Comparison of VOC measurements in Nashville, TE, during the Southern Oxidants Study (SOS) 1999

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Abstract

During the Southern Oxidants Study (SOS) 1999 Nashville campaign ambient air samples were analyzed at Cornelia Fort Airport (CFA) for organic compounds by two independent methods: 1) a gas chromatographic systems operated by NOAAs Aeronomy Laboratory, which performed immediate analysis of collected samples and 2) an in situ proton transfer reaction mass spectrometer (PTR-MS) system operated by the University of Innsbruck. The sample protocols were quite different for the different methods. The GC system sequentially collected and analyzed air samples each 60 minutes for VOCs. The in-situ PTR-MS system measured more than 20 VOCs on a time shared basis for 5 to 15 seconds respectively, once each 5 minutes. The PTR-MS system is not able to distinguish between isobaric species, therefore acetone and propanal (MVK and MACR) values measured by NOAAs GC were added up prior to comparison with the respective PTR-MS values. For all species mentioned above the different measurement methods show good agreement. In Figures 1 and 2 Isoprene and MVK&MACR values are shown.

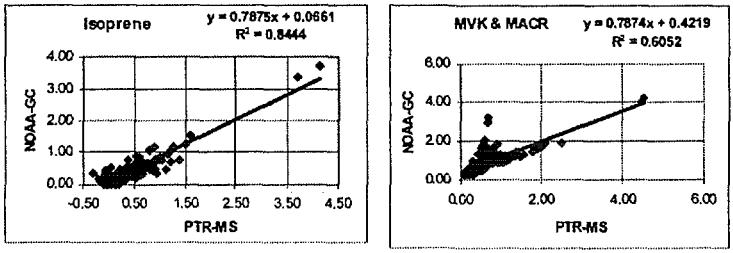

Figure 1: Scatter plots of coincident PTR-MS and GC measurements for isoprene and MVK & MACR for the time period June 18 – June 29 obtained during SOS 99 in Nashville, TE.

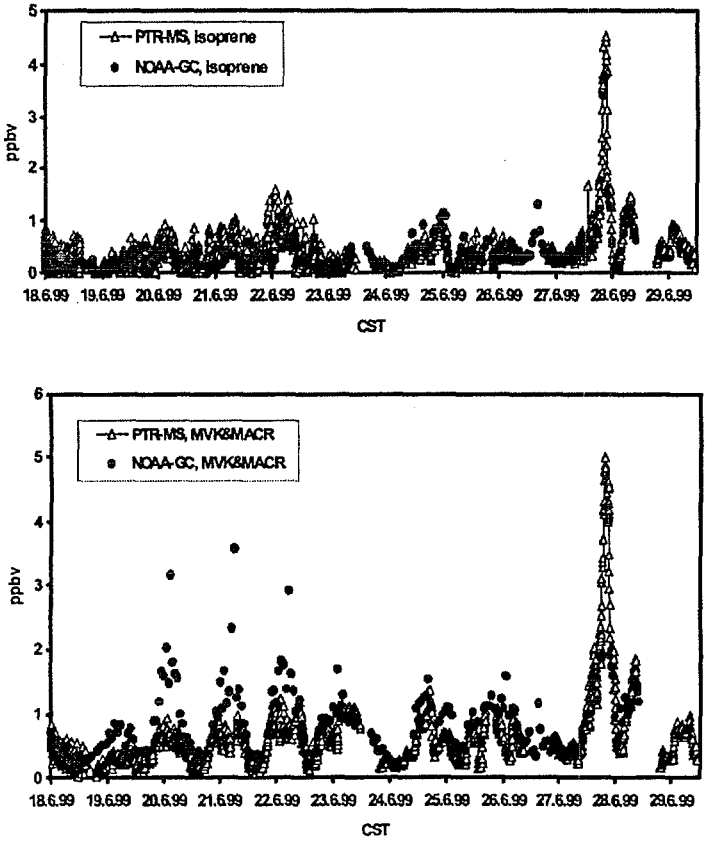

Figure 2: Synoptic variations for isoprene and its photooxidation products MVK & MACR for the time period June 18 to June 29 as observed at Cornelia Fort Airport in Nashville TE, during SOS 99. Open triangles represent in-situ PTR-MS results, full circles; NOAAs GC measurements.

In-Mouth Coffee Aroma: Breath-By-Breath Analysis of Nose-Space by PTR-MS While Drinking Coffee

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Abstract

PTR-MS combined with a fast response inlet-system was used to investigate breath-by-breath the evolution of the in-mouth coffee aroma. The time-intensity profiles of a series of 14 masses were monitored on-line. From an analytical perspective, the purpose of this contribution is to demonstrate the potential of PTR-MS for real-time nose-space analysis. From a flavour science perspective, we wish to examine possible differences between orthonasal and retronasal aroma profile and document temporal changes of the retronsal profile, while coffee is kept in the mouth.

Introduction

An objective of coffee flavour research is to find chemical quality markers for a coffee brew, which correlate with the sensory assessment of expert coffee tasters and which drive consumer preferences. Currently the majority of analytical investigations on coffee aroma are performed under equilibrium or dynamic headspace conditions. The volatile flavour compounds are either stripped by a flow of gas or extracted with solvents to be subsequently analysed by gas chromatography. While this has been extremely valuable to expedite our understanding of coffee aroma, one might wonder how well this reflects the coffee aroma profile as it is experienced during the actual situation of coffee consumption. Coffee drinking conditions have additional important factors such as mixing, mastication and salivation, heating and interactions with mouth mucousa. This can lead to significant alterations of the physical and chemical state of its constituents (e.g. melting, emulsification, adsorption) induce chemical transformations, and modify the release of volatile flavour compounds relative to headspace (HS) studies.

Here, we discuss some new developments of nose-space analysis. We present a method to sample and analyse on-line volatile organic compounds (VOC) directly released from humans through the nose when consuming food [1-4]. The main benefit of on-line nose-space analysis is the ability to investigate the aroma during the actual situation of consumption. We present a novel approach to breath-by-breath analysis of volatiles exhaled through the nose based on Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS). First we outline the method and then go on presenting breath-by-breath nose-space results on a series of volatile coffee compounds.

Nose-Space Analysis

The aroma (odour) of food products is related to VOCs that are released from foods and reach the olfactive epithelium in the upper part of the nose. When flavour active compounds interact with olfactive receptors, a sensory perception is triggered. VOCs can reach the olfactory epithelium from two distinct directions. Either they are sniffed directly through the nose, via the orthonasal pathway, or they reach the olfactive receptors through the oral cavity and the pharynx, via the retronasal pathway. The orthonasal aroma corresponds to an aroma, as it is perceived from a food held in front of the nose (sniffing). In contrast, the retronasal aroma corresponds to the aroma of a food, as it is perceived during food consumption (while

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drinking or eating). Nose-space analysis samples the air exhaled through the nose as food is being consumed and reflects the retronasal aroma composition. Hence by comparison of a HS VOC profile with a nose-space profile, we address the question how closely a HS profile reflects the odor of food being consumed.

The first real-time breath-by-breath analysis dates back to 1988 [5]; a recent review discussed the various methods for nose-space (in-vivo) analysis [6].

Experimental

Nose-space analysis aims at sampling and analysing the air exhaled through the nose while food is being consumed. For this, nose-space air is sampled via two glass tubes fitted into the nostrils (see Figure 1). The separation and diameter of the tubes are adapted in order to allow the person to breathe and eat freely. The air from both tubes is combined and a small fraction of the nose-space air (15 sccm/min analysis flow plus 15 sccm/min bypass flow) is sampled and introduced into the drift-tube of the PTR-MS. The nosepiece is heated to 38°C to prevent condensation on the glass tubes.

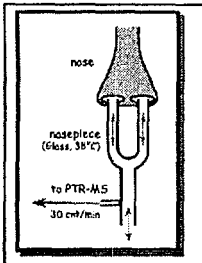

Figure 1: Nosepiece. The air exhaled during food consumption is sampled via the nosepiece and a small fraction introduced into the PTR-MS for on-line VOC analysis.

The PTR-MS technique has been extensively discussed in a series of review papers [7-10]. Briefly, it combines a soft, sensitive and efficient mode of chemical ionisation (CI), adapted to the analysis of trace VOCs, with a mass filter. In this study, 15 sccm/min gas is continuously introduced into the CI-cell (drift-tube). The drift-tube contains besides buffer gas a controlled ion density of H_3O^+. VOCs that have proton affinities larger than water (proton aff. of H_2O: 166.5 kcal/mol) are ionised by proton transfer from H_3O^+, and the protonated VOCs are mass analysed.

Results

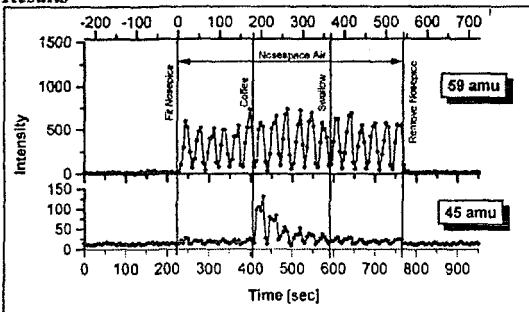

Figure 2: PTR-MS time-intensity profiles of VOCs during a typical nose-space experiment with coffee brew, for two selected masses - 59 and 45 amu. The experiment can be divided into five consecutive phases. First indoor air was sampled through the nosepiece in order to assess contributions from the laboratory background. We then measured the VOC composition of human breath during six consecutive breathing cycles, with the nosepiece being inserted into the nostrils, but without having coffee in the mouth. After approximately 410 sec, 5 ml coffee at 50°C were taken into the mouth and the nose-space air sampled for six additional breathing cycles, after which the coffee was swallowed and further six cycles monitored. At the end of the experiment, the nosepiece was removed from the nostrils and the indoor-air measured again. During the experiment, the nosepiece was heated to 38°C to avoid condensation.

As a starting point of the study, the HS profile of a coffee brew was measured by stripping the brew with indoor air. The coffee was prepared as follows. Using a standard coffee filter machine, 25 gram of roast&ground coffee was extracted with 500 ml water (Vittel 'Bonne Source'). 265 ml of the brew were put into a stripping vessel and the VOCs were stripped at

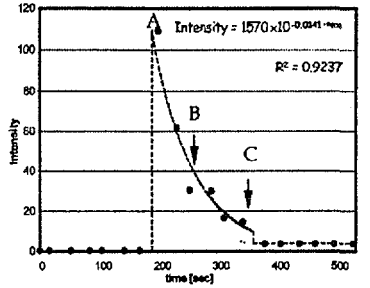

Figure 3: Exponential fit-curve to the intensity decrease of mass 45 as a function of time. Time zero was set at the moment where the nosepiece was put into the nostrils. Furthermore, we subtracted the averaged intensity originating from the human breath and the indoor-air from the raw data. Hence the intensity prior to taking coffee in the mouth is zero. Once coffee is taken into the mouth, the intensities at masses corresponding to coffee volatiles increased initially abruptly, but then decreased gradually as coffee was kept in the mouth. In order to assess quantitatively this decrease, we determined the maximum intensities at the individual breathing cycles and fitted an exponential function through these points. Once the coffee was swallowed, the nose-space intensities dropped to a value close to the one prior to taking coffee into the mouth.

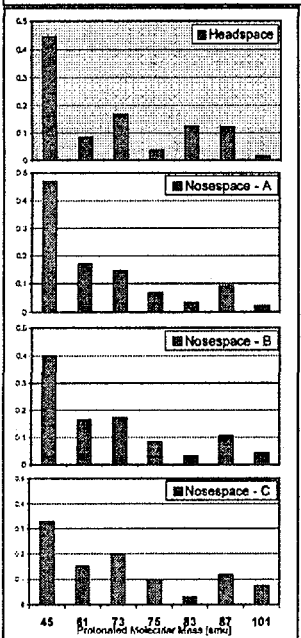

Figure 4: The top two frames allow comparing the orthonasal to the retronasal volatile profile. They are quite distinctive, indicating that traditional HS analysis might not reflect accurately the volatile profile, as it is experienced by consumer. The three bottom frames illustrate the evolution of the nose-space profile with time. A significant change with time is observed.

36 °C with an airflow of 15 sccm/min through the liquid for a period of one hour. The VOCs in the stripped gas were measured by PTR-MS. This spectrum represents an orthonasal reference profile to be compared with the retronasal data discussed below.

The brew used for the nose-space experiments was prepared similarly to the brew for the HS experiments. In order to minimize the experimental variability, a precise protocol was develop for the preparation and drinking of the coffee. A series of time-intensity profiles were taken by recording the intensities of a series of 14 masses using PTR-MS. The temporal course is shown in figure 2.

Discussion

The most striking observation of the nose-space time-intensity profiles is the strong decreases of signal intensity with time, while the coffee is kept in the mouth. In order to quantify the decrease we fitted an exponential decay curve through the maxima of the individual breathing peaks for each individual mass and determined the exponent, as shown for mass 45 in Figure 3.

Several processes can in principle be responsible for this decrease. One is stripping of volatiles from the liquid coffee. Based on measured partition coefficients and stripping experiments [11], we have to conclude that the observed decrease (exponents) is at least one order of magnitude too fast than can be explained by a simple volatile stripping argument. In fact, we observe for mass 45 (as well as for the others) a decrease of nose-space intensity by more than 50% within 2 min. In contrast, we measured reduction by just a few percent when stripping a liquid or a coffee solution with 100 sccm air for about 5 min. Hence this can only account for a marginal contribution to the

decrease of nose-space intensity.

Two other reasons for the fast decrease of VOCs in the nose-space can be put forward. (i) Diffusion of VOCs into the mouth mucosa will deplete the liquid coffee phase from volatiles, and hence reduce their nose-space concentrations. These compounds can be released back from the mucosa into the mouth-space once the coffee is swallowed and contribute to the lasting coffee-odour in the mouth. Currently we can hardly assess the quantitative importance of this effect, although experiments by Buettner et al. have shown that this can be quit significant [12,13]. (ii) The coffee that is taken into the mouth has a temperature of 50°C. Once in contact with the mouth tissue, the liquid starts to cool down and eventually reach 37°C. In a separate study we measured the temperature dependence of the partition coefficient for a series of coffee volatiles [14] and found that this phenomena can account for a significant if not for most of the decrease of the nose-space concentration. Quantitative studies are on the way to assess the relative contributions to the decrease of nose-space concentration with time.

Since we determined the exponents for the individual masses (Figure 3), we can calculate the volatile profile in the mouth as a function of time and follow the evolution of the mouth/nose-space. This is shown in Figure 4 for three selected times. The three bottom frames show the nose-space profiles for 0 (A), 85 (B) and 170 (C) sec after taking the coffee into the mouth. The frame Nosespace A corresponds to the nose-space profile as the coffee was just taken into the mouth. The spectra are normalised on the sum of the selected masses' intensities. While the coffee is kept in the mouth we can distinguish intensity changes that occur with time. This demonstrates at an analytical level and based on just a few selected compounds that the volatile profile is evolving rapidly in the mouth. It also suggests that a dynamic description of flavour might be more relevant to the situation of consumption than a static HS profile.

The top frame shows the intensities of the orthonasal profile (HS) at the same masses as for the nose-space at time zero, just below. Comparing both profiles, we see that they are distinctively different. This implies that the orthonasal HS profile is not an accurate description of the volatile profile as perceived during consumption.

Conclusions

The objective of this study was twofold. From an analytical perspective, we wanted to establish a nose-space method based on PTR-MS. From a flavour perspective we addressed two specific questions. First we wanted to assess the relation between the orthonasal and retronasal volatile profile. Second we were interested to see whether and how fast the retronasal volatile profile evolves with time.

Based on the results presented in this study, we believe that we have established a powerful approach that combines nose-space sampling with PTR-MS, to monitor at high time resolution the nose-space volatile profile. Considering flavour aspect, we have observed a fast exponential decrease of nose-space volatile intensities. For all VOCs discussed here, the intensities decreased by more than 50% within the two minutes of keeping coffee in the mouth. While several physical phenomena can contribute to this fast decrease, the most significant is probably the cooling of the coffee from the starting 50°C to 37°C in the mouth, although absorption on the mouth mucousa might also be important. More quantitative studies are needed to ascertain the relative contributions. The other flavour aspect is the comparison of the orthonasal (HS) with the retronasal volatile profile. This work revealed important differences between both profiles, documenting the value of analysing coffee flavour under conditions close to the situation of consumption.

Hence these first results, based on a limited number of volatile compounds, have demonstrated significant differences between orthonasal and retronasal volatile profiles and

revealed strong changes of the nose-space profiles while coffee is kept in the mouth. Further studies are on the way to extend these findings.

Acknowledgement

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