphur groups. Suppression of H_2S allows ammonia to become the dominant nucleophile allowing for the development of more desirable aroma profiles.

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