International Journal of Mass Spectrometry 424 (2018) 49–57

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Full length article

On-line analysis of coffee roasting with ion mobility spectrometry–mass spectrometry (IMS–MS)

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ARTICLE INFO

Article history:
Received 10 September 2017
Received in revised form
14 November 2017
Accepted 19 November 2017
Available online 22 November 2017

Keywords:
Ion mobility spectrometry–mass spectrometry (IMS–MS)
On-line analysis
Coffee roasting
Pyrazines
Fatty acids

ABSTRACT

On-line analysis of coffee roasting was performed using ion mobility spectrometry–mass spectrometry (IMS–MS) with corona discharge ionization. This is the first time that formation of volatile organic compounds (VOCs) during coffee roasting was monitored not only in positive but also in negative ion mode, and not only with mass spectrometry, but also with ion mobility spectrometry. The temporal evolution of more than 150 VOCs was monitored during the roasting of Brazilian *Coffea arabica*. Mass-selective ion mobility spectrometry allowed a separation of isobaric and isomeric compounds. In positive ion mode, isomers of alkyl pyrazines were found to exhibit distinct time-intensity profiles during roasting, providing a unique insight into the complex chemistry of this important class of aroma active compounds. Negative ion mode gave access to species poorly detectable by other on-line methods, such as acids. In this study, the release of fatty acids during coffee roasting was investigated in detail. These increase early on in the roasting process followed by a decrease at the same time as other VOCs start to be formed.

1. Introduction

Human beings are provided by nature with five senses: sight, hearing, taste, touch and smell. These warn us about danger, and fill life with delightful moments. Smell, for example, prevents us from eating spoilt food, but on the other, what would a good meal be without the delicious aroma? Mankind is therefore constantly trying to improve the aroma of food, and to understand the chemistry behind it.

From a chemist's perspective, aroma consists of volatile organic compounds (VOCs), and smell is an interaction between these VOCs and receptors in the nose. A specific aroma may be evoked by just a few VOCs, as raspberry is dominated by the ketones (4-(4-hydroxyphenyl)-butan-2-one) and α- and β-ionone [1]. For other aromas, however, a complex interplay of up to 40 VOCs is needed to create the final sensory impression [2]. Above a cup of coffee, for example, almost 1000 VOCs have been identified, and at least 20 of them are needed to reconstitute coffee aroma [3–15].

This variety of coffee aroma compounds is largely generated during the roasting of green coffee beans, in a complex interplay of various chemical reactions. One of these is the Maillard reaction, in which sugars react with amino acids to form aroma compounds such as alkyl pyrazines, which contribute a roasty note. Pyridines, in contrast, are formed by thermal degradation of trigonelline. Analysis of these reactions could provide a deeper understanding of how to treat coffee beans to elicit best flavour properties.

These analyses have traditionally been performed with gas chromatography. Samples are taken at different steps of the coffee roasting process and analysed off-line [11,16–20]. Direct monitoring of roasting is, however, preferable to gain insight into the complex pathways of chemical reactions of VOC formation. On-line analysis of VOC formation additionally saves the time and cost of sample preparation, and avoids process interruption. This approach has already been applied successfully for coffee roasting, especially using mass spectrometry coupled with different ionization methods: resonance enhanced multi photon ionization time-of-flight mass-spectrometry (REMPI-TOF-MS), single photon ionization TOF-MS (SPI-TOF-MS), [21–27] as well as proton-transfer-reaction mass spectrometry (PTR-MS). The first on-line analyses of coffee roasting with PTR-MS were performed using a quadrupole mass spectrometer [28–30], which is limited in

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https://doi.org/10.1016/j.ijms.2017.11.017

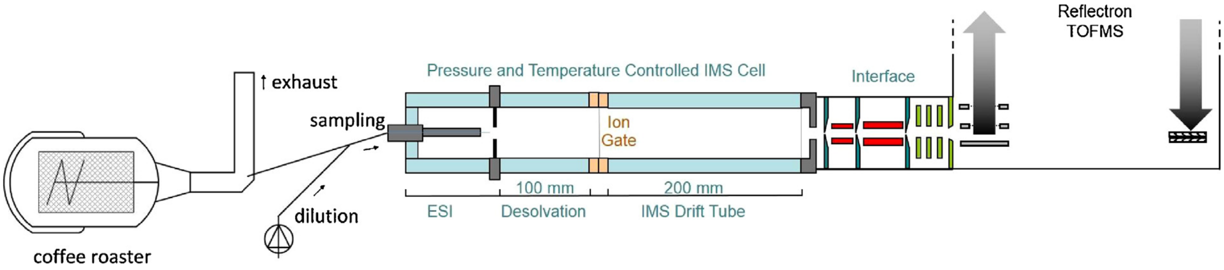

Fig. 1. Schematic setup of the coupling of the TOFWERK IMS-TOF to the coffee roaster.

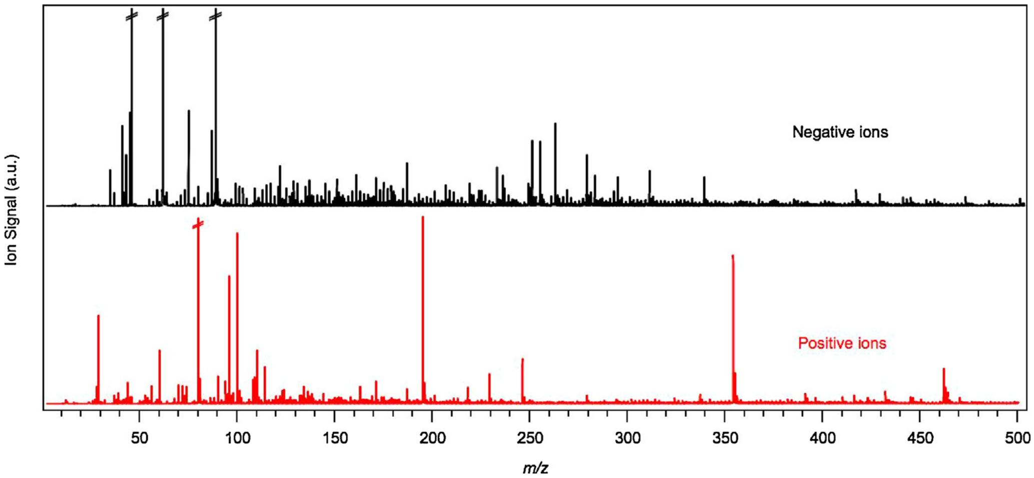

Fig. 2. Mass spectra summed over the entire roasting process in negative (top; scaled to the peak at *m*/*z* 265 as base peak) and positive (bottom; scaled to the peak at *m*/*z* 195 as base peak) ion modes. The largest peaks are truncated to better show the lower abundant species.

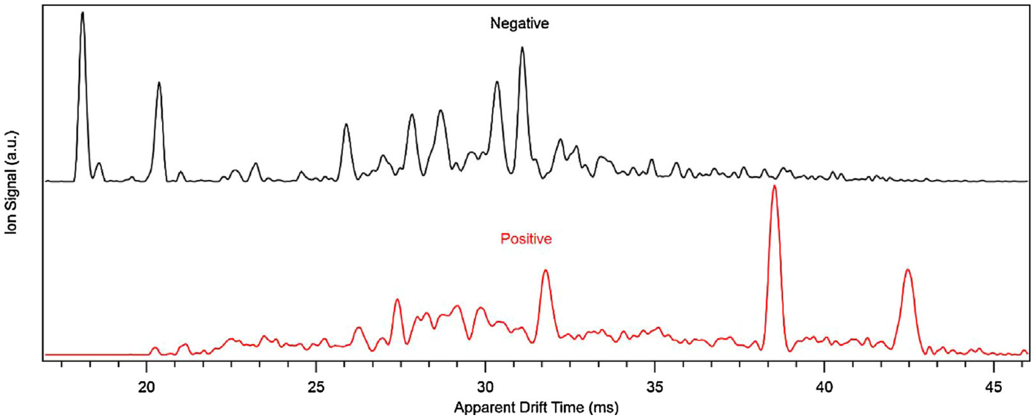

Fig. 3. Summed ion mobility spectra corresponding to the mass spectra of Fig. 2, in negative (top) and positive (bottom) ion modes.

sensitivity and mass resolution because it is a scanning instrument. Coupling the PTR source to a time-of-flight mass spectrometer (PTR-TOF-MS) was a step forward, as it delivers information about all ions simultaneously, and the higher mass resolution allows separation of some isobaric compounds. First PTR-TOF-MS studies of coffee roasting showed specific formation dynamics for different VOCs, and how these changed with different time-temperature roasting-profiles to the same roast degree [31–34]. Further studies shed light on how chemical reactions varied when roasting different coffees along the same time-temperature roasting profile [35]: Both the start of aroma formation varied as well as the dynamics of VOC formation.

While TOF-MS provides far more information and better mass resolution than a quadrupole MS, it is still unable to resolve multiple compounds of a single composition, such as isomers of alkyl pyrazines or of chlorogenic acids (CGAs). A partial solution to this problem is to perform a low resolution flash GC prior to injecting into the mass spectrometer. Even though experimental time resolution is reduced, on-line analysis can still be performed. This approach has been reported by Romano et al. for wine analysis and Ruzsanyi et al. for the analysis of human breath and of VOCs emanated through skin [36,37].

Both laser-based and proton transfer techniques exhibit some selectivity in the ionization process. For REMPI and SPI, VOCs must absorb light of the respective wavelength. In a PTR source, only molecules with proton affinities higher than water become ionized by H^+ transfer. In both methods only positive analyte ions are generated. A different ionization technique, allowing the analysis of a